Boreskov Institute of Catalysis of the Siberian Branch of Russian Academy of Sciences,
Novosibirsk, Russia

Russian Scientific and Cultural Center in Valletta, Malta

Russian Center of International Scientific and Cultural Cooperation under RF Government

Ministry of Education and Science of the Russian Federation

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EFCE CONFERENCE

XVIII International Conference on Chemical Reactors

CHEMREACTOR-18

Malta
September 29 – October 3, 2008

ABSTRACTS

Novosibirsk, 2008

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The organizers express their gratitude to

Ministry of Education and Science of the Russian Federation, Moscow, Russia

for the financial support

PLENARY LECTURES

PL-1

SUSPENSION POLYMERIZATION REACTIONS AND REACTORS

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The suspension polymerization process is a well established method to manufacture a number of important commodity plastics, including poly(vinyl chloride) (PVC). PVC is worldwide, by volume, the third largest thermoplastic with annual demands close to 30 Mton. Producers of polymers in general and of poly(vinyl chloride) in particular strive for certain customer specified properties such as e.g. thermal stability, tensile strength, processability and glass transition temperature. These properties are controlled by fundamental polymer properties such as the molar mass distribution (MMD) and the content of structural defects (branches and unsaturations). The latter influences to a large extent the thermal stability of the polymer product as thermal degradation reactions start at thermally labile structural segments in the polymer chains. Considering the great industrial importance of the vinyl chloride suspension polymerization process, it is critical to develop models linking polymer properties to the applied polymerization conditions such as polymerization temperature, amount and type of initiator, batch time, etc.

In the present contribution a fundamental kinetic model describing the free radical polymerization of vinyl chloride at the elementary reaction level while systematically accounting for diffusion limitations, is presented. In the presented kinetic model all occurring elementary reactions are grouped into four reaction families consisting of forward and reverse reaction steps: bond dissociation/radical recombination, radical addition/β-scission, hydrogen abstraction and chlorine shift reactions. By applying this set of elementary reaction families to all species in the reaction mixture, the reaction network is generated. All radical structures formed during the polymerization process are classified into seven groups according to the structure of their radical center. The formation of different structural defects in the polymer product can be directly linked to the presence of these distinct radical types and by deriving mass balances for these distinct radical species the structural defects content can be determined. The method of moments is applied to calculate the moments of the MMD.

As one of the reactive phases becomes highly viscous throughout the polymerization process, diffusion limitations play an important role. This is accounted for by calculating apparent rate coefficients for all elementary reactions. These apparent rate coefficients are built up from an intrinsic contribution and a diffusion contribution. The former is solely determined by the intrinsic rate coefficient of the considered elementary reaction step and is obtained via regression of experimental data and from literature, whereas the latter is systematically calculated using the Smoluchowski expression in which the diffusion coefficients are determined using the free volume theory [1].

The resulting kinetic model enables the calculation of conversion, moments of the MMD and the structural defects content as a function of polymerization time for a wide range of polymerization conditions. The developed model is validated by comparing model calculations to laboratory scale experimental data concerning the monomer conversion, the moments of the MMD and the structural defects content. A good agreement is obtained and from model calculations. It could be concluded that structural defects are predominantly formed at high monomer conversions when monomolecular reactions are favoured over bimolecular reactions [2].

The above described kinetic model is then combined with a reactor model to enable the simulation of polymerization reactors [3]. The mass balances and moment equations are solved together with the energy balances for the suspension, the reactor wall and the cooling jacket liquid. This extended set of equations allows calculating the monomer conversion, the polymer properties, the reactor temperature and pressure, the cooling agent flow rate and the temperature profiles as a function of batch time for a broad range of industrially relevant operating conditions. Also, the applied model allows to describe possible thermal runaway and/or reactor vessel explosions. Simulations have been performed for pilot scale and medium-size industrial scale reactors. Considering the good agreement of the model predictions with the pilot scale reactor experimental data it can be concluded that the proposed model is applicable in design, optimization and control of industrial poly(vinyl chloride) batch reactors.

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THE ROLE OF CATALYSIS IN FAST PYROLYSIS OF BIOMASS

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Fast pyrolysis of biomass is the process of thermal decomposition, in absence of oxygen at atmospheric conditions, with the aim to produce a high quantity of liquid product (bio-oil) that can be easily stored, transported and further processed. The technology has developed to a level of large scale demonstration and could be commercialized within the next five years. Potential applications of bio oil are manifold but, apart from direct combustion or co-combustion, up to now insufficiently developed. There is however a number of drivers that create an increasing interest in the technology.

One of the reasons that food/ feed industries, refinery companies and catalyst companies show a distinct interest these days, is the need for second generation biofuels. Fast pyrolysis is, to a large extent, a non-selective biomass conversion technique that accepts a wide variety of lignocellulosic feedstock materials such as forestry, agricultural or plantation residues, and industrial waste streams from e.g. from food/feed, bio-ethanol or bio-diesel production. On the other hand, this fairly simple liquefaction technique offers significant logistic advantages, allowing shipping to central sites (refineries, chemical plants, power stations) for large scale conversion to final products. In fact, fast pyrolysis has the potential to become a key process in various biorefinery concepts.

It has been recognized already in the early days of fast pyrolysis R&D [1], that the application of catalysis could be of major importance in controlling the oil quality and its chemical composition. Without any catalyst involvement, the bio-oil derived from fast pyrolysis is a mixture of hundreds different, highly oxygenated chemical compounds. This chemical “soup” also has some unfavorable properties like a high acidity, an insufficient chemical stability and a low combustion value. Besides, none of the compounds is present in the oil in quantities above a few weight percent.

Catalysis could be applied for a number of reasons, and at a number of different positions in the process. Lower pyrolysis temperatures, a higher chemical and physical stability, high yields of target components, and an improved miscibility with refinery streams, are all goals strived for. Catalyst materials could be impregnated in the biomass feed, mixed into the pyrolysis reactor, built in the process after the reactor for upgrading of the primary pyrolysis vapors, or be used to modify the condensed liquids.

This contribution is meant to review all opportunities and challenges in headlines, and discuss the consequences for process design.

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PL-3

DEVELOPMENT OF ZEOLITE-COATED MICROREACTORS

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Zeolites are crystalline materials with pores of subnanometric size that provide highly interesting properties. Thus, zeolites are capable of very specific interactions that have earned them nicknames that include «molecular sieves» and (with some exaggeration) «the inorganic equivalent of enzymes». Because of this, a number of applications have emerged, especially involving adsorption and catalysis. During the last 15 years synthesis methods have been developed that allow the preparation of zeolites not only as powders, but also as membranes and films on a variety of supports. This has given rise to the field of zeolite membranes, where outstanding separation properties have been demonstrated on a wide range of gas and liquid mixtures. Also, zeolite films have been deployed to increase selectivity on a variety of sensors, including semiconductor sensors, capacitors and mass sensing devices.

In recent years, a new interest has developed in deploying zeolite layers as active coatings on microreactors. The growth of zeolite films on the channels of microreactors enhance their performance by providing unprecedented fluid-solid contact area, at an affordable pressure drop. Of particular interest are the methods that allow a controlled growth of zeolite crystals in such a way that easy accessibility of reactants from the fluid phase is preserved.

The talk will discuss some of the emerging possibilities and limitations of zeolite-coated microreactors in the context of the research carried out by our group at the University of Zaragoza.

CATALYTIC CONVERSION OF HYDROCARBON FUELS: FROM MOLECULAR MODELING TO REACTOR OPTIMIZATION

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1. Introduction

Catalytic conversion of hydrocarbon fuels is discussed from several view points: experimental studies, development of homogeneous and heterogeneous reactions mechanisms, CFD simulations, mathematical optimization of operating conditions and catalyst laodings, experimental model evaluation, and technical applications. Applications cover synthesis of basic chemicals and hydrogen and high-temperature fuel cells (SOFC). Understanding and optimization of reactors for high-temperature catalysis require the knowledge of the physical and chemical processes on a molecular level. In particular, due to short contact times and high temperatures, at which reactions occur on the catalyst and in the gas-phase, the interaction of transport and chemistry becomes important. Recently, high-temperature catalysis has been extensively discussed, in particular in the light of the synthesis of basic chemicals and hydrogen, and high-temperature fuel cells. Catalytic partial oxidation and autothermal reforming of natural gas, higher alkanes, diesel surrogates, and alcohols over noble metal catalysts at short contact times offer promising routes for the production of synthesis gas[1], olefins[2], and hydrogen. High-temperature catalysis is also present in solid oxide fuel cell (SOFC) operated at 800 °C. For any fuel other than hydrogen, catalytic reactions are likely to occur in the anode of a SOFC leading to a complex chemical composition at the anode-electrolyte interface[3]. Today, the challenge in catalysis is not only the development of new catalysts to synthesize a desired product, but also the understanding of the interaction of the catalyst with the surrounding reactive flow field. Sometimes, the exploitation of these interactions can lead to the desired product selectivity and yield.

2. Reaction mechanisms and coupling to the reactive flow field

The development of a reliable surface reaction mechanism is a complex process. A reaction mechanism should include all possible paths for the formation of the chemical species under consideration in order to be «elementary-like» and thus applicable over a wide range of conditions. The mechanism needs to be evaluated by numerous experimentally derived data, which are compared with theoretical predictions based on the mechanism. Here, the simulations of the laboratory reactors require appropriate models for all significant processes in order to evaluate the intrinsic kinetics. Sensitivity analysis leads to the crucial steps in the mechanism, for which refined kinetic experiments and data may be needed. Recently, kinetic Monte-Carlo simulations (kMC) have been used to achieve a better understanding of the interaction of adsorption, diffusion of adsorbed species, surface reactions, and desorption on three-dimensional catalytic nano-particels. Those simulations are fed with parameters (activation energies, thermodynamics etc) derived from DFT simulations of the species adsorbed on the individual particle crystal surfaces. Then, the reaction rates of individual steps can be derived from kMC as function of surface coverage, gas-phase concentration, and temperature. Based on those rates, rate equations in the concept of the mean-field approximation (MF) can be derived, which then can be used in CFD simulations.

3. Mathematical optimization of reactor design

A newly developed optimization approach will be discussed that is in particular suitable for better engineering of monolithic reactors with strong interaction between chemical reactions on the catalytic surface and in the gas-phase, and mass and heat transport[4]. As example of such a system, the catalytic oxy-dehydrogenation of ethane to ethylene in a platinum coated catalyst is chosen. The objectives of the optimization is the maximization of the product yield depending on inlet (temperature, species composition, mass flow) and operating reactor conditions (wall temperature and catalyst loading along the channel).

4. High-temperature catalysis in monolithic reactors

High-temperature catalysis is frequently carried out in monolithic structures. An efficient approach, which still includes all fundamental aspects, can based on the combination of simulations of a representative number of channels with the simulation of the temperature profiles of the solid structure treating the latter one as continuum[5]. This approach is the basis for the computer code DETCHEM$^{\text{MONOLITH}}$, which has been applied to model the transient behavior of catalytic monoliths. The code combines a transient three-dimensional simulation of a catalytic monolith with a 2D model of the single-channel flow field based on the boundary layer approximation. It uses detailed models for homogeneous gas-phase chemistry, heterogeneous surface chemistry, and contains a model for the description of pore diffusion in washcoats. The application of the code for catalytic partial oxidation and reforming of natural gas, higher alkanes, diesel surrogates, and alcohols to synthesis gas, olefins, and hydrogen will be discussed and the results will be compared to experimentally derived data.

5. High-temperature catalysis in Solid-Oxide Fuel Cells

Several groups[3] applied the following approach for the analysis of temperature, species concentrations, and current density profiles as well as the efficiency and power density of solid oxide fuel cell at direct internal reforming conditions: The heterogeneous chemistry model of the catalytic reactions in the anode structure uses a multi-step reaction mechanism for the steam reforming of the fuel[6]. The porous media transport is modeled using the Dusty Gas Model, and electrochemistry is modeled using modified Butler-Volmer setting assuming. Coupling of those models will exemplarily be discussed for an anode-supported SOFC operated with methane containing fuels and a Ni/YSZ anode structure.

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PL-5

CATALYTIC PARTIAL OXIDATION OF METHANE TO SYNGAS

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This presentation deals with a study of the methane Catalytic Partial Oxidation (CPO) process performed with a multiscale approach that goes from surface characterization aspects to chemical reactor analysis.

First, Rh/α-Al_2O_3 systems at increasing metal load (0.5, 2, 4 wt%) were prepared and characterized with various techniques in concert. Activity tests in annular reactor were used to study the conditioning process of these materials. The results suggested that, during the conditioning period, the catalyst surface undergoes a reconstruction process that tends to eliminate defective sites. The changes of the surface are more important for a highly heterogeneous surface, such as that of low Rh-load (0.5%) samples. The final stable catalysts are very active and robust with reduced tendency to C-formation.

The kinetics of the partial oxidation of CH_4 to synthesis gas were investigated over a 4 wt% Rh/α-Al_2O_3 catalyst by means of the short contact time annular reactor, which allowed to operate out of thermodynamic control with negligible pressure drops and nearly isothermal conditions on the reactive layer. The high flexibility of the annular reactor allowed to perform an extensive experimental campaign.

Data were collected feeding CH_4/O_2/inert gas mixtures, varying temperature, GHSV, O_2/CH_4 ratio, reactant dilution (1 to 27% CH_4 v/v) and adding CO, CO_2 and H_2O to the standard feed. Steam reforming (SR), CO_2 reforming (DR), water gas shift (WGS), reverse-WGS (R-WGS), H_2 and CO combustion tests were also carried out to refine the study.

A quantitative analysis of the experimental data was performed through a 1D mathematical model of the reactor, which incorporated a molecular indirect-consecutive kinetic scheme.

The molecular kinetic scheme consists of CH_4 total oxidation and reforming, the WGS and the R-WGS reactions, and H_2 and CO post-combustion reactions. The scheme provides an accurate description of reactants conversions and products distribution and accounts for the observed effects in a very large experimental field. An immediate picture of the main reaction pathways of the process are thus provided, as well as its major kinetic dependencies such as: (1) the negligible kinetic role of CO_2 reforming in the mechanism; (2) the comparable intrinsic kinetics of CH_4 steam reforming and total oxidation under differential conditions; (3) the need for independent kinetic expressions for the direct and the reverse WGS reaction, when far from equilibrium.

Moreover, a thermodynamically consistent C_1 microkinetic model for the conversion of CH_4 to syngas on Rh-based catalysts was also developed. It was verified that the model is able to predict correctly the behavior of several reacting mixtures, including CH_4/H_2O (SR) and CH_4/CO_2 (DR) reforming, CH_4/O_2 (CPO), H_2/O_2 and CO/O_2, CO/H_2O (WGS). Using the microkinetic model, a detailed analysis of the reaction mechanisms of CH_4 CPO, by the identification of the Rate Determining Step and the main elementary paths that occur under different operating conditions. In addition, the possibility of modeling in detail the surface chemistry allowed to propose also a possible explanation of the main molecular pathways involved in the process. Adopting a systematic reduction methodology, a hierarchy of models for CPO was proposed and overall molecular rate expressions were derived. In doing so, the molecular models are not based on an assumed mechanism and the effective parameters are not determined by regression of experimental data, but are directly related to the rate constants of the elementary reactions of the full microkinetic model.

Finally, results concerning reactor-engineering related aspects will be presented. The analysis has been carried out both experimentally and theoretically, by means of a dedicated adiabatic experimental study and of a comprehensive mathematical model of the CPO-reformer, incorporating the previously derived kinetics. Among others, this study allowed to clarify the mechanism of reactor light-off and blow-out and to pinpoint the governing phenomena at steady-state.

KEY-NOTE PRESENTATIONS

100 ANNIVERSARY OF PROFESSOR M.I. TEMKIN

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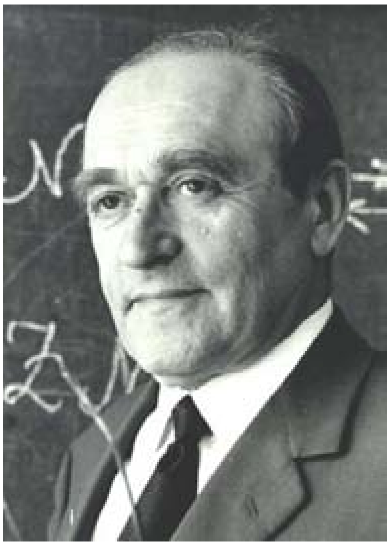

Prof. M.I. Temkin (1908-1991)

September 2008 marks 100 anniversary of Prof. M.I. Temkin. He is considered as one of the founders of modern kinetics of complex catalytic reactions. Prof. Temkin had been working in Karpov Institute of Physical Chemistry in Moscow from 1932 after graduation from the Moscow State University till the last days of his life (1991), heading for more than 50 years Laboratory of Chemical Kinetics. Being a disciple of famous scientists Prof. A.N. Bakh (the father of Russian biochemistry) and Prof. A.N. Frumkin (the father of Russian electrochemistry) he was also working with the Nobel prize winner Prof. N.N. Semenov and Prof. Michael Polanyi in Manchester. Prof. Temkin is famous for developing the theory of catalytic processes on nonuniform surfaces. Independently with Prof. J. Horiuti he developed the theory of stationary reactions. Together with his co-workers M.I. Temkin proposed a gradientless flow-circulation method, frequently used nowadays, for investigating heterogeneous catalytic kinetics.

The important feature of Temkin's school is a unique blend of fundamental and applied research. A particular example is kinetics of ammonia synthesis, which serves as a basis for reactor design and intensification of industrial processes. Another trade mark is logarithmic adsorption isotherm, frequently referred as Temkin isotherm. A seminal paper by Prof. Temkin written in the 50-s was devoted to thermodynamic analysis of molten salts and is still widely cited nowadays.

Personal reflections on the experience working with Prof. M.I. Temkin as a PhD student and a research associate will be given.

KN-2

GETTING TO THE POINT: FROM MOLECULAR TO PROCESS SCALES

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Advanced techniques have been developed and implemented in our laboratories which are capable of linking molecular and process scales. Evolution and achievements of the Temporal Analysis of Products (TAP) – technique have been recently described in a special issue of «Catalysis Today» (2007, 3/4) [1] In our paper, the new trends in non-steady-state catalytic kinetics are presented in which a size of perturbation is insignificantly small in comparison with the catalyst reactant capacity («point-like» perturbation) and also a catalyst amount is insignificantly small with the reactor loading («a needle in haystack catalysis»). In our non-steady-state high throughput monitoring, most of experiments are performed in thin-zone reactors TAP-reactors, TZTR, in which a thickness of the catalyst zone is very small compared to the reactor length. (1999, Shekhtman & Yablonsky [2]). A key advantage of the TZTR is that the catalyst bed can be changed uniformly by exposing the catalyst to a long series of small pulses at values of conversion up to 80% (it is much higher than in the differential plug-flow reactor, PFR) [4]. The TZTR very simplifies both an experimental realization and theoretical analysis. The theory of TZTR-reactors was developed in our papers in detail [2-5]. Preliminarily, a new configuration of the TZTR has been proposed in which the reaction zone is collapsed to the surface of a single micron-sized catalyst particle in a bed of inert particles [6]. The particle occupies less than 0.3% of the cross-sectional area of the microreactor, so that the reaction zone can be considered as a point source. In a typical experiment, the microreactor was packed with approximately 100, 000 quartz particles (210-250 microns in diameter) and a single platinum catalyst particle (300-400 microns in diameter) usually positioned in the bed. An important advantage of this configuration is that for the most reactions, even very fast ones, concentration and temperature gradients can be assumed to be negligible.

In this paper, the results of the probabilistic theory of reaction-diffusion process in the TAP-reactor with a single particle of this configuration are presented. The approach is illustrated by the examples of CO oxidation over the platinum catalyst and a series of Pd/PdO catalysts and hydrocarbon selective oxidation over modified VPO catalysts. A variety of non-steady-state experiments is performed and analyzed, i.e. data of single pulse-response and multi-pulse-response experiments with different reactants and products, pump-probe and uptake/release experiments, temperature programmed desorption and reaction experiments, pulse-response experiments with varying pulse intensity and spacing etc. Information obtained during the «single pulse experiment» and train of pulses will allow distinguishing times of different reactions. The approach allows obtaining unique quantitative information on catalyst properties for particular catalyst state: (1) Determination of the *total* number of active sites. This number can be found for every reactant and product in the course of multi-pulse experiment. The total number of active sites is also estimated in the straightforward single-pellet experiment in the domain of high conversion (95-100 %); (2) Determination of the number of *working* active sites; (3) Estimation of apparent kinetic parameters of the catalyst (kinetic parameters of reactants and products, their times of delay. The approach is focused on establishing direct, reproducible correlations between changes in surface composition and changes in catalyst activity.

This development is complemented by the development of advanced techniques that can characterize in 3D the flow field and transports (mass heat and momentum) of the process scale heterogeneous systems where the developed catalyst will be used. These techniques also assist in defining the proper flow and transport conditions suitable for the developed catalyst to function efficiently and properly as per the goals set for its development. In this presentation these techniques will be presented and sample of results that link both molecular and process scales will be discussed and outlined.

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KN-3

PROBLEMS AND PROSPECTS FOR IMROVEMENT OF THE OIL-REFINING REACTOR DESIGN

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The key strategic tasks facing the Russian oil-refining sector are increasing the oil conversion level and shifting to the European quality petroleum products.

The report has considered main problems and prospects of the improvement of the reactor design for the most important secondary oil-refining processes, including catalytic cracking, catalytic reforming, hydrotreating and hydrocracking.

The evolution of catalytic cracking reactor design due to shifting from a bead catalyst to a microspheroidal catalyst was discussed. Design features of moving-bed reactors with process beads, microspheroidal catalyst boiling-bed reactors, reactors with a riser and short-time contact reactors were considered.

Main advantages and shortcomings of moving-bed reactors with large-sized catalyst granules, microspheroidal catalyst fluidized-bed reactors and riser reactors with catalyst powder were reviewed.

The most important structural elements of the reactor for a new VGO catalytic cracking complex of OAO TAIF-NK built in Nizhnekamsk on the basis of Russian technology developed by RAS Institute of Petrochemical Synthesis (INKhS), OAO VNII NP and OAO VNIPIneft were discussed. It was demonstrated that application of a number of new design solutions permitted to achieve high performance being competitive in the world market.

Modification of the catalytic reforming reactor design in going from fixed-bed units to moving-bed units was considered. Features of reactors with an axial gas mixture inlet, with movement along a central pipe downwards and a radial outside-in inlet were discussed.

The operation experience of hydrocracking units built in Russia on the basis of both domestic and foreign processes was generalized. Features of fixed-bed and boiling-bed reactors operated in process units at Ufa, Omsk, Perm, Yaroslavl, and Ryazan plants were analyzed.

Main lines of the reactor design improvement for operating oil-refining units were indicated.

Prospects of the construction of new up-to-date catalytic cracking, reforming, hydrotreating and hydrocracking units were considered.

CATALYTIC DISTILLATION: PROSPECTS AND PROBLEMS

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The chemical industry is among the most energy- and material-intensive branches of material production. The prospects of increasing the efficiency of chemical engineering processes are connected with a thermodynamic optimization of existing processes, which can give a decrease in the energy consumption by 25-30%, and with the development of new processes and apparatuses.

Chemical production is an interrelated triad of the units of feedstock preparation, chemical conversion and the separation and purification of reaction products. Since the separation unit duty depends on conversion degree, there must be an optimum value of conversion degree, which balances the cost of a reactor, a separation unit and raw materials. This optimum exerts an influence on process parameters (temperatures, pressure, compositions) and equipment dimensions. The best, from the standpoint of energy- and resource-saving, variants of process flowsheets are based on the integration of a reactor and a separation system in a single apparatus. Owing to such a combination of different processes, in a number of cases a virtually complete conversion of reagents is achieved, selectivity is increased, energy consumption is reduced by a factor of 2-3, and an abrupt decrease in metal-capacity occurs. Distillation processes are the most versatile separation technique, and it is not surprising that among hybrid reactive mass transfer processes, catalytic distillation processes have gained the widest occurrence. The present paper deals with the prospects of development and the problems of the study of catalytic distillation at the modern stage.

Practical implementation of catalytic distillation advantages requires the carrying-out of in-depth physicochemical studies in order to understand the mechanism of the interaction of combined processes that have a nonlinear character and to reveal their potential in full.

Reactive mass transfer processes are thoroughly studied by a number of scientific teams in Russia, USA, Germany, UK and Holland. The key issue is the creation of scientifically founded strategy of the development of methods for the calculation and design of reactive mass transfer processes. To solve this problem, foreign researchers mainly direct their attention to the methods of mathematical modeling and numerical experiment. These calculation methods make it possible to mainly analyze separate steady states, and because of that, alternative, sometimes more effective, variants of the process implementation often remain out of the sight of researchers. However, it is now clear that some multiple steady states do occur for chemical reactions with small heat of reaction (e.g., methyl acetate synthesis), with large heat of reaction (e.g., ethylene glycol synthesis), and with intermediate heat of reaction (e.g., MTBE synthesis). In contrast to the approach specified above, the technique of the study of reaction-mass transfer systems which was developed in Russia is based on qualitative methods of thermodynamic-topological analysis with the use of the concept of the process weak model. This allows one to analyze simultaneously a full set of process steady states, providing the selection of the most effective variants of the process organization.

Energy management has received surprisingly little systematic study on aspects specifically for catalytic distillation, although traditional methods for distillation, heat and power integration are useful. There are two directions of energy efficiency enhancement. One of the two is connected with the decrease of driving force. The use of thermally-coupled columns, based on the model of thermodynamically reversible distillation, is an example that can give a reduction in energy capacity up to 30-40%. Recently, a first industrial catalytic divided wall column was developed and tested by joint efforts of Sulzer and BASF, which was used for obtaining pure methanol in methyl acetate hydrolysis in the production of polyvinyl alcohol. The integration of a catalytic distillation unit with a rectification column in a single shell made it possible to abruptly reduce the total number of apparatuses and, as a consequence of a decrease in the residence time of flows in an apparatus, to minimize the reverse reaction of methyl acetate formation and to obtain pure product methanol in addition to energy and metal saving.

Another direction of catalytic distillation enhancement has an aim to increase kinetic coefficients because lowering driving force tends to increase dimensions of column and reactor or to decrease conversion degree of reagents. Physicochemical intensification of processes, based on a synergism arising at a molecular level (Marangoni effect, diffusion-hydrodynamic Rayleigh instability, chemical turbulence) and characterizing the transition from macrotechnology to microtechnology, was found effective, with catalytic distillation being most promising between different hybrid processes.

At present, there is a continuing demand for conceptual design methods developing for catalytic distillation with the aim of prompt advancement of new products, made by new technology, to a market.

This work was financially supported by the RFBR project 08-03-00745.

ISOTOPIC TRANSIENT KINETICS STUDY TO IDENTIFY REACTION MECHANISMS

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Steady State Isotopic Transient Kinetic Analysis (SSITKA) is one of the most promising for study of kinetics and reactions mechanism in situ. Being properly unsteady-state, it allows to study kinetics under the steady state where the rates of the reaction steps, as well as concentrations of adsorbed species remain unchanged. Experimentally the dynamics of label transfer from feed molecules to reaction products is registrated after stepwise change of isotope composition in feed gas. Qualitative and quantitative analysis of isotope responses allows to reveal the key elementary steps involving the labeled molecules, to determine concentration of intermediate species, as well as the rate and sequence of their transformation on the catalyst surface [1].

This overview includes discussions of the experimental features, the mathematical formalism used in transient analysis and for evaluation of kinetic parameters. The results of SSITKA study in ethylene epoxidation over silver, selective NO reduction with methane over Co-ZSM-5 and fiberglass based catalysts are also represented.

Investigation of the ^{18}O isotope transfer dynamics showed that different surface oxygen species are involving in epoxidation and deep oxidation of ethylene. Formation of epoxidizing oxygen $[O_e]$ proceeds via two pathways: from nucleophilic $[O_n]$ and through sub-surface ones. Both concentrations of active oxygen, and the rates of ethylene epoxidation and deep oxidation were evaluated. The corresponding reaction rate coefficients were estimated to be about 10^6-10^7 s^{-1}. This example clearly demonstrates that, despite of relatively low time resolution of the SSITKA (~1 s), it allows to estimate the rates of very fast (microsecond scale) processes [1].

More detailed SSITKA study was performed for selective NO reduction with methane over Co-ZSM-5, where three isotopic labels (^{15}N, ^{13}C and ^{18}O) were used. It was found that two parallel reaction pathways on cobalt cations and $Co^{2+} - OH$ pairs takes place. It was shown that reaction turnover number (TON) over $Co^{2+} - OH$ sites was more than an order of magnitude higher compared with that of Co cations. The isotope studies were carried out at rather wide feed gas composition and temperatures. It allowed to find kinetic equations for key reaction steps and evaluate their rate coefficients and activation energies [2-4].

SSITKA allows to study not only the kinetics of catalytic (chemical) reactions, but mass transfer processes also. Indeed, the study of NO and water diffusion in the bulk of Pt-containing fiberglass catalyst clearly showed that diffusion of such polar molecules can be stimulated by their chemical interaction with the catalyst active sites. In the case of nitrogen oxide the diffusion can be stimulated by NO reaction with Pt species, whereas in the case of water – by interaction with Broensted acid sites [5].

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CATALYTIC TECHNOLOGIES APPLYING ARTIFICIALLY CREATED CATALYST NONSTATIONARITY AND SORPTION-CATALYTIC PROCESSES

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The review is dedicated to catalytic processes performed under artificially created catalyst nonstationarity. It is shown that the highest technological effect can be achieved for a controlled combination of the thermal nonstationarity with the composition nonstationarity of the catalyst surface. In the elaboration of a new technology, when choosing the main active factor (e.g., periodic concentration changes), it is necessary to take into account the other factors (the dynamic changes in the temperature and the pressure). Otherwise, in place of the expected improvement in the characteristics as compared with stationary processes, one may obtain a zero and even negative effect.

The development of non-stationary and adsorption-catalytic processes is very tedious task, which requires consideration of a large number of different factors and their combined action on different-scale levels of the process. The diversity of methods for the development of unsteady state conditions and their combinations is even reflected in the yet uncertain terminology used in the literature – the terms «non-stationary catalysis», «sorption-enhanced catalytic processes», «multifunctional reaction/separation processes», «chemical looping», «reaction chromatography processes» are often used.

It should be noted that many fundamental regularities typical for stationary processes are not in principle present in the processes with catalysts in the unsteady state. Particularly, in non-stationary processes, even in formally adiabatic catalyst beds, the temperature in the bed may substantially deviate from the adiabatic value. This difference is determined, in addition to the dynamic effects associated with the regeneration heat exchange and the travel of thermal fronts in the catalyst layer (a property typical of conventional reverse processes with the thermal nonstationarity of the catalyst), by the possible dynamic redistribution of released heat, which occurs in different reaction stages and phases in both space and time (this is a unique property of systems with the sorption nonstationarity). Depending on the chosen strategy of the realization of a non-stationary mode, the maximum temperature in the process can be either substantially lower or higher than the adiabatic temperature in an equivalent stationary process. The use of the sorption capacity of the catalyst allows one to carry out individual reaction stages within certain phases of the technological cycle, which opens up wide prospects for the varying of the reactant concentrations on the catalyst surface. In many cases, the correct arrangement of this process in combination with the temperature factor allows one to overcome the equilibrium limitations and reach higher yields of target products as compared with analogous stationary processes. It is interesting that in many cases, the parameters of non-stationary modes substantially depend on the factors that play a minor role or have an indirect effect on the stationary technologies. These factors include the energy of the reactant bond with the catalyst surface, the heat capacity of the catalyst, its specific surface, etc.

Prospective for application of unsteady catalytic and sorption-catalytic processes are analyzed for different case applications: VOC incineration, NOx reduction, purification of automotive exhausts, the Claus process, H_2S decomposition, SO_2 oxidation, hydrogen and syngas production by steam conversion of methane and CO, the Deacon process, selective oxidation of hydrocarbons and others.

The following advantages of the sorption-catalytic technologies over the stationary methods can be mentioned:

- principally new options for heat management, possibility to perform highly-exothermal reactions in packed adiabatic beds without catalyst overheating;
- a decrease in the energy consumption in processing of low-concentration gases;
- an increase in the efficiency of cleaning of exhaust gases;
- the shift of equilibrium in thermodynamically limited reactions;
- the enhanced selectivity of partial «anaerobic» oxidation processes using the chemisorbed oxygen as a «soft» oxidant.

In many cases, these advantages may include the reduction in the capital costs in and also, paradox as this may look at the first glance, the simplification of technological schemes and the enhancement of their operation stability.

In general, unsteady state and sorption-catalytic ideology discovers new degrees of freedom for process development and may become the basement for new generation of highly-efficient catalytic technologies in the nearest future.

ORAL PRESENTATIONS

Section 1. Kinetics of catalytic reactions
The Section is dedicated to the 100th anniversary of Professor M.I. Temkin, the outstanding specialist in the field of physical chemistry and chemical kinetics

Section 2. Physico-chemical and mathematical fundamentals of the processes in chemical reactors

Section 3. Catalytic processes' development and reactors design: modeling, optimization, new catalyst application

Section 4. Catalytic technologies in fuel and energy production
– production of hydrogen
– production of environmental friendly fuels
– environmentally friendly engineering

Section 5. Catalytic processing of renewable sources: fuel, energy, chemicals

Section 1.

Kinetics of catalytic reactions

The Section is dedicated to the 100th anniversary
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of physical chemistry and chemical kinetics

KINETICS OF AMMONIA SYNTHESIS AT CATALYST POISONING WITH OXYGEN

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Effect of oxygen sorption on the catalyst of ammonia synthesis on stationary and non-stationary kinetics of the reaction was studied.

$$N_2 + 3H_2 = 2NH_3 \qquad (1)$$

Experiments were carried out using a glass flow-circulation unit at the pressure of stoichiometric nitrogen–hydrogen mixture from 420 to 650 kPa and temperatures of 240 and 285°C. CA-1B industrial catalyst of synthesis with the following composition (prior to reduction) was used: K_2O - 1, CaO - 3, and Al_2O_3 was 4.4 weight percents; the rest was Fe_3O_4. The surface according to BET was 9,1 m^2/g. We used the fraction of 0,1-0,2 mm. So the reaction proceeded in kinetic regime. Poisoning of reduced catalyst with oxygen was carried out by circulation of a mixture of water vapor (0.1 volume percents) with hydrogen at 310°C for half an hour. After such treatment, the water vapor was absent in the gas phase. Each of three poisonings increased the quantity of absorbed oxygen on about 4% calculated for the number of surface catalyst atoms.

Rate of synthesis for stationary condition was described by the Temkin, Morozov and Shapatina equation simplified for our experimental conditions [1],

$$W = \frac{k_+ P_{N_2} P_{H_2}^{2m}}{\left(\ell K P_{N_2} P_{H_2}^2 + P_{NH_3}^2\right)^m} \qquad (2)$$

were k_+ is the rate constant for forward reaction, ℓ is the constant, which value for poisoned catalyst is close to the value for the reduced one, and K is the equilibrium constant of the reaction (1). The first term of denominator is significantly less than the second one, so the general equation has slight distinction from the Temkin and Pyzhov equation. The constant k_+ decreased with each oxygen sorption - in 8-10 times after three oxygen poisonings.

According to the Temkin theory of ammonia synthesis, the pre-exponential factor of k_+, k_+^0 constant is equal to the product of constant and Γ_s/f, where Γ_s is the maximum quantity of chemisorbed nitrogen atoms, f is the factor of surface unhomogeneity, $f = (Q_{max} - Q_{min})/RT$; Q_{max} and Q_{min} are the maximum and the minimum differential heat of nitrogen adsorption.

Evaluation of Γ_s/f can be done using the data on the rate of ammonia formation at non-stationary reaction proceeding after the change of the flow rate [2]. The experiments showed that Γ_s/f changed insignificantly at the catalyst poisoning. So poisoning results in the increase of activation energy of rate constant k_+. Noteworthy that this conclusion is true when the quantity of surface oxygen is low in comparison with the number of surface catalyst atoms. After three oxygen poisonings, this corresponds to the increase of its activation energy by 2,0-2,5 kcal/mol.

According to the Temkin theory, the increase of activation energy of k_+ means that the effect of oxygen sorption on the catalyst consists in the increase of activation energy of nitrogen chemisorptions at a fixed heat of nitrogen chemisorption. So activation energy of nitrogen adsorption rate depends not only on the heat of nitrogen chemisorption but also on the quantity of oxygen on the catalyst. Earlier such conclusion was made on the base of studying of the effect of oxygen sorption on the catalyst of ammonia synthesis on the rate of isotope exchange in molecular nitrogen and on the rate of nitrogen adsorption [3].

This conclusion is in agreement with studies of Ertl et. all [4], in which a significant increase (about 300 times at 430 K) of the rate of nitrogen adsorption on a Fe (100) single crystal surface after evaporation of potassium on it was observed [5]. It was concluded that activation energy of activated complex at nitrogen chemisorption reduced at the decrease of work function of electrons.

Oxygen sorption on a properly reduced catalyst leads to re-oxidation of promoters and to the increase of activation energy of nitrogen chemisorptions [6].

Results of this study show that this conception can be applied for description of kinetics of ammonia synthesis at poisoning of promoted catalyst with oxygen-containing gases.

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THE STUDIES OF THE MULTIROUTES MECHANISMS IN HOMOGENEOUS CATALYTIC PROCESSES

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In this report the key problems and methods based on the Horiuti-Temkin theory of the stationary reaction kinetics, which are useful for mechanistic studies of the multiroutes reactions will be presented. The following questions are discussed:

1. The physico – chemical and topological components of the «reaction mechanism» notion [1].
2. The kinetic and bipartite graphs as a geometric image of the mechanism topological structure [2].
3. The multiroute mechanisms and the new rational strategy for kinetic model design [3].
4. The multiroute mechanisms as characteristic feature of the reaction catalyzed with metal complexes [4].
5. The artificial creation of the multiroutes mechanisms and the conjugation knots analysis [3].
6. The chain mechanisms and conjugated reactions in the real catalytic processes [5].
7. The chain reaction schemes with autocatalysis and critical phenomena in the catalysis with metal complexes [5, 6].

Financial support of RFBR, grant № 07-03-00315.

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KINETIC MODELING OF LACTOSE OXIDATION OVER SUPPORTED PALLADIUM AND GOLD CATALYSTS

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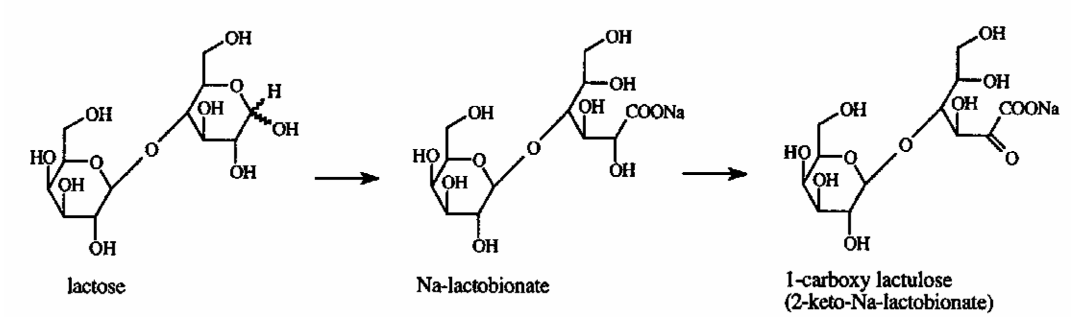
Introduction

Lactose, an abundant disaccharide, can be oxidized resulting first in lactobionic acid, and then in 2-keto-lactobionic acid [1-3].



Oxidation of sugars is very sensitive to several factors such as pH and the oxygen feed rate. The «*in situ*» catalyst potential measurements give important information about red-ox state of the catalyst surface.

Experimental

Lactose oxidation was studied in the present work using such measurements over Pd/C and Au/Al_2O_3 catalysts. Catalytic experiments were performed at 60-90°C and pH from 6 to 10 at different oxygen flow rates. Samples of the liquid phase were periodically taken and analyzed by HPLC with Biorad Aminex HPX-87C column (t =80°C and flow 0.4 ml /min).

Kinetics

Langmuir type of kinetics was applied to describe the concentration behavior leading to the following rate expression for lactobionic acid consumption

$$r_{LA} = \frac{k_3 K_L C_L \sqrt{K_o P_{O_2}}}{(1+\sqrt{K_o P_{O_2}} + K_L C_L + K_{OH} C_{OH^-})^2} \qquad (1)$$

For gold catalysts it was proposed that initially adsorption of oxygen occurs on edges, corners and perimeter of nanoparticles, migrating further to faces, where it is transferred into inactive in catalysis oxide. In order to explain experimentally observed electrochemical potential behavior of gold catalysts reduction of oxygen in alkali media with involvement should be assumed.

An expression for the catalyst potential is

$$E=\frac{RT}{2F}\ln\left(\frac{k_7\sqrt{K_O P_{O_2}}+k_8(1-\frac{k_8}{k_5\sqrt{K_o P_{O_2}}}\frac{1}{(1+\sqrt{K_o P_{O_2}}+K_L C_L+K_{OH}C_{OH^-})}-e^{-k_5\sqrt{K_o P_{O_2}}\,t})}{k_6 C_{OH^-}}\right) \tag{2}$$

For kinetic modeling eqns. (1) and (2) were used. Oxygen concentration was calculated from its solubility. Analogously to lactose oxidation of lactobionic acid takes a form

$$r_{LBA}=\frac{k'' C_L C_{OH^-}\sqrt{K_o P_{O_2}}}{(1+\sqrt{K_o P_{O_2}}+K_A C_L+K_{OH^-}C_{OH^-})^2} \tag{3}$$

The system of differential equations was solved with the aid of regression software MODEST applying simplex - Levenberg-Marquardt method. The degree of explanation was equal to 99.42%. Modelling results, partially presented in Figure 1, showed very good agreement between experimental and calculated values.

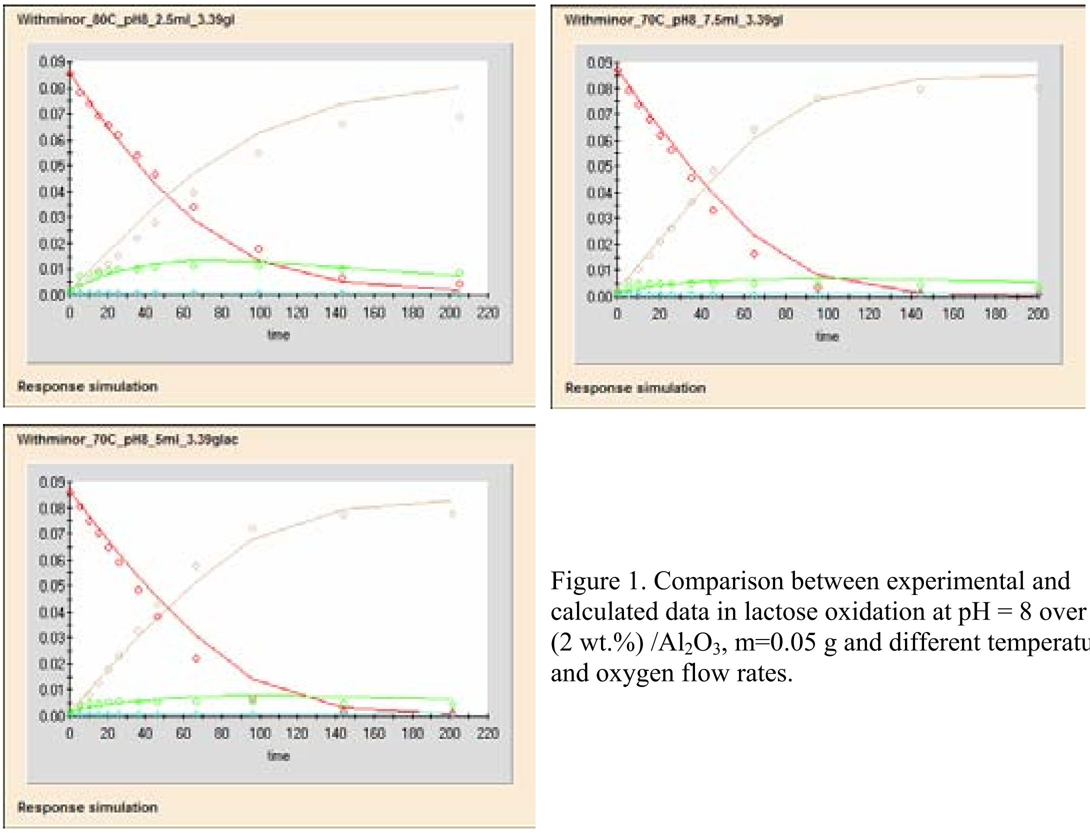


Figure 1. Comparison between experimental and calculated data in lactose oxidation at pH = 8 over Au (2 wt.%) /Al_2O_3, m=0.05 g and different temperatures and oxygen flow rates.

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PARTIAL OXIDATION OF TOLUENE UNDER CATALYST UNSTEADY STATE: KINETICS AND MODELLING

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Experimental and theoretical studies during the last decades have proved that the efficiency of process can be increased considerably if the reaction is performed with the catalyst in unsteady state. The physical basis for it lays in an ability to regulate the ratio between the adsorbed species interacting on the catalyst surface. Cyclic reduction and re-oxidation of the catalyst is one of the ways to support of the catalyst in unsteady state and to reach an improved performance in catalytic partial oxidation reactions. This operation is industrially used in the DuPont process of butane oxidation to maleic anhydride over a vanadium-phosphorous catalyst [1]. The reason to apply this cycle was to improve the selectivity by a decrease of the concentration of surface oxygen, which is thought to be responsible for total oxidation. The common objectives of the use of periodic operation in catalytic reactors are to provide an increased conversion, selectivity, and reduced deactivation [2]. An important mechanistic information could be extracted from the transient behavior of the reaction after a fast change of the composition of reaction mixture over the catalyst.

The goal of this work is modelling of toluene oxidation into benzoic acid (BA) vanadia/titania catalyst under periodic reactor operation.

On the base of the developed unsteady state kinetic model the theoretical analysis of the reactor performance under unsteady state conditions was carried out. The unsteady state conditions on the catalyst surface are supposed to be created by forced oscillations of concentration of BA in the reactor inlet. The influence of various parameters like cycle split, length of period of forced oscillations in the reactor was investigated with respect to the conversion of the benzene. It is shown that under periodic reactor operation an average toluene conversion was up to several times higher than the steady state value. This was due to presence a different surface oxygen species: nucleophilic lattice species and electrophilic surface species participating in the parallel routes of the toluene oxidation. The latter species could be formed easier in the presence of gaseous oxygen providing the decrease of selectivity.

Acknowledgment

The authors acknowledge to RFBR (Grant № 06-03-32473-a) for the financial support.

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KINETICS OF LIGHT ALKANE OXIDATION: FROM DETAILED MODELING TO PROCESS DEVELOPMENT

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Oxidative transformations of light alkanes (LA) from methane to butanes attract not only scientific, but also industrial attention, since these processes may open a potentially efficient way to produce valuable chemicals and intermediates (alcohols, aldehydes, acids, olefins) from relatively cheap and abundant feedstocks (natural and associated petroleum gases). However, these reactions suffer from low selectivities to target product(s) due to their higher reactivity as compared to LA. Their accessible yields are determined by kinetic factors, i.e. overall reaction network and kinetic parameters of «elementary» reactions. Therefore, deep fundamental understanding of both homogeneous and heterogeneous reactions at near to elementary reaction step level is of prime importance for process development.

The processes under consideration with high probability proceed via so-called heterogeneous-homogeneous reaction schemes. This means that both gas-phase and surface transformations of initial and intermediate species are of crucial importance for the overall reaction rate and product distributions. In the case of «homogeneous» LA oxidation heterogeneous transformation proceed over the reactor walls and various «inert» inserts, as well as on the surface of soot and other carbonaceous particulates formed as by-products. On the other hand, it was demonstrated by several authors (see, e.g., [1,2]) that catalytic oxidation of LA proceeds via the formation and further transformations of free radicals (FR). As a result, the overall process can be represented by a kinetic scheme that includes homogeneous and heterogeneous elementary reactions of initial reactants (alkane, oxidant), reactive intermediates such as FR and molecular products including target products of partial oxidation, e.g. olefins and/or oxygenates. Recently we have formulated the set of main ruling principles for the development of kinetic model applicable to processing of hydrocarbon gases and able to describe the major regularities of LA partial oxidation and used for the process development [3]. They include

- thermodynamic consistency;
- model fullness;
- independence of kinetic parameters;
- openness of the description.

Also, the approach to modeling heterogeneous reactions of free radicals was developed (see [3,4]) that allows one to combine gas-phase and surface reaction steps within a uniform description of the reacting system. Based on the above principles and approaches, the kinetic model for oxidative transformation of C_1-C_2 hydrocarbons has been developed, that can be further expanded to a broader description of LA oxidation.

In this presentation the first results of the model application to the processes of practical interest will be discussed. They include:

- high-pressure non-catalytic partial oxidation of methane and methane-ethane mixtures to methanol;
- catalytic oxidative coupling of methane to higher hydrocarbons, including olefins;
- oxidative dehydrogenation and cracking of C_2-C_4 alkanes.

Special attention will be paid to:

- reciprocal influence of different alkanes during their co-oxidation;
- effects of additives (such as peroxides) onto both homogeneous and catalytic LA oxidation;
- contribution of macrokinetic factors (heat and mass-transfer) to the yield of target product(s).

Also, some examples of process optimization using the model(s) under discussion will be provided.

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KINETICS OF STARCH OXIDATION USING HYDROGEN PEROXIDE AS AN ENVIRONMENTALLY FRIENDLY OXIDANT AND AN IRON COMPLEX AS A CATALYST

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1. Introduction

Native starch has been used for a long time in the preparation of different products (intermediates to paper industry), due to its large availability and low cost. An environmentally friendly oxidizing agent, hydrogen peroxide, was used in starch oxidation in this work to suppress the amount of by-products. Iron tetrasulfonatophthalocyanine complex (FePcS) was applied as a catalyst, since very low catalyst amounts of this catalyst are needed resulting in a pure oxidized starch, leading to the residual iron content lower compared to iron salts. Typically, large amounts of products are needed for determination of the degree of substitution [1] and thus oxidation kinetics has not been studied previously in detail using this catalyst. The aim of this work was to determine the kinetics of starch oxidation with hydrogen peroxide in the presence of FePcS catalyst.

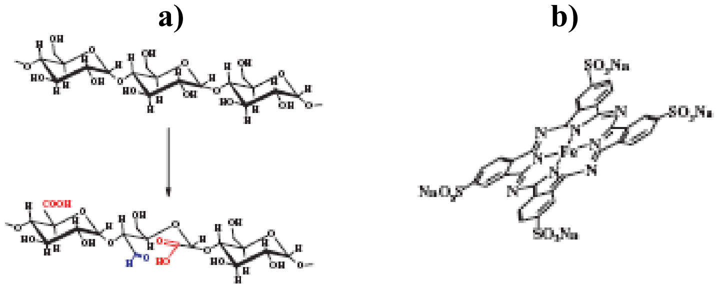

Fig. 1. a) Reaction scheme for starch oxidation and b) catalyst structure [1].

2. Experimental section

Starch oxidation was performed in a semibatch glass reactor (V_L=1000 ml). Typically 260 g starch and 140 mg catalyst were used in the experiments. pH was kept constant by continuously adding 2M NaOH The main parameters were pH and the hydrogen peroxide flow rate (between 11 and 22 ml/h). The reaction temperature was 55 °C and the experiments were typically carried out for 7 hours. Carboxyl and carbonyl contents of the oxidized starch were determined by Smith procedures, according to which the sample is titrated with NaOH for the carboxyl content and with HCl for the carbonyl content. Additionally, the carbonyl and carboxyl contents were analyzed with HPLC by using an acidic hydrolysis method [2]. The yield was determined by drying and weighing the product. The residual iron content was determined by ICP. SEM pictures were obtained from the native and oxidized starch.

3. Results and discussion

Kinetics of starch oxidation given as degree of substitution of carboxylic groups, is shown in Fig. 2. In the beginning of experiments, oxidation mainly occurred on the surface of the starch granules, but after a certain reaction time (240 min) starch partially depolymerized and swelled, resulting in the formation of reducing end units and increase of surface, leading to enhanced reaction rates (Fig. 2). Glucose units and its oxidized monomer units were detected by HPLC after hydrolysis of polymer (Fig. 3a). SEM pictures showed a loss of smoothness of the starch granules, which is desirable due to a bigger contact surface of the starch with a reagent (Fig. 3b). Higher yields of oxidized starch were achieved using lower amounts of H_2O_2, but at the cost of lower DS values. Higher pH (8-10) favored carboxyl formation and neutral pH (7) favored carbonyl formation. A mathematical model was developed.

Table 1. Degree of substitution and yield of oxidized starch at different reaction conditions

#	a / b / c	$^{d}DS_{COOH}$ /100AGU	$^{d}DS_{CO}$ /100 AGU	^{d}yield %
1	55/8.4/22	0.92	2.05	87
2	55/8.4/11	0.46	1.87	96
3	55/7.0/22	0.68	2.15	89
^{e}4	52/10.0/5	0.45	0.66	98
5	52/7.0/5	0.28	1.55	99

[a] temp. °C [b] pH [c] H_2O_2 flow (ml/h) [d] after 420 minutes
[e] 500 ml reactor, 130 g starch and 70 mg cat, 4h

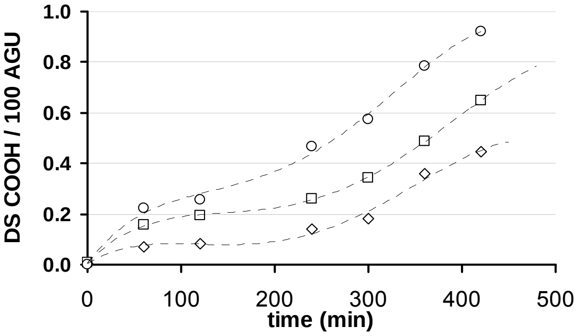

Fig. 2. Kinetics in starch oxidation at 55°C at pH 8.4 and H_2O_2 flow of 22 ml/h (○), at pH 7 and H_2O_2 flow of 22 ml/h (□), at pH 8.4 and H_2O_2 flow of 11 ml/h (◊).

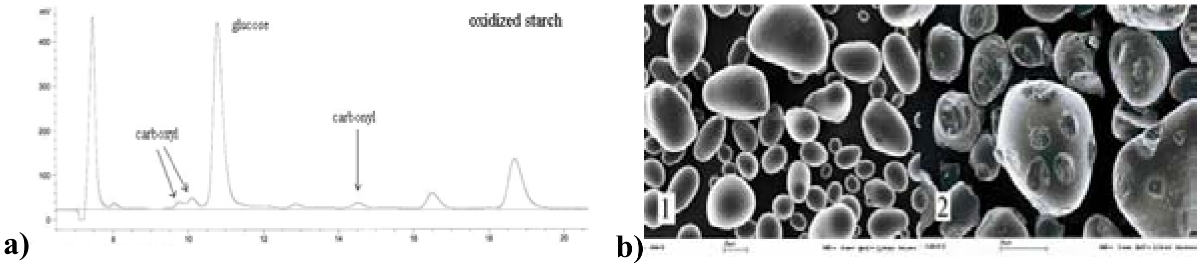

Fig. 3. a) Carboxyl and carbonyl contents identified by hydrolytically breaking down starch to single glucose units and analyzed with HPLC, b) SEM pictures of native (1) and oxidized starch (2).

4. Conclusions

Kinetics of starch oxidation was studied at 55 °C over FePcS catalyst using H_2O_2 as an oxidant. Higher yields were obtained with less lower oxidant amounts, and more alkaline conditions favored carboxyl formation, while neutral conditions favored carbonyl formation. HPLC succeeded to identify carboxyl and carbonyl contents by breaking down the polymer to single units.

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DESIGN OF CATALYTIC SYSTEMS BASED ON THE KINETIC CONJUGATION PRINCIPLE

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The theory of conjugated reactions was developed at the beginning of 20 century and is interesting now for catalytic systems design. A few conjugated catalytic processes were designed by Likholobov's group on the base of information about probable mechanisms [1]. The most interesting one is conjugated oxidation ofcarbon monoxide and water to carbon dioxide and hydrogen peroxide, respectively (1)(formally, reaction (1) is result of conjugation exoergic reaction (2) and endoergic one (3).

$$CO + H_2O + O_2 = CO_2 + H_2O_2 \qquad (1)$$

$$CO + 1/2O_2 = CO_2 \qquad (2)$$

$$H_2O + 1/2O_2 = H_2O_2 \qquad (3)$$

The complex of Pd(0) c PPh_3 is the key intermediate in this process [1]. We have proposed another mechanism for reaction (1), including hydride palladium complex as a key intermediate (4-6) [2].

$$PdBr_2 + CO + H_2O \rightarrow HPdBr + CO_2 + HBr \qquad (4)$$

$$HPdBr + O_2 \rightarrow BrPdOOH \qquad (5)$$

$$BrPdOOH + HBr \rightarrow PdBr_2 + H_2O_2 \qquad (6)$$

This mechanism is established for systems PdX_2-$CuBr_2$-solvent (X – Br, I; solvent –1,4-dioxane, tetrahydrofurane). If cyclohexene is added to the system $PdBr_2$-$CuBr_2$-tetrahydrofurane under reaction (1) conditions (30^0, atmospheric pressure of CO and O_2 mixture), the new conjugated reaction is initiated - hydrocarboxylation of cyclohexene to cyclohexane carboxylic acid. This fact is one of the proofs of mechanism (4-6) correctness, because hydride palladium complexes are the real catalysts of alkenes carbonylation processes. Carbonylation of cyclohexene is carried out under more hard conditions without conjugation [3]. A number of alkenes were carbonylated in our systems under mild conditions.

It is possible to design catalytic systems for reactions with thermodynamic or kinetic limitations using information about probable mechanism of these reactions. We term this approach «kinetic conjugation principle of reactions». Problem of selectivity is discussed for conjugated processes. Financial support of RFBR (Grant 08-03-00258).

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OP-I-8

KINETICS OF CARBON MONOXIDE OXIDATION OVER CuO/CeO_2 CATALYSTS

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Introduction

Ceria supported CuO catalyst have been reported as very active in low temperature CO oxidation catalyst [1,2] due to its high capacity to storage and supply oxygen [3] the CO oxidation is believed to follow Mars-Van Krevelen (MVK) mechanism, but also Langmuir-Hinshelwood (LH) mechanism is reported in literature [4]. In this work the kinetics of pure CO oxidation over CuO/ceria catalysts has been investigated and the experimental data were fit with several mechanistic models.

Experimental

CuO/CeO_2 catalyst was prepared by wet impregnation with CuO loading of 7% in weight (being real value 6.9), dried and calcined in air at 400°C for 5 h. Previous to kinetic experiments, catalyst was reduced in hydrogen stream at 300°C for 1 h. The catalyst was characterized by BET, XRD, H_2-TPR, CO-TPD, O_2-TPD and oxidation-reduction cycles.

Kinetic experiments were carried out in differential regime, with gas total flow rate of 200 cm^3/min and for several feed stream composition, being the catalyst particles size of 0.16-0.25 mm. The experiments were carried out at four temperatures (in the range 300 to 353 K) and the obtained 61 experimental data were fit to power law rate and several mechanistic rate equations (LH and MVK).

Genetic algorithm (GA) was used to optimization of rate equations parameters, by minimizing the objective function $\sum_{i=1}^{N}\left(r_{\exp}-r_{calc}\right)^2$. The initial population of 100 individuals, mutation fraction of 0.1 and 200 generations were found as optimal values for running the GA.

Results

The OSC capacity of the catalyst measured at 120°C by CO-He-O_2 steps (Figure 1) reveals that after oxygen step followed by helium step, CO_2 is produced after switching to CO, being supplied the necessary oxygen by ceria lattice (calculated to be 0.18 mmol O_2/g). This agrees with CO-TPD (not shown), in which the preadsorbed CO is removed in form of CO_2, with

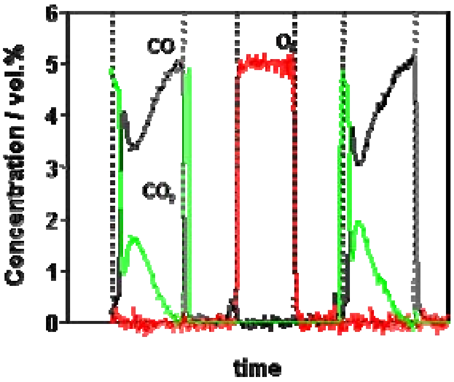

Figure 1. CO, CO_2 and O_2 evolution during 5%O_2→He→5%CO steps at 120ºC.

maximum CO_2 formation rate around 120°C.

According to Weisz-Prater criterion, the kinetic experiments were carried out in kinetic regime (calculated Weisz-Prater number of 0.019<< 0.3).

By comparing Figures 2(a) and 2(b) we can realize than at low partial pressures, CO oxidation rate increases more rapidly with oxygen than with CO, while at higher partial pressures the effect of oxygen on CO reaction rate is more pronounced than the effect of CO.

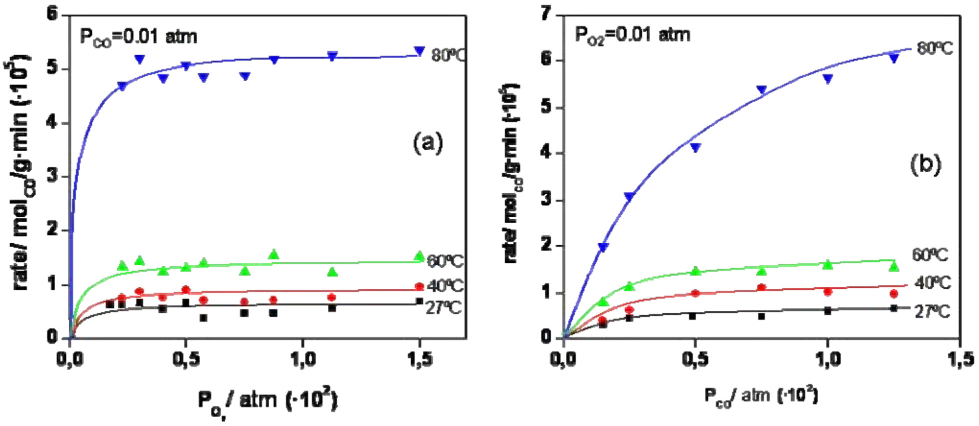

Figure 2. CO oxidation rate in function of partial pressure of (a) oxygen and (b) CO with constant catalyst weight.

The model adequacy was checked by applying F-test, being the best the one with the higher F-value. In Table 1 are listed the results of three of the checked models, being the second and third models a LH and MVK models, respectively (note that for all models calculated F-value>tabulated F-value, which makes the regression meaningful).

Table 1. Apparent activation energy and statistical parameters for some the the checked models.

Rate equation	Ea (kJ/mol)	SSR (10^{-8})	F value	F_t
$r_{CO} = k\cdot P_{CO}^{a} P_{O_2}^{b}$	51.5	6.555	13.7	2.540
$r_{CO} = \frac{k\cdot P_{O_2}}{(1+K_{CO}\cdot P_{CO})^2}$	54.8	63.914	10.8	2.540
$r_{CO} = \frac{k\cdot P_{CO}\cdot P_{O_2}{}^{n}}{0.5\cdot k_{CO}\cdot P_{CO} + k_{O_2}\cdot P_{O_2}{}^{n}}$	61.2	6.547	13.8	2.386

Conclusions

Among different rate equations, the best fit is for one derived from Mars-Van Krevelen mechanism, whose optimal parameters were found by genetic algorithm-based optimization techniques. In the best model the apparent activation energy of 61.2 kJ/mol and n (oxygen partial pressure exponent) of 0.1 are obtained.

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CHAOTIC DYNAMICS IN THE THREE-VARIABLE KINETIC MODEL OF CO OXIDATION ON PLATINUM GROUP METALS

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The most widely studied heterogeneous catalytic reaction is CO oxidation on the metals of platinum group. In particular, some conditions for such nonlinear effects as steady state multiplicity, oscillations, and chaotic dynamics were described. In many cases, the kinetic models, describing the complex irregular oscillations of reaction rate, have a large number of variables and parameters. One of the effective methods for analysis of nonlinear dynamics is the separation of fast, moderate and slow motions in the model under consideration [1]. Then the dynamics of the whole system is determined by the structure of limit sets of the subsystems of both fast and moderate motions.

Using the hierarchical method, we have studied the scenarios of rise of chaotic dynamics for the CO oxidation reaction in the framework of a rather simple kinetic model that describes the behavior of the dimensionless concentrations of CO (x) and oxygen (y) absorbed on the catalyst surface, as well as the dynamics of the concentration of oxygen embedded into the subsurface metal layer (z):

$$x' = K_1(1-x-y) - K_{-1}x - K_3xy\,,$$

$$y' = 2K_2(1-x-y)^2 - K_3xy\,,$$

$$z' = K_4y(1-z) - K_5xz\,.$$

The assumptions on the reconstructive properties of the catalyst surface are as follows:

1. A surface modification occurs and the activation energy of the interaction between the adsorbed species sharply increases when the adsorbed oxygen concentration y exceeds some critical value.
2. A surface reconstruction occurs and the constant of oxygen adsorption decreases when the embedded oxygen concentration z exceeds some critical value.
3. Oxygen and CO adsorption and interaction between them are faster then the oxygen embedding and the interaction between the embedded and adsorbed oxygen, i.e., z is a slow variable.

This work is a continuation of [2], which was devoted to the development of a low-dimensional kinetic model of CO oxidation on a metallic catalyst surface and the theoretical study of arising nonlinear phenomena and relaxation oscillations of the reaction rate. In the paper [2], the conventional Langmuir-Hinshelwood mechanism of catalytic CO oxidation was considered under assumption of the possibility of a metal surface modification in the course of catalytic reaction due to the oxygen penetration into subsurface layers.

The rate of changing the third coordinate z is smaller then the rates of the other reaction stages, and the dynamic properties of the whole system are inherently determined by the structure of limit sets of the one-parameter family of submodels with two variables x, y and parameter z. These submodels have a hysteresis of steady states and two maximal families of periodic solutions at some K_i values (i = 1, -1, 2, 3). For each family, the periodic solutions at one of the boundaries degenerate into the homoclinic orbit that is a saddle-loop separatrix. In this case the periodic solutions are highly parametric sensitive. Moreover, there are two scenarios of the chaotic dynamics birth in the model at some values of K_4 and K_5, namely: by means of a cascade of period-doubling bifurcations and owing to the mixed-mode oscillations (see Fig. 1).

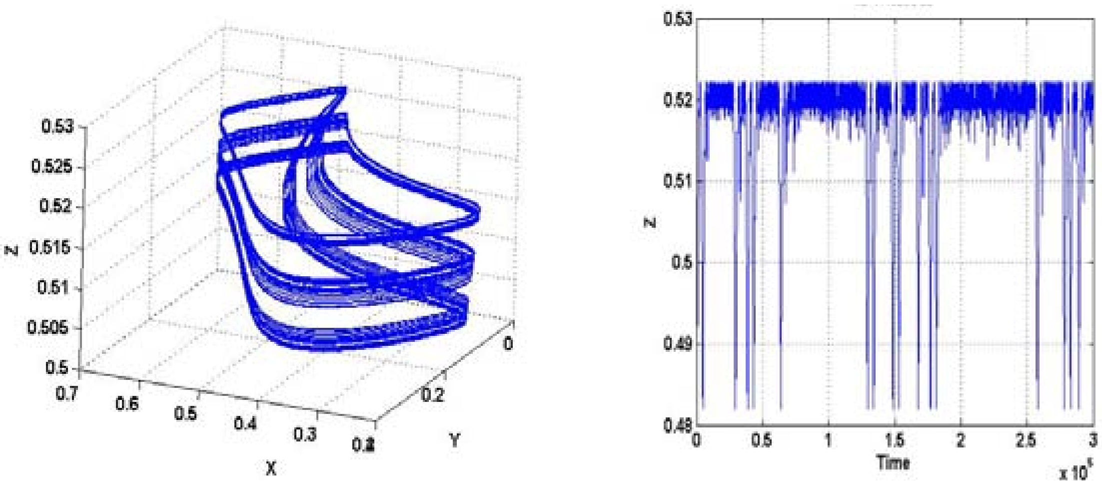

Figure 1. The examples of a strange attractor as a result of the cascade of period-doubling bifurcations (left part) and chaotic oscillations as a result of the development of mixed-mode oscillations (right part)

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OP-I-10

ADSORPTION OF COMPLEX MOLECULES WITH DIFFERENT ORIENTATION IN MONOLAYER ON SQUARE LATTICE. MONTE CARLO AND TRANSFER-MATRIX TECHNIQUES

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The most of the studies of adsorption are devoted to the monomolecular adsorption, but the statistics and thermodynamics of multisite one is the interesting problem to date. This situation is mainly associated to three difficulties which make the complex molecules statistics different from the usual single particle statistics [1]. Namely, 1) no statistical equivalence exists between particles and vacancies, 2) the occupation of a given lattice site ensures that at least one of its nearest-neighbor sites is occupied, and 3) an isolated vacancy cannot serve to determining whether that site can ever become occupied. Moreover, there is a problem of different molecular orientation in adlayer [2]. The aim of this study is investigation of complex molecules adsorption on square lattice with different molecular orientations in adlayer.

To describe adsorption of complex molecules on homogenous surfaces we used the general lattice gas model. One of the simplest kinds (do not taking into account the dimer adsorption) of complex molecules which can variously orientate on the surface is quadrangular pyramid. Such molecules can adsorb by two different ways: 1) adsorbed molecule occupies one site (on top adsorption); 2) adsorbed molecule occupies four sites (on facet adsorption).

To take into account own size of the molecules we involve infinity strong repulsive interactions between nearest-neighbor particles (adsorption to nearest-neighbor sites around adsorbed molecules is prohibited). The model was studied with grand canonical ensemble. The model parameters are chemical potential μ, temperature T and Δ – difference between the adsorption heat on facet and on top adsorption.

One of the methods used for calculations was transfer-matrix technique. The transfer-matrix is generated for stripe cut out from the square lattice with M sites along X axis and with infinity length along Y axis. Along X axis periodic boundary conditions are used. For our model the state of the surface in whole can be described as set of lattice site states, each ones can be in six states. On the other hand, we used the standard Monte Carlo method. The sites were arranged in a square lattice of side L $(N=L\times L)$, with conventional periodic boundary conditions. With this method phase diagram was made.

The multiple-histogram reweighting and finite-size scaling techniques (the fourth-order Binder's cumulant of the order parameter) have been used to estimate the phase diagram of the system. In the case of a first-order transition the density distribution *P(ρ)* had a double peaked structure. The second-order phase transition was estimated from the intersection of the reduced fourth-order Binder's cumulant.

The isotherms and dependencies of lattice coverage as functions of chemical potential were calculated and shown in Fig. 1. The dependence of coverage on chemical potential has no monotonous behavior at sufficiently higher value of Δ, it means that with increasing of pressure in gas phase the quantity of free sites growths too. This phenomenon is explained with mutual influence of two factors: nonlinear shape of molecules and its different orientation in adlayer. However, isotherms, as it follows from general thermodynamic lows, are monotonous increasing functions. The analysis of the results allows us to conclude the effect of non-monotonous changing of coverage depends on appearing of specific ordered phases on the surface (Fig. 2). In the case of Δ=*30 kJ/mol* the phase diagram was made up with Monte Carlo technique. There are three well-defined regions which correspond to the ordered structures.

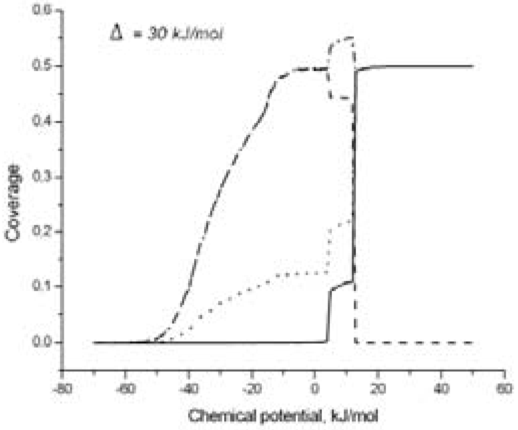

Fig. 1. Dependencies of lattice coverage. Solid line – adsorption on top; dash line – adsorption on facet; dot line – adsorption isotherm; dash dot line – total coverage.

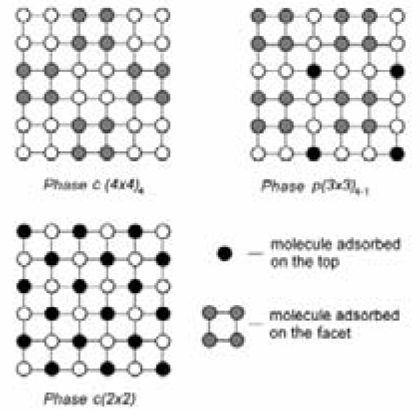

Fig. 2. Ordered structures observed on the surfaces in our model.

Conclusions: (1) there is the effect of non-monotonic changing of the coverage versus pressure for the model under consideration; (2) in the some ranges of chemical potential values the existence of chess-like specific phase is shown (Fig. 2). The cause of the existence of given phase is established to be the nonlinear shape of one of the adsorption active complexes and different orientation of the molecules in adlayer; (3) for the value of Δ=*30 kJ/mol* the phase diagram was calculated. It was shown that there are two three-critical point in it.

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OP-I-11

KINETIC ASPECTS OF METHANE OXIDATION BY O_2 AND N_2O OVER V_2O_5/SiO_2

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Nitrous oxide has been explored as an oxidant in the different catalytic reactions [1] including methane partial oxidation [2-4]. According to [4], the relationship between the rates of methane oxidation by O_2 and N_2O over V_2O_5/SiO_2 depends on the reaction temperature. The aim of the present work is to study the mechanistic causes of the temperature affect on the relative rates of methane oxidation by oxygen and N_2O.

Steady-state catalytic runs were performed in fixed-bed quartz reactor (11 mm i.d.) over 1.4%V_2O_5/SiO_2 prepared with chemical vapour deposition method and 3.6%V_2O_5/SiO_2 prepared with the impregnation. The support was fumed silica A-380 (380 m^2/g). The catalyst granules (0.5-1mm) were diluted with quartz granules to improve a temperature control. Inlet concentration of methane was 30 vol.%, N_2O 30 vol.%, O_2 15 vol.%.

Figs. 1a and 1b show the dependence of reaction selectivity on methane conversion over 1.4%V_2O_5/SiO_2 catalyst. As seen, the selectivity dependencies for the main reaction products (formaldehyde and CO) on methane conversion are similar; the CH_2O/CO ratio is in a little dependence on the oxidant.

Fig.1a. 550°C

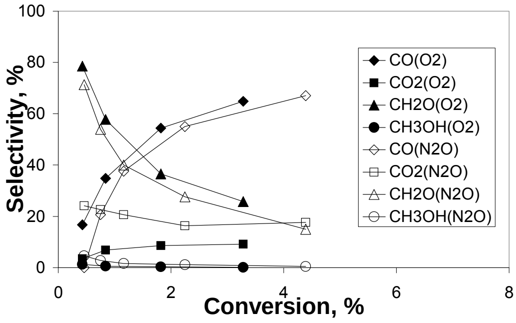
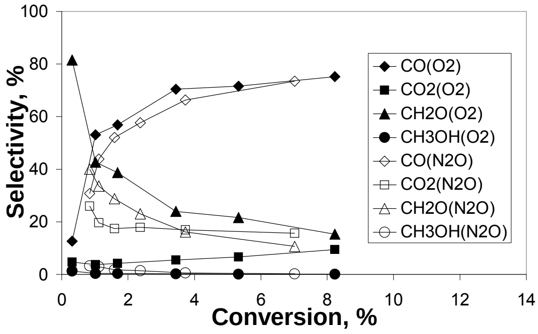


Fig.1b. 575°C



The temperature increasing leads to inversion of the levels of the reaction rates (Fig. 2a). The obtained activation energies for N_2O and O_2 are equal to 116 and 232 kJ/mole, correspondingly. The qualitatively same result was obtained for 3.6%V_2O_5/SiO_2 catalyst with energy activation 158 kJ/mole for N_2O and 227 kJ/mole for O_2.

Attempts to explain the different action of N_2O and O_2 using different versions of the «two-step» mechanism of the Mars-van Krevelen type had no success. Quite satisfactory explanation can be made using the following scheme of the surface chain reaction mechanism like mechanism proposed by Kazansky for CO oxidation over V_2O_5/SiO_2 catalyst [5]:

(1) $[V^{5+}O^{2-}V^{5+}] + CH_4 \rightarrow 2V^{4+} + \text{products}$ chain generation

(2) $V^{4+} + N_2O \rightarrow [V^{5+}O^{-}] + N_2$

(3) $V^{4+} + O_2 \Leftrightarrow [V^{5+}O^{2-}]$

(3a) $[V^{5+}O^{2-}] + V^{4+} \rightarrow 2\,[V^{5+}O^{-}]$ chain propagation (steps 2-4)

(4) $[V^{5+}O^{-}] + CH_4 \rightarrow V^{4+} + \text{products}$

(5) $[V^{5+}O^{-}] + V^{4+} \rightarrow [V^{5+}O^{2-}V^{5+}]$ chain termination

For such mechanism, an inversion of the reaction rate position becomes possible (Fig. 2b). The reaction rate simulation was made using the realistic values of the pre-exponential factors [6]: $k_{1,o} = 10^{12}$, $cm^3/(mole \cdot s)$; $k_{2,o} = 10^{11}$, $cm^3/(mole \cdot s)$; $k_{3,o} = 10^{12}$, $cm^3/(mole \cdot s)$; $k_{-3,o} = 5 \cdot 10^{13}$, s^{-1}; $k_{3a,o} = 10^{14}$, s^{-1}; $k_{4,o} = 10^{12}$, s^{-1}; $k_{5,o} = 10^{10}$, s^{-1}; activation parameters: $(E_i/R, K)$: $E_1/R = 20000$; $E_2/R = 0$; $E_3/R = 0$; $E_{-3}/R = 30000$; $E_{3a}/R = 15000$; $E_4/R = 10000$; $E_5/R = 5000$; and concentrations: $[R] = [N_2O] = 2[O_2] = 1.25 \cdot 10^{-5}$, $mole/cm^3$ (30 vol.% at 1 atm).

Fig2a. Experimental data

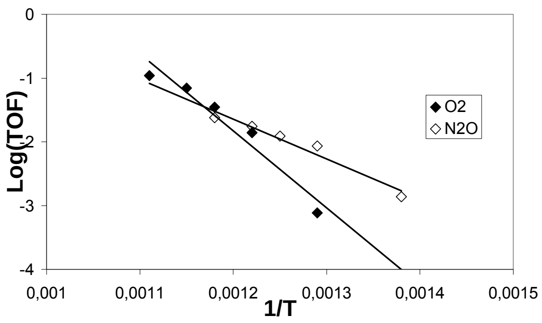
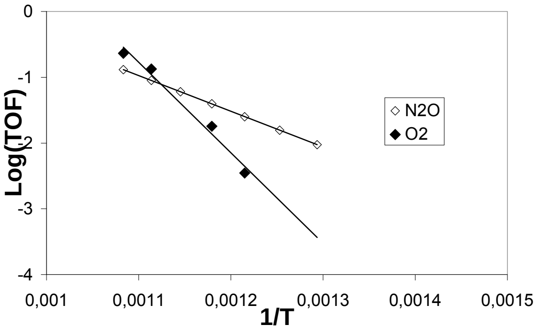


Fig2b. Simulated data



Simulated data are in a qualitative accordance with experimental data. It can be also noted that participation of both O^{-} anion-radicals and O^{2-} ions in the reaction of partial methane oxidation with N_2O over MoO_3/SiO_2 is assumed in [7]. Besides, the mechanism, proposed in [7], is, in fact, the surface chain mechanism like mechanism analyzed in the present work.

Obtained results allow to make conclusion that N_2O as an oxidant is more appropriate for low-temperature oxidation reactions proceeding on easy reducible oxide catalysts.

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KINETIC STUDIES IN STRUCTURED REACTOR WITH THE FRAGMENT OF MONOLITH CATALYST

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The kinetic study of high-temperature processes at relevant experimental conditions, in particular, realized on monolithic catalysts at short contact times, is a complicated task which demands the use of special structured reactors of small scale. In analogy to the case of monolithic reactors for industrial applications, such model reactors allow to realize the investigations at high space velocities, and the impact of mass transfer, pressure drop and temperature gradients along the catalyst length can be minimized. The advantages of annular and metallic plate-type structured reactors for kinetic measurements under severe conditions were shown for the case of CH_4 and CO combustion over a PdO/γ-Al_2O_3 catalyst [1]. Catalyst units for these reactors were prepared specially via coating some ceramic or metallic surface by a thin catalyst layer.

In structured reactor used for the study of partial oxidation of methane (POM) into syngas over LaNiPt–catalyst, separate structured elements of a real monolith are tested in a quartz tube at short contact times [2]. The aim of present work is the analysis of such structured reactor behavior for a monolithic catalyst based on a honeycomb α-Al_2O_3 support with triangular channels.

Experimental

For the purpose, the triangular fragments of a porous monolithic LaNiPt/α-Al_2O_3 catalyst with one separate straight channel with wall thickness 0.2 mm, side of the channel 2.3 mm, and length of 10-20 mm were used for the experiments. Thus, the catalyst shape and structure corresponded completely to a real catalytic system. The POM testing of the fragments was performed in a plug-flow quartz reactor of 4 mm ID at atmospheric pressure. The temperature of the catalytic bed was varied in the range of 600-900 °C and controlled precisely by thin thermo-couples placed along the catalyst length. The reaction mixture contained 3–12 % of methane and 1.5–6 % of oxygen flowing with the rate in the range of 5–30 l/hour, i.e., at 4–15 ms contact time.

Impact of inter-phase mass transfer

The axial profiles of mass transfer rates between gaseous flow phase and the catalyst wall were determined on the basis of the approaches developed for local Sherwood number in honeycomb monolith matrices [3,4]. The simulation was fulfilled for all range of temperatures and gas velocities given above. The analysis of inter-phase mass transfer influence on the reaction rate in this structured reactor was performed on the base of a one-dimensional model with evaluated mass transfer correlations and the restrictions on the catalyst activity for studied operation conditions were defined, while the reaction occurs in the chemical or chemical-diffusion- controlled regime.

POM reaction

A number of experimental runs with variation of contact time, temperature and feed composition was fulfilled to study the dependence of the reagent (CH_4 and O_2) and product (H_2, CO, CO_2) concentrations on the operation conditions. In all cases, the rise of temperature and/or contact time leads to the increase of product selectivity. At high temperatures, when oxygen is absent in the gas phase, such impact reveals the importance of indirect pathway of methane oxidation as well as the rise of CH_4 conversion and CO selectivity indicates the methane transformation through reforming reactions following the deep oxidation. At contact time of 4.7 ms and temperatures below 750 °C, syngas is formed in the presence of oxygen. It could be supposed that the syngas generation can proceed by the direct selective oxidation of methane.

The data were processed to estimate the rates and its kinetic parameters of the main independent reaction pathways on the catalyst developed. The experimental points for data processing were selected with minimal influence of mass transfer according to the analysis given above as well as with minimal temperature gradients. The kinetic characteristics of deep methane oxidation as well as steam and dry reforming were determined, and the contribution of the direct route of partial oxidation of methane was evaluated.

Thus, the studies performed show that the suggested construction of the small scale reactor with separate structured element of a real catalyst is promising for the kinetic studies under severe conditions. This reactor can be used also as effective tool to predict the characteristics of catalyst behavior for real industrial conditions.

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OP-I-13

A STUDY ON THERMAL COMBUSTION OF LEAN METHANE – AIR MIXTURES: SIMPLIFIED REACTION MECHANISM AND KINETIC EQUATIONS

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The combustion of lean methane – air mixtures combined with the recovery of the heat of reaction is an important problem for the mining industry, as methane concentration in mine ventilation air is usually below 1 vol.%. Since the flowrates of this air from a single ventilation shaft usually exceed 500,000 m^3/h, the methane gas should be somehow utilized rather than released into the atmosphere. One of the most reasonable options seems to be the combustion of CH_4 in reverse-flow reactors with the simultaneous heat recovery. Both catalytic and non-catalytic (thermal) reverse-flow reactors are intensively studied. In both types of reactors homogeneous combustion occurs in the gas phase. Therefore, the knowledge of the mechanism and kinetics of the combustion is crucial in the design and simulation studies.

The homogeneous oxidation of methane is undoubtedly a free-radical reaction which may consist of several (or even hundreds) of elementary reactions. Detailed kinetic mechanisms are used to describe, on a molecular level, the transformation of the reactants into a number of by-products. An extensive literature survey did not yield any unique kinetic mechanism for the homogeneous combustion of methane. The process is often described based on elementary reactions (from around a dozen to several tens to as many as 835). These reactions are described by kinetic equations which are then coupled numerically to yield the concentrations of reactants, by-products and end-products of the process. Highly detailed and complex combustion mechanisms obtained by several authors using numerical simulations may differ widely. From the practical standpoint, simulations based on several hundred reactions are not only tedious, but also numerically unreliable due to the accumulation of numerical errors in the strongly nonlinear differential equations. Moreover, the open literature does not provide any clue as to which of the whole variety of the models should be used in a specific case. Consequently, alongside these complex kinetic models attempts have been made to describe homogeneous combustion using a simplified single-step (or containing less than ten steps, at most) model of the process, which would bypass the most of free-radical reactions. In a study presented at CHEMREACTOR – 17 and then published (Gosiewski et al., 2007a) it is demonstrated that single-step kinetic models derived from various sources lead to divergent simulation results. In another study (Gosiewski et al., 2007b) the kinetics of homogeneous combustion over a monolith was studied based on a simple, single-step reaction scheme leading to CO_2 and H_2O. At that time, this scheme was regarded as satisfactory as the relevant experiments did not show the presence of CO in the gaseous product. However, the problem of CO formation is by no means resolved, as some authors (Slepterev et al., 2007) clearly point out that the combustion of methane at comparable concentrations, at temperatures of up to 900 °C, may lead to temporary presence of substantial amounts of CO.

The previous studies carried out on a monolith packing were thus extended onto combustion in a free space. These studies were done in an empty cylindrical reactor (10 mm x 210 mm), over a temperature range of 500 °C to 890 °C and for methane concentrations from 0.5 vol.% to 1.4 vol.%; the flowrate of the feed gas was kept at 120 l/h. Since the reactions might potentially occur in the inlet and outlet tubes of the vessel, the gas velocity was chosen such that the combustion only took place inside the reactor itself. The study corroborates earlier results obtained elsewhere (Slepterev et al., 2007), that the combustion in a free space, over certain temperature ranges, occurs with the production of considerable amounts of carbon monoxide, and only at higher temperatures does it lead to carbon dioxide. It can therefore be assumed that the oxidation of methane in this system is a consecutive reaction. A comparison between methane combustion in a free space and the same process over a monolith reveals that the ignition temperatures for the mixture methane – air differ considerably. This temperature is about 300 °C higher for the combustion in a free space (around 830 °C for the free-space oxidation and 530 °C for the monolith combustion). The results obtained so far have shown that the mechanism of the reaction strongly depends on the environment in which the combustion occurs. Furthermore, whereas the monolith combustion is a fairly stable process, the free-space oxidation is unstable and the results may be difficult to reproduce. We may theorize that the large surface area of the monolith channels may have a major effect upon the products of the combustion by activating oxidizing radicals. For the combustion conditions investigated a number of hypothetical simplified reaction mechanisms were studied. The estimation of kinetic parameters for these mechanisms will be presented together with a comprehensive analysis of the results thus obtained.

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OP-I-14

KINETICS OF THE CONVERSION OF METHANE−OXYGEN−STEAM MIXTURES IN FILTRATION REACTOR

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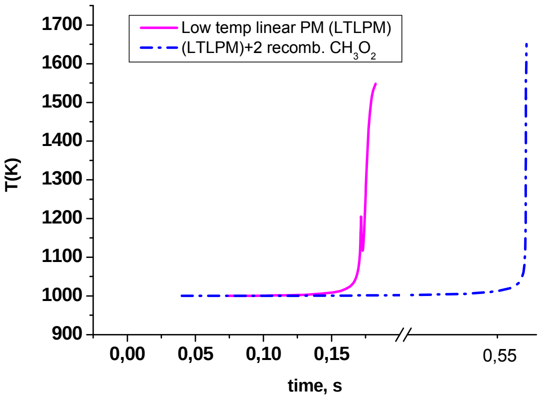
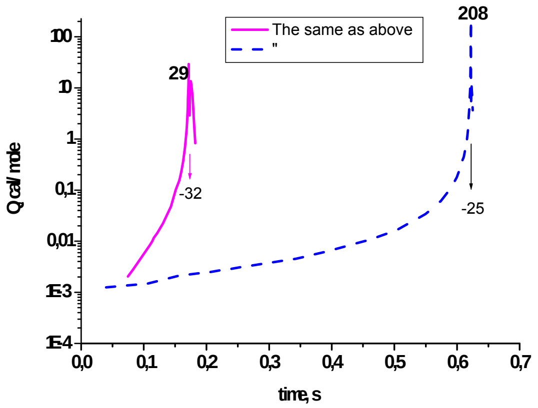
We consider the inclusion of detailed kinetics in a model of the conversion of methane-oxygen-steam mixtures to syngas proceeding in the regime of filtration combustion (FC) in an inert porous medium. The study is motivated by the energy-saving effect, which might be achieved due to super adiabatic regime (SA) of FC. A number of previous FC studies showed that it is primarily kinetics that determines both conditions for materialization of SA and parameters of the combustion wave. A number of questions arose in development of a kinetic scheme adequate to formation of stationary FC wave. For example, to what extent the concepts of gas-phase kinetics can be applied to gas mixture conversion in a very small (size of a solid pore) stream reactor? In particular, how to describe, in this case, the surface kinetics? If the FC wave is not kinetically uniform, that the using standard programs (such as CHEMKIN, GRI-Mech, etc.) may appear most simple in order to descript it? Those programs are supplied usually with extensive databases, which must be reduced anyway. But should perform the reduction similar to [1-3], i.e. using the stationary concentrations method?

To answer all those questions, we used the approach developed [4] for investigation of the properties of kinetic models describing primarily ignition, particularly, in methane oxygen mixtures – in absence [5, 6] and presence [7, 8] of water. This approach allows one to select so-called critical fragments of the reaction scheme and is applicable not only to ignition but to each significant stage along the FC wave. On other hand, we may take into account that the initial and following stages mechanisms rule the further processes.

This is illustrated by two figures bellow, which present the solution for undistributed kinetic problem for initial stage of conversion of the studied mixture under the atmospheric pressure in a reactor with d=0.6 cm. Compared are two variants of low-temperature linear peroxide model (LTLPM) of ignition. Both models also incorporate primary sources of hydrogen, including non-linear ones. In the first case, two reactions of CH_3O_2 radicals with active intermediates CH_2O and CH_3OH, accelerating the accumulation of branching peroxide, were added to the model, while in the second case – two more quadratic reactions of CH_3O_2, decelerating the process. One can see that both kinetics have two rising stages. During the first of ones the oxygen is consumed and heat is accumulated, faster and slower, respectively.





While, the maxima of both heat release and temperature prove to be much greater just in the case of the initial reaction rate slowing down with the quadratic reactions (at right), one of which is highly exothermic. The last, apparently, is one of stronger preheating sources in the reaction zone. Thus, in this case the system got more energy for an initiating of following heat absorption stage, being be trigger of all possible endothermic processes. Then, the gradually weakening brunched oxygen cycle competes with equally hardening oxygen-free one, and the second rising stage begins. Judging by the reactions which contribute to heat release on this stage, the H atoms and CH_3 radicals, released from the peroxide form, play a leading part in it, while the role of oxidizer comes to water. Thus, if one will be extended at now the responsible variant of model by observable number of reactions of these active agents and their interactions product, then it has be reached a good level of the description of the mixed chain-heat process of combustion oneself. The kinetic features of the system are analyzed responsible for the influence of different factors on the process regimes.

The work is supported under project No.6025 on the RAS Presidium Program of physical-chemical investigations «New Approaches to the Fuels Chemistry and Power Engineering».

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HYDROCRACKING OF LONG CHAIN LINEAR PARAFFINS

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Hydrocracking is a fundamental process in refinery practice, becoming increasingly important for fuel upgrading. Usually a bifunctional catalyst is employed, with metallic sites promoting the hydrogenation/dehydrogenation step of the reaction, coupled with acid sites responsible of the isomerisation/cracking events. Kinetic modelling of such a process is a hard task, due to the complexity of the reaction network involved. Furthermore, analytical and experimental problems arise when dealing with complex feeding mixtures, as well as when investigating the reactivity of long chain paraffins. Up to now detailed kinetic schemes have been developed for relatively light paraffins only, mainly based on the so called single event approach [1-4]. Empirical models have been drawn for complex feeding mixtures [5-8]. The aim of the present work was then to set up an experimental apparatus allowing to test the reactivity of two model reactants, namely n-C16 and n-C28. Conversion and products distribution has been determined under different reaction conditions, aiming at defining a kinetic model for the scale up of the process.

Experimental

A continuous mini-pilot plant was set up, equipped with a downflow tubular reactor, loaded with 5 g of a catalyst made up of platinum over amorphous silica-alumina (particle size 40-60 mesh). Particular care was put in keeping hot all the feeding and product lines, to avoid solidification of the heavier species. Products analysis has been carried out by gas chromatography on both the outcoming liquid and gaseous fractions. The reaction operating conditions have been varied following a factorial experimental design with four variables: pressure (20-80 bar), temperature (270-330°C), contact time (0.33-1.0 h^{-1}) and H_2/wax feeding ratio (0.05-0.15 wt/wt).

Results and discussion

The operating conditions of the central test have been selected so to obtain 50% conversion. This operation led to draw a preliminary deduction on the role of reaction conditions on catalyst activity and selectivity. The results of the kinetic tests carried out on n-C16 and n-C28 as model reactants can be summarised as follows: *a*) an increase of temperature and/or of contact time always induced an increase of both conversion and light products fraction, the latter effect being more evident for n-C16 than for n-C28, likely due to the higher contribution of secondary cracking reactions; *b*) an increase of pressure always depressed conversion, without significant influence on product distribution in the case of n-C16, but with a lowering of the light fractions in the case of n-C28; *c*) an increase of H_2/wax feeding ratio slightly improved conversion with a small increase of the light products fraction.

At first, kinetic modelling has been attempted by considering the following reaction scheme:

$$\text{n-Cx} \rightarrow \text{iso-Cx} \rightarrow \text{cracking products}$$

By using a simple PFR model with first order isomerisation reaction, apparent activation energy values of 31.2 and 31.1 kcal/mol were obtained for n-C16 and n-C28, respectively. The reaction order with respect to H_2 was -0.54 in the case of n-C28, whereas for n-C16 a non reliable value was obtained. Indeed, the assumption that H_2 partial pressure was equal to total pressure was unacceptable at low pressure and a different approach is needed. Attention is now focused on the development of a more detailed reaction scheme, aimed at designing a tool to provide a reliable description of the behaviour of the two model compounds here analyzed and suitable to be extended to the interpretation of the hydrocracking of real feedstocks.

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KINETICS IN THE HYDROGENATION OF β-SITOSTEROL TO β-SITOSTANOL OVER DIFFERENT Pd CATALYSTS

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Introduction

Nowadays, one of the most important problem for human health is high concentration of fats in food. Therefore, a lot of attention has been devoted to β-sitostanol, which was proved to inhibit cholesterol absorption [1], and is thus a constituent of some margarines available on the consumer market. The aim of the present work was to evaluate the catalytic activity of several materials in the hydrogenation of β-sitosterol, which is a product from pulping industry, in order to achieve a high selectivity towards β-sitostanol and to determine the reaction kinetics over the most promising catalyst. The main reaction scheme is presented in Fig 1.

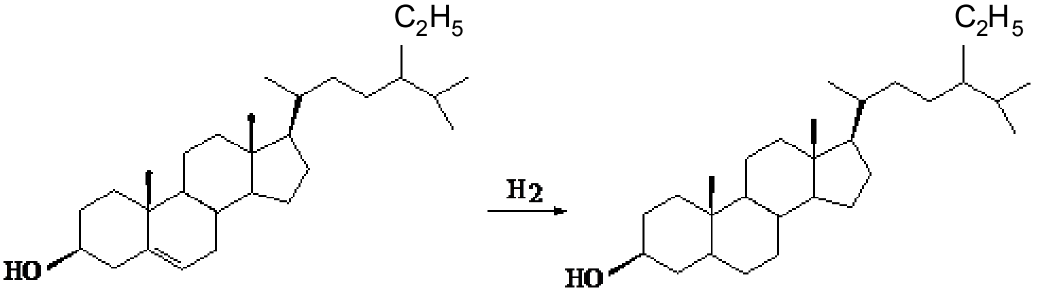

Fig. 1. Reaction scheme for β-sitosterol hydrogenation.

Experimental

The kinetic experiments were performed in a shaking reactor using 1-propanol as a solvent. The volume of the liquid phase was 110 mL and the pressure was set to 4 bar. The raw material according to results obtained from GC-MS analysis were: 82 wt.% β-sitosterol, about 7 wt.% campesterol, 9 wt.% β-sitostanol and 1 wt.% campestanol. The β-sitosterol hydrogenation was carried out in the presence of 1-propanol, and several supported Pd catalysts. The samples were withdrawn periodically from the reactor which operated at 60°C to 80°C. After addition of an internal standard solution consisting of heneicosanoic acid and betulinol, the reaction mixture was evaporated under nitrogen and silylated at 60°C for 45 min with BSTFA-TMCS-pyridine solution and analyzed by a GC equipped with an HP-1 column. Several catalyst characterization methods (CO-chemisorption, nitrogen adsorption, XRD) were applied. Furthermore, rapid UV analyses were applied for the reaction mixtures, being prior calibrated using GC analyses.

Results and discussion

Typical kinetic curves over Pd/C (Aldrich) at 80°C and 4 bar are displayed in Fig. 2.

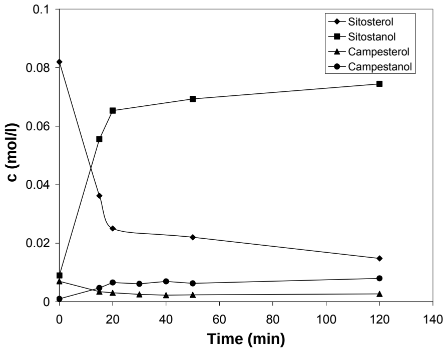

Fig. 2. Hydrogenation of β-sitosterol over Pd/C (360 mg) at 80°C and 4 bar overall pressure.

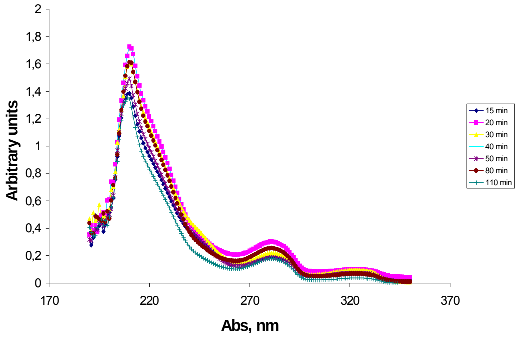

Fig. 3. UV-spectra of the reaction samples as a function of time.

Preliminary experiments demonstrated the crucial role of the catalyst. For instance, Fig 2 shows that maximum conversion of only 80 % could be achieved with lower (360 mg) catalyst amounts. The reaction was, however, 100% selective, since neither sitostane no sitostanone were found in GC-MS analysis.

Due to high selectivity, a fast analytical tool, e.g. UV spectroscopy could be used to measure the amount of ethylenic double bonds. Fig 3 shows the UV-spectra for the reaction mixture demonstrating in a reliable way, how the concentration of β-sitosterol is decreasing with time. The catalyst screening with the following Pd supported catalysts, Pd-SBA-15, Pd-MCM-41, Pd-CNF, Pd-C (Sibunit) as well as the kinetic experiments and the catalyst reuse with the most promising catalyst were performed and the results will be discussed in the final presentation.

Conclusions

Several supported palladium catalysts were screened in β-sitosterol hydrogenation. Catalyst deactivation was found to be crucial using lower amounts of Pd/C. Very high selectivity towards the desired product, β-sitostanol was achieved. A fast analytical tool, i.e. UV-spectroscopy was applied to monitor the reaction products.

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OP-I-17

MECHANISM OF FORMATION OF ETHYLENE BY SELECTIVE HYDROGENATION OF ACETYLENE OVER CERIA SUPPORTED GOLD CATALYST

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Ethylene is by far the basic petrochemical product most demanded with a production over 130 millions tons per year worldwide. Industrially, ethylene is usually formed by pyrolysis of hydrocarbons in the presence of steam. Acetylene is a by-product of ethylene production and acts as a poison for the catalyst used for the synthesis of polyethylene from ethylene, and should therefore be removed by selective hydrogenation. There are several types of catalysts suitable for hydrogenation of acetylene and they are usually using palladium. However, these catalysts still need to be improved, as the problem of selectivity at higher temperature and of oligomerization is not completely overcome. Gold has been found to be active for the hydrogenation of several reaction, such as acroleine, 1,3-butadiene, or even α,β insaturated ketones, but this propensity for hydrogenation has only rarely been studied for the alkynes molecules.

The present study was undertaken in an attempt to put in evidence the properties of hydrogenation of gold on a support not yet reported in the literature, namely ceria in order to propose a mechanism of selective hydrogenation of acetylene. The choice of ceria was made because we are able, with a method of preparation developed in our group, to perfectly control both the deposition and the dispersion of gold, so that nanoparticules of 2 nm are obtained. The method of preparation is based upon the direct anionic exchange (DAE) of the gold species with the hydroxyl groups of the support, and was reported in a previous publication [1].

The activity and selectivity has been measured between 30 and 400°C at different H_2/C_2H_2 ratio (R), namely, 3, 5, 7, 10, 30 and 60. The selectivity towards ethylene is of 100% up to 300°C independently of the different C_2H_2/H_2 ratios. The conversion follows a volcano shape trend for C_2H_2/H_2 ratio equal to 3, 5 or 7 with a deactivation above 300°C concomitant with the loss of selectivity, i.e. with maxima at 300°C. For higher H_2/C_2H_2 ratio, i.e. 10, 30 or 60, ***the conversion remains of 100%.*** The decrease of selectivity in C_2H_4 is due ***to the formation of*** CH_4**,** the formation of C_2H_6 was never observed contrary to all the results reported, the literature, mainly on Pd, in.

The activity measurements were completed by a kinetics study by varying the partial pressure of acetylene at constant hydrogen pressure and vice-versa in order to determine the apparent order of reaction. ***The order towards C_2H_2 was found to be negative and equal to -1.0 whereas the order toward hydrogen was found to be equal to 1.0***. The coverage of the surface byC_2H_2 is therefore constant and the rate is only a function of the hydrogen coverage which explains the increase of conversion at constant temperature when the hydrogen partial pressure increases.

Concentration of surface hydrocarbonaceous deposits accumulated during different treatments was also determined by temperature programmed oxidation (TPO). Hydrocarbon overlayer was observed to form immediately, and its presence appeared to be having a blocking effect only at very high concentration, the decrease of activity being due to the fact that these layers of carbonaceous deposits slow down the diffusion of the reactants towards the active sites. A large excess of hydrogen suppressed the formation of carbonaceous lay down and increased the over-hydrogenation of acetylene. Two types of carbon were identified, the first one formed at low temperature is not involved in the hydrogenation, the second one formed above 300°C is formed by surface carbenes which are key intermediates in the formation of methane.

At the issue of the presentation, a detailed mechanism of the various reactions pathways of acetylene hydrogenation on Au/CeO_2 will be presented.

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OP-I-18

KINETIC STUDIES OF PROPANE DEHYDROGENATION OVER Pt-Sn/Al$_2$O$_3$ CATALYST

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Introduction

One of the most selective processes to produce short-chain alkenes is the direct catalytic dehydrogenation of the corresponding alkanes. The kinetic study of isobutane dehydrogenation over different catalysts was represented in various publications [1,2,3]. Also kinetic study of propane dehydrogenation was performed over three different catalysts [4]. In this study the kinetics of propane dehydrogenation was performed over a commercial catalyst containing 0.6% Pt, 0.8% Sn and 0.85% K.

Experimental Section

The dehydrogenation reactions were carried out in a continuous-flow fixed-bed micro reactor with a 10 mm inside diameter under atmospheric pressure and 580, 600 and 620 °C, with a molar ratio of 0.8 for propane to hydrogen. Based on our previous research, internal and external mass transfer resistances can be neglected in this study [5].

Kinetic Modeling

Several kinetic models were tested in this research. The following mechanisms were used to derive some of the kinetic models.

Mechanism I

$$C_3H_8\,(g) + S \longrightarrow C_3H_8....S$$
$$C_3H_8....S + S \longrightarrow C_3H_6....S + H_2....S$$
$$C_3H_6....S \longrightarrow C_3H_6\,(g) + S$$
$$H_2....S \longrightarrow H_2\,(g) + S$$

Mechanism II

$$C_3H_8\,(g) + 2S \longrightarrow C_3H_7....S + H....S$$
$$C_3H_7....S + S \longrightarrow C_3H_6....S + H....S$$
$$C_3H_6....S \longrightarrow C_3H_6\,(g) + S$$
$$2H....S \longrightarrow H_2\,(g) + S$$

Mechanism III

$$C_3H_8\,(g) + S \longrightarrow C_3H_8....S$$
$$C_3H_8....S + 2S \longrightarrow C_3H_6....S + 2H....S$$
$$C_3H_6....S \longrightarrow C_3H_6\,(g) + S$$
$$2H....S \longrightarrow H_2\,(g) + 2S$$

Mechanism IV

$$C_3H_8\,(g) + S \longrightarrow C_3H_7....S....H$$
$$C_3H_7....S....H + S \longrightarrow C_3H_6....S....H + H....S$$
$$C_3H_6....S....H \longrightarrow C_3H_6\,(g) + H....S$$
$$2H....S \longrightarrow H_2\,(g) + 2\,S$$

Mechanism V

$$C_3H_8\,(g) + S \longrightarrow C_3H_7....S....H$$
$$C_3H_7....S....H \longrightarrow C_3H_6\,(g) + H....S....H$$
$$H....S....H \longrightarrow H_2\,(g) + S$$

Mechanism VI

$$C_3H_8\,(g) + S \longrightarrow C_3H_8....S$$
$$C_3H_8....S + S \longrightarrow C_3H_7....S + H....S$$
$$C_3H_7....S + S \longrightarrow C_3H_6....S + H....S$$
$$C_3H_6....S \longrightarrow C_3H_6\,(g) + S$$
$$2H....S \longrightarrow H_2\,(g) + 2S$$

Kinetic models which are presented in Table 2, will be referred to in the form «model I-a» or «model II-b», where the Roman numeral indicates the mechanism and the letter (a or b) indicates Rate Determining Step (RDS). Letter «a» refers to the adsorption of propane over solid catalyst and «b» refers to the surface reaction.

Table 2: Proposed reaction rate equations based on above mentioned mechanisms.

Model	Rate Equation	Model	Rate Equation	Model	Rate Equation
1	$k'(P_P - \frac{P_{Pr}P_{H_2}}{K_{eq}})$	7 (III-b)	$\frac{k'(P_p - \frac{P_{pr}P_{H_2}}{K_{eq}})}{(1+K_pP_p+K_{pr}P_{pr}+(K_{H_2}P_{H_2})^{0.5})^3}$	13 (VI-b)	$\frac{k'(P_p - \frac{P_{pr}P_{H_2}}{K_{eq}})}{(1+K_pP_p+K_{pr}P_{pr}+(K_{H_2}P_{H_2})^{0.5}+K'P_{pr}P_{H_2}{}^{0.5})^2}$
2 (I-a)	$\frac{k'(P_P - \frac{P_{Pr}P_{H_2}}{K_{eq}})}{1+K_{PrH_2}P_{Pr}P_{H_2}+K_{Pr}P_{Pr}+K_{H_2}P_{H_2}}$	8 (IV-a)	$\frac{k'(P_p - \frac{P_{pr}P_{H_2}}{K_{eq}})}{1+K_{PrH_2}P_{pr}P_{H_2}+(K_{H_2}P_{H_2})^{0.5}+K'P_{pr}P_{H_2}^{0.5}}$	14	$\frac{k'(P_p - \frac{P_{pr}P_{H_2}}{K_{eq}})}{1+K_{PrH_2}P_{pr}P_{H_2}+K_{pr}P_{pr}}$
3 (I-b)	$\frac{k'(P_P - \frac{P_{Pr}P_{H_2}}{K_{eq}})}{(1+K_PP_P+K_{Pr}P_{Pr}+K_{H_2}P_{H_2})^2}$	9 (IV-b)	$\frac{k'(P_p - \frac{P_{pr}P_{H_2}}{K_{eq}})}{(1+K_pP_p+K'P_{pr}P_{H_2}^{0.5}+(K_{H_2}P_{H_2})^{0.5})^2}$	15	$\frac{k'(P_p - \frac{P_{pr}P_{H_2}}{K_{eq}})}{1+K_{pr}P_{pr}+K_{H_2}P_{H_2}}$
4 (II-a)	$\frac{k'(P_P - \frac{P_{Pr}P_{H_2}}{K_{eq}})}{[1+K'P_{Pr}P_{H_2}{}^{0.5}+K_{Pr}P_{Pr}+(K'''P_{H_2})^{0.5}+K_{H_2}P_{H_2}]^2}$	10 (V-a)	$\frac{k'(P_p - \frac{P_{pr}P_{H_2}}{K_{eq}})}{1+K_{PrH_2}P_{pr}P_{H_2}+K_{H_2}P_{H_2}}$	16	$\frac{k'(P_p - \frac{P_{pr}P_{H_2}}{K_{eq}})}{(1+K_{H_2}P_{H_2})(1+K_pP_p+K_{pr}P_{pr})}$

5 (II-b)	$\dfrac{k'(P_P-\frac{P_{\text{Pr}}P_{H_2}}{K_{eq}})}{(K^{///}P_{H_2})^{0.5}[1+K^{//}\frac{P_P}{P_{H_2}^{0.5}}+K_{\text{Pr}}P_{\text{Pr}}+(K^{///}P_{H_2})^{0.5}+K_{H_2}P_{H_2}]^2}$	11 (V-b)	$\dfrac{k'(P_p-\frac{P_{pr}P_{H_2}}{K_{eq}})}{1+K_pP_p+K_{H_2}P_{H_2}}$	17	$\dfrac{k'(P_p-\frac{P_{pr}P_{H_2}}{K_{eq}})}{(1+(K_{H_2}P_{H_2})^{0.5})^2}$
6 (III-a)	$\dfrac{k'(P_p-\frac{P_{pr}P_{H_2}}{K_{eq}})}{1+K_{pr}P_{pr}+(K_{H_2}P_{H_2})^{0.5}+K_{\text{Pr}H_2}P_{\text{Pr}}P_{H_2}}$	12 (VI-a)	$\dfrac{k'(P_p-\frac{P_{pr}P_{H_2}}{K_{eq}})}{(1+K_{pr}P_{pr}+(K_{H_2}P_{H_2})^{0.5}+K'P_{pr}P_{H_2}^{0.5}+K_{prH_2}P_{pr}P_{H_2})}$	P: Propane(A) Pr: Propylene(B) H_2=Hydrogen(C)	k': Rate Constant K_{eq}: Equilibrium Constant K: Adsorption Constants

Results and Discussion

Optimization programs in MATLAB software were used to minimize the absolute error and find the optimum values for rate equation constants. The results were presented in Table 3:

Table 3: Optimization results.

Model 1	Model 2	Model 3	Model 4	Model 5	Model 6
$k^{/}=3088.7\exp(\frac{-78.69}{RT})$	$k^{/}=28681.3\exp(\frac{-86.25}{RT})$ $K_{pr}=0.8443\exp(\frac{4.72}{RT})$ $K_{H_2}=4.3211\exp(\frac{0.07}{RT})$ $K_{prH_2}=1.3325$ $MSE=0.015$	$k^{/}=1631.1\exp(\frac{-64.67}{RT})$ $K_p=0.0609\exp(\frac{17.29}{RT})$ $K_{pr}=0.3123\exp(\frac{7.43}{RT})$ $K_{H_2}=0.0822\exp(\frac{18.99}{RT})$ $MSE=0.015$	$k^{/}=5.32\times10^{6}\exp(\frac{-113.74}{RT})$ $K_{pr}=7.45\times10^{-7}\exp(\frac{89.07}{RT})$ $K_{H_2}=0.2179\exp(\frac{9.36}{RT})$ $K'=0.1952$, $K'''=10.917$ $MSE=0.011$	$k^{/}=4.67\times10^{4}\exp(\frac{-85.45}{RT})$ $K_{pr}=5.91\times10^{-6}\exp(\frac{54.89}{RT})$ $K_{H_2}=0.9398\exp(\frac{2.84}{RT})$ $K''=0.5158$, $K'''=1.5814$ $MSE=0.011$	$k^{/}=48\exp(\frac{-46.09}{RT})$ $K_{pr}=2.27\times10^{-8}\exp(\frac{108.47}{RT})$ $K_{H_2}=4.78\times10^{-17}\exp(\frac{263.25}{RT})$ $K_{prH_2}=0.1616$ $MSE=0.015$
Model 7	**Model 8**	**Model 9**	**Model 10**	**Model 11**	**Model 12**
$k^{/}=136.2\exp(\frac{-49.83}{RT})$ $K_{pr}=1.25\times10^{-22}\exp(\frac{355.2}{RT})$ $K_{H_2}=0.0027\exp(\frac{28.48}{RT})$ $K_p=9.11\times10^{-8}\exp(\frac{102.19}{RT})$ $\mathrm{MSE}=0.015$	$k^{/}=7811.9\exp(\frac{-83.95}{RT})$ $K_{H_2}=0.0016\exp(\frac{36.03}{RT})$ $K_{prH_2}=0.1013$ $K'=0.0982$ $\mathrm{MSE}=0.015$	$k^{/}=1146.1\exp(\frac{-66.82}{RT})$ $K_{H_2}=0.0004\exp(\frac{45.78}{RT})$ $K_p=0.0008\exp(\frac{35.46}{RT})$ $K'=0.2012$, $\mathrm{MSE}=0.015$	$k^{/}=2647.6\exp(\frac{-77.09}{RT})$ $K_{H_2}=9.7\times10^{-5}\exp(\frac{52.22}{RT})$ $K_{prH_2}=0.2093$ $\mathrm{MSE}=0.023$	$k^{/}=36.7\exp(\frac{-42.74}{RT})$ $K_p=3.33\times10^{-17}\exp(\frac{248.65}{RT})$ $K_{H_2}=2.77\times10^{-6}\exp(\frac{94.92}{RT})$ $\mathrm{MSE}=0.023$	$k^{/}=1395.5\exp(\frac{-70.66}{RT})$ $K_{pr}=0.0087\exp(\frac{18.06}{RT})$ $K_{H_2}=3.54\times10^{-6}\exp(\frac{80.79}{RT})$ $K'=0.2341$, $K''=0.2006$ $\mathrm{MSE}=0.011$
Model 13	**Model 14**	**Model 15**	**Model 16**	**Model 17**	
$k^{/}=1064.6\exp(\frac{-66.09}{RT})$ $K_p=0.0067\exp(\frac{18.92}{RT})$ $K_{pr}=1.43\times10^{-5}\exp(\frac{69.31}{RT})$ $K_{H_2}=0.0002\exp(\frac{51.24}{RT})$ $K_{prH_2}=0.2019$, $MSE=0.011$	$k^{/}=3799.8\exp(\frac{-80.04}{RT})$ $K_{pr}=0.0006\exp(\frac{36.62}{RT})$ $K_{prH_2}=0.4821$ $\mathrm{MSE}=0.023$	$k^{/}=2509.2\exp(\frac{-76.79}{RT})$ $K_{pr}=0.0374\exp(\frac{12.45}{RT})$ $K_{H_2}=1.02\times10^{-6}\exp(\frac{82.14}{RT}$ $\mathrm{MSE}=0.023$	$k^{/}=1432.1\exp(\frac{-72.56}{RT})$ $K_p=1.67\times10^{-17}\exp(\frac{252.55}{RT})$ $K_{pr}=2.95\times10^{-6}\exp(\frac{80.69}{RT})$ $K_{H_2}=5.25\times10^{-7}\exp(\frac{91.06}{RT})$ $MSE=0.015$	$k^{/}=781.6\exp(\frac{-64.69}{RT})$ $K_{H_2}=3.3\times10^{-5}\exp(\frac{63.52}{RT})$ $\mathrm{MSE}=0.046$	

In this study, F-test (Fishers test) method was used for evaluation of kinetic models. So, for each model, analysis of variance table (ANOVA table) was prepared. MSE (Mean of Squares Error) that has been presented in Table 3 is a parameter which was calculated in ANOVA table. Based on ANOVA Table for investigated models, all models from statistical point of view are acceptable but based on MSE values, models 4, 5, 12, 13 are better than the others.

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OP-I-19

ACTIVITY AND DEACTIVATION OF ACIDIC CATALYSTS AT THE DEHYDRATION OF GLYCEROL

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Itroduction. In recent years, the increasing of biodiesel production has resulted in a price decline of raw glycerol, which make the aqueous glycerol as attractive compound for the synthesis of fine and crude chemicals [1]. The conversion of glycerol to acroleine opened a new route for a production of acrylate monomers from renewable raw materials [1-3]. The dehydration of glycerol in gaseous phase on acidic catalyst proceeds via formation of 3-hydroxypropionaldehyde (3-HPA) and 2-hydroxyacetone (2-HOAC) [1, 4]. The highest observed selectivity to acrolein was 55-70%. Moreover a formation of a large amount of by-products (25-40%) and catalyst deactivation was reported. In order to understand the mechanism of acrolein formation, we investigated the catalytic activity of solid supported phosphates (Al_2O_3/PO_4, TiO_2/PO_4) and selected SAPO samples in the dehydration of glycerol. Additionally the reactivity of 3-HPA and 2-HOAC toward dehydration and deactivation of acid catalysts in presence of water was studied.

Experimental. Al_2O_3-PO_4, TiO_2-PO_4 catalysts are prepared by impregnation methods, using H_3PO_4 solution and corresponded support or by sol-gel co precipitation of metal hydroxides with H_3PO_3. SAPO-34 and SAPO-11 were prepared by hydrothermal synthesis. The crystal structure of catalysts were characterised by X-ray diffraction, elemental analysis, XPS and thermal analysis (TG/DTA, TPO and NH_3-TPD). The gas-phase dehydration of glycerol and C3-hydroxy carbonyl compounds was conducted under atmospheric pressure in fixed-bed reactor. Before reaction catalyst were pre-treated for 5h in presence of water stream at 350°C, The reactions products of glycerol dehydration were condensed analysed by GC. The reactions product of 3-HPA and 2-HOAC thermolysis or decomposition were also analysed by online MS (Omni-Star; GSD-200C, Balzer-Pfeiffer-Vacuum) and GC/MS (Varian/Saturn).

Result and Discussions. Gas-phase dehydration of glycerol to produce acrolein was investigated at 325°C. The glycerol conversion and selectivity to acrolein and to side products depended on reaction conditions and strength of acids site. Other by-products included acetone, acetaldehyde, propionaldehyde, allylalcohl and 2-HOAC. Moreover a large amount (~ 25 %) of C6 compounds (Adol-condensation of 2-HOAC) were identified by GC/MS.

The conversion and selectivity to decomposition products observed for the reaction of 3-HPA and 2-HOAC are also strongly dependent on the texture and acidity of solid phosphoric acids. With the increase of intrinsic acidity and the reactions temperature the rise in conversion was observed. Additionally the decomposition C-C bond of glycerol and 2-HOAC and depositions of cokes was found. (Fig. 1a-c). This is due to the further decompositions of carbonyl compounds which are thermodynamically favourable at higher temperature.

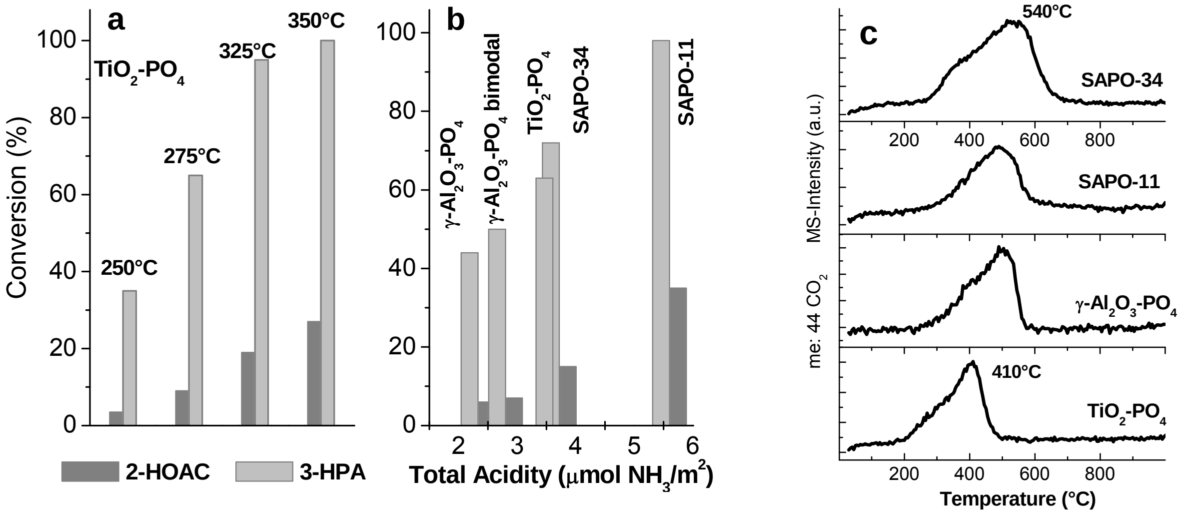

Fig. 1a-c. Conversion of 2-HOAC and 2-HPA over TiO_2-PO_4 at different temperatures (a) and different catalysts at 275°C (b) and the amount of carbon deposits (c) over catalysts after reaction with 2-HOAC at 310°C in the presence of water (DTA-MS Analysis).

Conclusions. Supported phosphates and SAPOs showed the different activity for the gas-phase dehydration of glycerol and degradation of 2-hydroxy acetone and 3-hydroxy propionaldehyde in the presence of water. The total acidity, the texture of the supported phosphates and the reactions temperature strongly influenced both conversion and distribution of the products. The experimental data showed that in the presence of the acidic catalysts 2-HOAC was stable until 240°C. In contrast, 3-HPA was dehydrated to acroleine and was subject of condensation to cyclic C_6 compounds already at 120°C. The side products were identified with GC-MS. Deactivation was observed for all of acid catalyst, but a oxidative treatment with air at the reactions temperature about 450°C was found to be sufficient to regenerate the deactivated catalysts and recovery of acidity and activity.

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OP-I-20

GAS PHASE OXIDATION OF FORMALDEHYDE INTO FORMIC ACID ON A V/Ti CATALYST: 1. REACTION KINETICS

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Introduction

Formic acid (FA) is produced commercially by a multi-stage hazardous technology. The Boreskov Institute of Catalysis has developed the one-stage gas-phase process of FA production by oxidation of formaldehyde (F) over the V_2O_5/TiO_2 catalyst. The goal of this work was to investigate reaction kinetics.

Experimental

Kinetic experiments were performed in a differential reactor with external circulation loop providing ideal mixing regime, at ambient pressure and range temperature 100-180 °C under variation of concentrations of F, oxygen and steam. The catalyst fraction was 0.25-0.5 mm. V/Ti catalyst (11%V_2O_5/90%TiO_2) was used. The BET was 140 m^2/g.

Results and discussion

The products of F oxidation over V_2O_5/TiO_2 catalyst are FA, CO and CO_2, and methyl formate minor quantity. In the range temperature 100-180 °C parallel-consecutive network of products formation is determined.

Reaction mechanism determined by IR spectroscopy and experimental kinetic data obtained resulted in the kinetic equations for the reaction rates according to reaction network. The kinetic parameters were calculated by minimizing the function, which represents the difference between the experimental and the calculated rates.

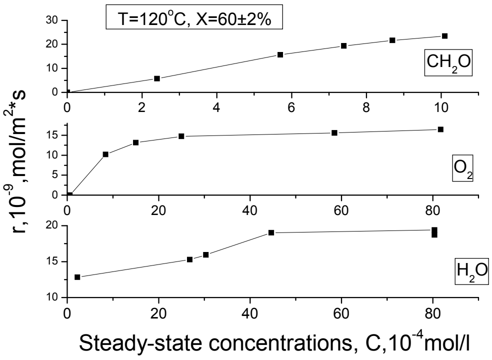

Fig. Effect of the concentrations on FA formation rate.

The work was supported by the Russian Foundation for Basic Research, Grant 06-03-32473-a, Grant 06-03-08137-ofs.

OP-I-21

DEACTIVATION KINETICS OF PLATINUM-BASED CATALYSTS IN DEHYDROGENATION OF HIGHER ALKANES

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Abstract: The deactivation of promoted Pt /Al_2O_3 catalyst in dehydrogenation of C_{10}-C_{14} normal alkanes to the corresponding mono-olefins was studied. A simple kinetic model for catalyst decay was obtained. The model was based on a reversible main reaction and concentration-independent, *n*th-order decay law. It was checked both through integral analysis of experimental data and nonlinear estimation functions of temperature-time data of a commercial plant and the model parameters were evaluated. The results of both approaches were consistent. The deactivation rate law was found to be of the second-order. The activation energies of the dehydrogenation and catalyst decay were found to be E_A =60 kJ/mol and E_d=230 kJ/mol, respectively.

Keywords: Dehydrogenation of alkanes; Pt/Al_2O_3 catalyst; Kinetics; Catalyst deactivation.

Introduction: In commercial practice, the activity of dehydrogenation catalyst drops slowly with time on stream. To achieve a constant conversion, the reaction rate is maintained by a programmed increase of the feed temperature.

The previous deactivation modeling by temperature-time trajectories were based on a single irreversible primary reaction and *n*th-order, concentration–independent deactivation [1, 2, 3]; however, in this work the main reaction was considered to be reversible and its consequence on the interpretation of the results was considered. The kinetic parameters were estimated using commercial temperature-time data and the results were compared with those of integral method of analysis of experimental data.

Experimental: The reactor tests were performed in a fixed-bed, isothermal reactor at 743 K and 0.7 barg using industrial feedstock with a H_2/hydrocarbon molar ratio of six. HP/PONA column of 50 m length, 0.2 mm diameter and 0.5 μm fill thickness and FID detector were used for liquid product analysis. The industrial data were provided by a commercial plant for three sets of runs, with start of run and end of run temperatures of 743 and 768 K, respectively.

Modeling: To achieve a constant conversion, Eq. (1) should be satisfied:

$$k_A(T)a(t,T) = k_{A0}\,\frac{X_{Ae}(T)\ln\left(1 - X_A(T)/X_{Ae}(T)\right)}{X_{Ae}(T_0)\ln\left(1 - X_A(t=0,T_0)/X_{Ae}(T_0)\right)} \qquad \text{Eq. (1)}$$

Where k_A is the rate constant, T temperature, t time, a catalyst activity, X_{Ae} paraffin conversion, and the subscript 0 refers to initial values. Assuming a reversible main reaction and concentration-independent, *n*th-order decay law, the kinetic parameters of model were obtained by genetic algorithm using commercial plant data. The experimental data were analysed through integral method of analysis.

Results and discussion: Both approaches showed a second-order decay law (Table 1) which was observed elsewhere for analogous reaction systems [4]. The model also fitted experimental results fairly (Figure 1).

Table 1. Kinetic parameters from experimental and industrial data

Experimental Data			Industrial Data		
k_{A0} (m^3/kg.hr)	k_{d0} (hr^{-1})	n	k_{A0} (m^3/kg.hr)	k_{d0} (hr^{-1})	n
9.2e+6	5.03e+12	2.0	5.3e+6	2.1e+12	1.9

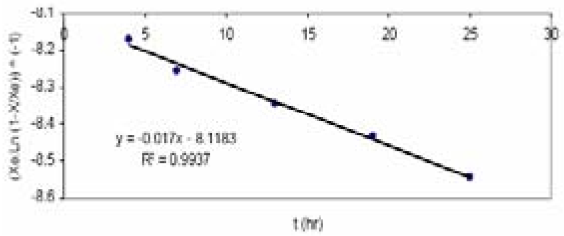

Figure 1. Integral analysis of experimental conversion –time data with *n*=2

The difference observed might be due to the fact that the commercial reactor was considered as isothermal in the model. It is nearly the case for the commercial reactor, because of the low level of conversion and the high volume of diluents present. However, because of the endothermicity of the reaction, the average bed temperatures should be slightly lower than the feed temperatures being used in calculations.

Conclusions: A second-order catalyst decay law was found to fit fairly long-term experimental and plant data for dehydrogenation of higher alkanes. The resulted kinetics is useful in dynamic simulation of commercial plants, especially, since the plant data and commercial feed were used in kinetic parameter estimations.

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ON THE DYNAMICS OF NH_3 FORMATION DURING REGENERATION OF NO_X STORAGE CATALYTIC MONOLITH

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Introduction

The NO_x storage and reduction catalyst (NSRC) is designed for abatement of nitrogen oxides emissions from diesel and lean-burn gasoline engines, where direct NO_x reduction is hindered due to an excess of oxygen in the exhaust gas. In the course of a longer lean phase (economical engine operation with lean fuel mixture, typically lasting for several minutes) the NO_x are adsorbed (stored) on the catalyst surface in the form of nitrites and nitrates (Epling et al., 2004). Several NO_x adsorbing components (Ba, K, Na, Ca, Li, Mg, etc.) can be used simultaneously in the NSRC washcoat, with particular temperature dependence of the effective NO_x storage capacity related to the basicity of the used components (Kobayashi et al., 1997). Then, the accumulated NO_x are desorbed and reduced within a short rich phase (excess of reducing components – CO, H_2 and hydrocarbons – in the exhaust gas, lasting several seconds). The exhaust gas enrichment can be realised by controlled (post-)injection of rich fuel mixture or other techniques (DieselNet, 2008).

Several nitrogen compounds can be produced during the regeneration phase in periodically operated NO_x storage and reduction catalyst (NSRC) for conversion of automobile exhaust gases. Besides the main product N_2, also NO, N_2O, and NH_3 can be formed, depending on the regeneration phase length, temperature, and gas composition (Epling et al., 2007; Kočí et al., 2008).

Experiments

This contribution focuses on experimental evaluation and kinetic modelling of the NO_x reduction dynamics during catalyst regeneration phase. Hydrogen, CO and C_3H_6 are examined as the reducing agents. Particular attention is devoted to the formation of ammonia that is identified as a main by-product and an important intermediate of the NO_x reduction under rich conditions (Cumaranatunge et al., 2007). An industrial NSRC monolith sample of $PtRh/Ba/CeO_2/\gamma\text{-}Al_2O_3$ type is employed in nearly isothermal laboratory microreactor (Kočí et al., 2008; Monolith, 2008). The NO_x storage/reduction experiments are performed in the temperature range 100-500 °C in the presence of CO_2 and H_2O.

Modelling

Spatially distributed NSRC model is developed (Kočí et al., 2008), considering the following ammonia reaction pathway: NH_3 is formed by the reaction of H_2 with NO_x and it can further react with oxygen and NO_x deposited on the catalyst surface, producing N_2. Considering this scheme with ammonia as an active intermediate of the NO_x reduction, a good agreement with experiments is obtained in terms of the NO_x reduction dynamics and selectivity. Reduction front travelling in the flow direction along the reactor is predicted, with the NH_3 maximum on the moving boundary. When the front reaches the reactor outlet, the main NH_3 peak is observed in the exhaust gas (Kočí et al., 2008).

Under certain operating conditions, a smaller NH_3 peak is observed experimentally at the reactor outlet just after the beginning of the regeneration phase (before the main NH_3 peak). We show that this more complex, double NH_3 peak dynamics can be described by the same spatially distributed model with proper values of kinetic parameters governing the rate of NH_3 formation and decomposition.

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STOCHASTIC MODELS FOR THE IMAGINATION OF SURFACE WAVES IN CATALYTIC REACTIONS OF CARBON MONOXIDE OXIDATION ON PLATINUM METALS

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We intend to compare the specific features of the statistical lattice models (based on the Monte-Carlo technique) for imitating the oscillatory and autowave dynamics in the adsorbed layer during carbon monoxide oxidation over Pt(100) and Pd(110) single crystals differing by the structural properties of catalytic surfaces. The statistical lattice model constructed for $(CO+O_2)/Pd$ reaction takes into account the change of surface properties due to the reversible penetration of the adsorbed oxygen into subsurface layer: $O_{ads} \leftrightarrow O_{sub}$ [1]. The statistical lattice model has been constructed for the $(CO+O_2)/Pt(100)$ reaction which takes into account the change of surface properties due to the adsorbate-induced reversible surface transformation hex ↔ 1×1 [2]. The model reproduces qualitatively the hysteresis and the oscillations of reaction rate, O_{ads}, CO_{ads} coverages, hex and 1×1 surface phases under the conditions close to the experimental ones. Autowave processes on the model surface accompany the oscillations of the rate of CO_2 formation and the concentrations of the adsorbed species in both cases. The existence of the reaction zone between the moving adsorbate islands characterised by the elevated concentration of the free active centres has been shown [2]. The presence of the narrow reaction zone was found experimentally by means of the field ion probe-hole microscopy technique with ~ 5 Å resolutions, Fig. 1 [3]. The simulated structure of the reaction zone is shown in Fig. 2.

In both cases (Pt(100), Pd(110)) the synchronous oscillations of the reaction rate and surface coverages are exhibited within the range of the suggested model parameters under the conditions very close to the experimental observations [1,2]. These oscillations are accompanied by the autowave behaviour of surface phases and adsorbates coverages. The intensity of CO_2 formation in the CO_{ads} layer is low, inside oxygen island it is intermediate and the highest intensity of CO_2 formation is related to a narrow zone between the growing O_{ads} island and surrounding CO_{ads} layer («reaction zone»), Fig. 2. The boundaries of oscillatory behavior and hysteresis effects have been revealed. The possibility for the appearance of the turbulent patterns in the case of Pt(100) [2] and Pd(110), the spiral [4] and elliptic waves on the surface in the cases under study has been shown.

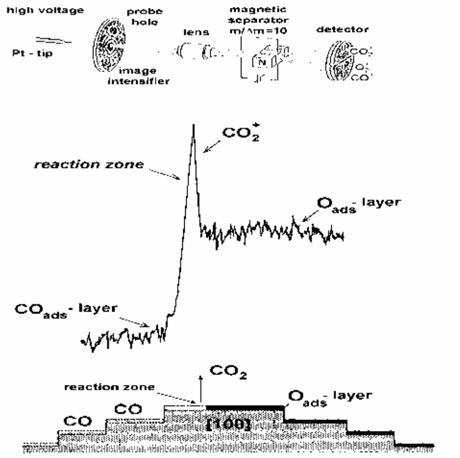

Fig. 1. Scheme of the FIM mass-analysis implemented by the probe-hole technique. Reaction-diffusion front monitored during CO + O_2 reaction on the Pt(100) – oriented Pt field emitter – experiment [3].

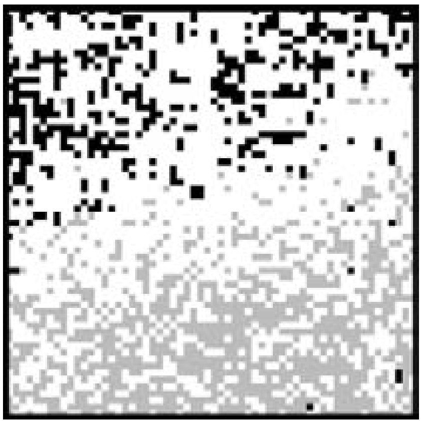

Fig. 2. Fine structure of the reaction zone. Black cells – O_{ads} on (1x1) surface, grey cells – CO_{ads}, white cells – empty Pt centres: Monte-Carlo simulation [2].

The elliptic waves in the form of the propagating islands and spirals of adsorbed oxygen appeared on the model surface, if we take into account the anisotropy of the CO_{ads} diffusion due to missing row reconstruction of the Pd(110) plane induced by the adsorption [5]. We found that, if this effect is taken into account, such integral characteristics as the reaction rate and surface coverages do not change. However, the propagation of the wave on the reconstructed Pd(110)-(1x2) surface becomes noticeably anisotropic. In addition, the hysteresis in oscillatory behaviour has been found in simulation experiments under step-by-step variation of oxygen partial pressure, i.e., two different oscillatory regimes could exist at one and the same parameters of the reaction [6, 7]. The parameters of oscillations, as well as the shapes of the surface patterns (cellular, target, turbulent, spiral and stripe oxygen waves) depend on the dynamic prehistory of the system (shape-memory effect).

Both experimental and simulation studies has been reviewed in [8, 9].

The study was supported by RFBR grant # 08-03-00454.

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OP-I-24

NONLINEAR PHENOMENA AND MECHANISMS IN CATALYST DEACTIVATION

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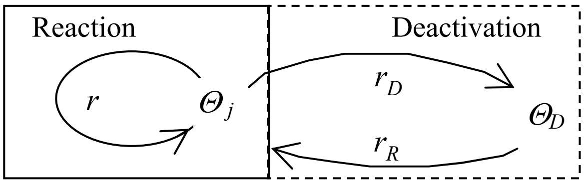
There are several phenomena in catalyst deactivation that are considered as nonlinear ones. Those are the volcano-shape of catalyst activity vs. time, the changing of selectivity during deactivation, the drastic drop of catalyst activity after long stable work, etc.

As a matter of fact, only some of them are caused by nonlinear mechanisms of deactivation. The others are related to the simultaneous action of several linear processes.

In this report, four types of nonlinear deactivation kinetics will be analyzed, caused by: 1 – combined effect of deactivation and self-regeneration; 2 – simultaneous formation and poisoning of active centers; 3 – precursors interaction in adsorbed layer; 4 – ions diffusion in catalyst bulk.

Deactivation and self-regeneration

Deactivation (r_D) and self-regeneration (r_R) are assumed to be slow steps external to catalytic cycle (r):



$$-\frac{da}{dt} = \frac{w_D}{w_j} r^o \frac{a - a_S}{1 - a_S} \qquad (1)$$

where r, r_D, r_R are rates of reaction, deactivation and self-regeneration;

Θ_j is the intermediate (coverage) participating in the rate limiting step of catalytic cycle;

Θ_D refers to the coverage excluded from the catalytic cycle due to deactivation;

r^o is the reaction rate on fresh catalyst; a_S is the "residual" activity;

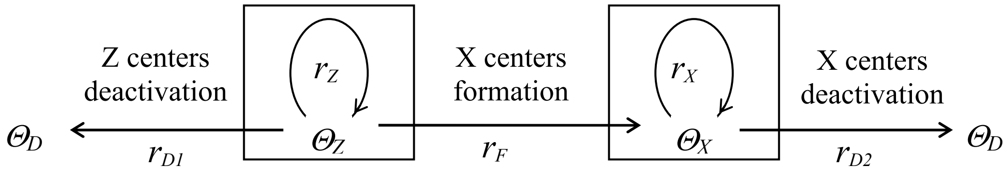
$w_j = r_j / \Theta_j$, $w_D = r_D / \Theta_j$ are weights of rate limiting step and of deactivation step.

According to [1, 2] the general equation for such a reversible deactivation has a form (1) in terms of relative activity $a = r / r^o = 1 - \Theta_D$. The «residual» or «stationary» activity (a_S) is achieved when the rate of deactivation (r_D) becomes equal to the rate of self-regeneration (r_R).

When a formal fitting of such deactivation experiments is applied, the nonlinear kinetics is usually required $da / dt = - k_P a^n$, at $n \geq 2$. Therefore, the apparent nonlinear kinetics of deactivation can be caused by self-regeneration phenomenon that accompanied the linear intrinsic mechanisms of reaction and deactivation.

«Qualitative» deactivation

In some catalytic processes, the formation of active centers and their deactivation occur simultaneously, during the reaction. Schematically it can be presented as a catalytic cycle on Z - type centers (reaction rate r_Z) with slow deactivation (r_D) and slow transformation (r_F) of Z to X - type centers (reaction rate r_X):

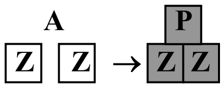
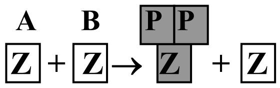
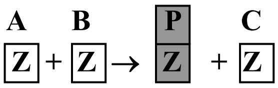


(2)

Such a «qualitative» deactivation leads to the volcano–shape nonlinear dependences of activity vs. time. Nevertheless, the mechanisms and intrinsic kinetics of each of three processes in scheme (2) can be linear.

Interaction in adsorbed layer

Most of nonlinear deactivation mechanisms can be reduced to binary interactions in the adsorbed layer, because of a very low probability for more than two species to interact on the surface. In this case, only three types of nonlinear binary interactions can be formulated:

Double-center adsorption	Surface dimerization	Surface disproportionation
		
1 molecule of precursor poisons 2 active centers 2 Z → 2 PZ	2 molecules of precursor poisons 1 active center 2 Z → 1 PZ	1 molecule of precursor poisons 1 active center 2 Z → 1 PZ

Z – active center, AZ, BZ – precursors of poison or coke, PZ – blocked center.

General deactivation equations for these schemes take following nonlinear forms [1]:

$$-\frac{da}{dt} = w_D\,(\Theta_i^o\Theta_j^o)\,a^2, \qquad -\frac{da}{dt} = 2\,w_D\,(\Theta_i^o\Theta_j^o)\,a\sqrt{a} \tag{3}$$

Diffusion of ions in catalyst bulk

The mobility of ions and atoms in solid catalysts is widely observed and can influence the catalytic reaction significantly. It concerns the mobility (diffusion) of oxygen ions in metal oxides [3], of chlorine in metal chlorides [4], etc. Since ions diffusion in bulk is caused by reaction on the surface, it affects the state of surface, and consequently affects the reaction dynamics. Because the capacity of bulk is much higher than that of the surface, ions mobility increases the working period of the catalyst (decreasing its deactivation). It makes acceptable the non-stationary cyclic regime of the process with reaction and catalyst recovery periods.

Such a regime provides usually higher selectivity than the stationary one in oxidation processes. In other processes it can increase the «catalyst life», or «poison resistance».

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OP-I-25

EFFECT OF CATALYST FRACTAL DIMENSION ON THE RATE CONSTANT OF HETEROGENEOUS CATALYTIC REACTION

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In present study we develop a theoretical approach**,** which reveals a relation between the catalyst fractal dimension and the rate constant. Based on the fractal approach [1] we derive the following dependence between pre-exponential factor of the reaction rate constant and catalyst fractal dimension:

$$\ln k_0 = A - BD_F = A - B\left(1 - \left(\frac{r_0}{r_m}\right)^{D_F - 2} \cdot \frac{r_m}{d}\right)^{-1} \qquad (1)$$

where $A = \ln k_{0R} + 2\ln\left(R/r_0\right)$, $B = \ln\left(R/r_0\right)$, k_o is the experimental value of the pre-exponential factor, k_{0R} is a size independent fraction of the pre-exponential factor, r_m gives the most probable radius of particles of active component which is obtained from the probability distribution function of active component, d gives particle size of an active component obtained from the study of specific adsorption of probe molecules with characteristic linear size r_0.

On the other hand, we show the following relation between activation energy, *E*, and fractal dimension:

$$\ln(E-E_0) = \ln(\pi\varepsilon) + D_F \ln(R/r) \qquad (2)$$

where E_0 gives activation energy of activated complex on isolated active site, R gives the radius of disturbed area of the surface, r is the radius of adsorbed molecule (active site), ε gives reorganization energy of one atom or molecule of the surface, D_F is the surface fractal dimension.

Hence, the rate constant of heterogeneous catalytic reaction may be expressed by the following equation:

$$k = k_{0R}\left(\frac{r_0}{r}\right)^{D_F - 2} \exp\left(-\frac{E_0 + \pi\left(\frac{R}{r}\right)^{D_F}\varepsilon}{RT}\right) \qquad (3)$$

We performed an experimental study to verify eq.1 and eq.2. We study the carbon monoooxide oxidation on silica, alumina, zeolite and acetone hydrogenation over dispersed metals. The fractal dimension was determined applying the FHH (Frenkel–Halsey–Hill) equation [2] to nitrogen isotherm adsorption. Experimental study of kinetic carbon monooxide oxidation and acetone hydrogenation were carried out in a fixed-bed reactor at atmosphere pressure.

Fig.1 shows experimental and theoretical dependencies between pre-exponential factor and average size of particles. There is a good correspondence between experimental data (solid squares) and theoretical results (solid lines). Fig. 2 represents a plot of ln(E-E$_0$) against the D$_f$, E$_0$=33±1 kJ/mol. Since this experimental data give rise to a good fit to the line predicted by the eq.2. Dependence between rate constant and fractal dimension is also discussed.

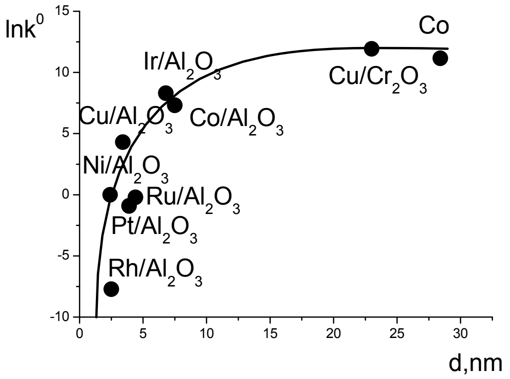

Figure 1. Dependence of pre-exponential factor on average size of particles

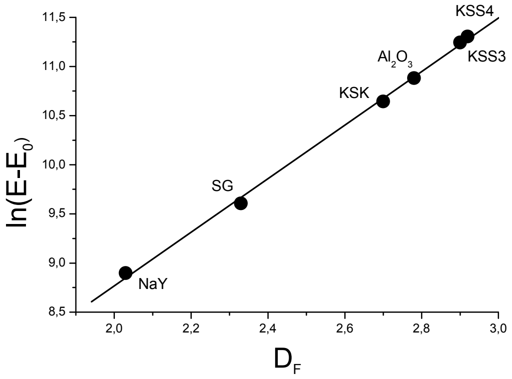

Figure 2. Dependence of activation energy on fractal dimension

Thus, in frame on fractal geometry of active component of catalyst we derive a relation (3) between rate constant and geometrical characteristics of catalyst. Theoretical results are in a good agreement with experiments. Our approach allows to determine activation energy of activated complex and disturbance energy of catalyst surface and radius such disturbance. It provides getting additional information about heterogeneous catalytic reaction mechanism and allows separating the chemical and structural contribution of catalyst to activation energy of heterogeneous catalytic process. Our approach opens new avenues for understanding structure sensitivity in heterogeneous catalysis.

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Section 2.

Physico-chemical and mathematical fundamentals of the processes in chemical reactors

OP-II-1

CHEMICAL NANOREACTORS AS BASE FOR NOVEL TECHNOLOGY(IES) OF NANOMATERIALS

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Rapid development of nanotechnologies causes demand for development of new technological approaches for production of nanostructured materials.

The traditional approach for creation of ultradisperse materials includes two stages: dispersion of substance and consolidation of disperse (or ultradisperse) powder.

The most progressive method of dispersion in chemical technology is mass crystallization, and the most widespread ways of consolidation are sintering or pressing.

This approach is well developed and successfully applied in production of materials, as a rule, the constructional materials with degree of dispersion more than 0.1 microns.

Direct application of this approach for preparation of nanomaterials with a dispersion degree in the range of 1 - 100 nanometers causes significant difficulties.

In this report scientific bases of technological processes for synthesis of functional nanomaterials with the characteristic degree of dispersion in the range of 1 −10 nanometers are analyzed in detail.

This approach includes two basic stages: colloid synthesis of nanoparticles and their self-assembly.

The main advantage of colloid synthesis is that it allows to receive nanoparticles of the defined shape and with very narrow size distribution.

It is reached by application of some techniques, including chemical nanoreactors which allow to control nanoparticle shape and sizes.

Basic techniques of nanoparticle self-assembly are considered. An opportunity to receive the nanoparticles of the defined size and shape is very important at programmed self-assembly.

MONTE CARLO SIMULATION OF ADSORPTION ON SUPPORTED NANOPARTICLES

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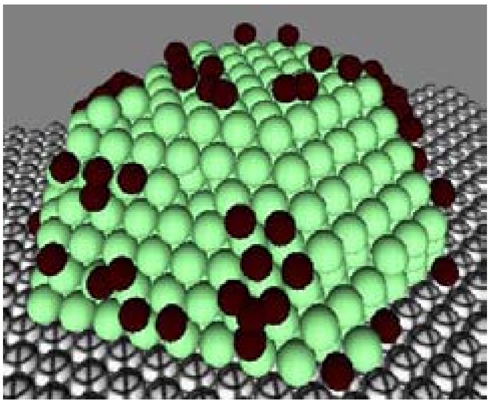
Introduction

Most of commercial catalysts consist of nanometer scale particles (1-100 nm) deposited on a porous support. Experimental researches of catalytic processes are rather expensive and hard to conduct and often there is no way to make direct measurements of interesting parameters. For successful interpretation of obtained results suitable mathematical models are required [1].

The computer model for simulation of metallic nanoparticles and adsorption on their surface has been developed. This model can be used for investigation of steady state of supported nanocrystals and adsorbate systems. The Metropolis algorithm is employed to archive the configuration with minimal potential energy. Using this approach it is possible to simulate bigger, than molecular dynamics allows, particles in a time period sufficient for putting the system in thermodynamic equilibrium. For evaluation of the system energy the model can use the many-body potentials. Here we have chosen the tight-binding second moment approximation (TB-SMA) potential which shows rather good agreement with experiments for fcc metals in case if sufficiently long interaction range is taken into account [2]. The model allows to simulate systems with up to several thousands atoms deposited in any type of crystal lattice. Type of adsorption can be specified by spatial configuration of adsorbate, particle and support atoms given in internal coordinates. It is possible to simulate adsorption on different faces, sites or adsorption near different defects.

Model

In TB-SMA potential interaction between atoms depends on their type and distance between them. For metals it is reasonable to suppose that atoms can be located only in cells of crystal lattice and hence there is a finite set of all possible distances. So one can preliminarily calculate terms of TB-SMA equation for all pairs of atom types and for all distances up to cut off radius, where interaction values become vanishingly small. On that assumption we have used the lattice gas model for representation of particle atoms spatial distribution. This allowed to significantly speed up interaction energy evaluation and neighbours enumeration – the most expensive parts of simulation in terms of computational resources. Because of lattice gas model use, there is no need to support dynamic lists of neighbour atoms, but similar lists can be prepared before simulation for each lattice cell and such lists don't need to be refreshed during simulation. No suggestions about lattice type are made by the simulation algorithm, so the model easily can be adopted for any kind of crystal.



Supported Pt particle with atoms adsorbed on (111) face

On attempt to execute a diffusion act an atom is selected from the list of lattice cells with active atoms (atoms of the particle which can take part in diffusion process). This list is dynamically updated on each successful diffusion act and is in actual state during the whole simulation. The second lattice cell is picked from the neighbor list of the first one and an attempt to change their content is being done according to Boltzmann distribution. This approach gives higher acceptance rate than mathematical diffusion because amount of unlikely jumps from the middle of the particle to a free space is reduced. Also in that way the system reaches an equilibrium state in a less amount of steps in comparison with realistic diffusion.

An adsorbed atom forms some spatial configuration with adsorbent atoms. Set of such configurations defines adsorption type. It can be adsorption on top, on bridge, on hollow sites, on three or four atoms, on steps or other defects. For our model this set can be specified in internal coordinates. For each given configuration a lattice pattern is being built for all possible orientations in space. Obtained patterns can be effectively matched against the lattice. It allows quick search of places on the simulated particle which are suitable for some kind of adsorption. Adsorbed atoms don't have to be placed in lattice cells, their position is determined by vector beginning form some lattice cell. Length of this vector is comparable with distance between atoms in the crystal. Therefore a list of adjacent adsorbed atoms can be build by enumeration of neighbor lattice cells which, as described above, can be done quickly.

Simulations

We have used this model for adsorption simulation on supported Pt nanoparticles with different values of pressure and parameters of interaction between the particle and adsorbate. An influence of adsorption on particle form has been investigated.

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IMPROVEMENT OF CALCIUM FLUORIDE CRYSTALLIZATION IN A FLUIDIZED BED REACTOR WITH MULTIPLE INLETS

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Abstract

The limited natural resources of fluorspar, calcium fluoride, and the world consumption of fluorspar for chemicals production, stabilised around 4 million of tons in 2004 (World Mineral Statistics, 2004) require to make an effort in the sustainable management of the raw material as well as the valorization and recycling into the production processes.

The fluoride recovery process to obtain synthetic calcium fluoride consists on a crystallization process in a fluidized bed reactor, which is proposed as an alternative to the conventional precipitation in the BREF document on Best Available Technology in common waste water and waste gas treatment and management systems in the Chemical Sector (European Commission, 2003).

Previous works were focused on the study of the fluoride removal and recovery as synthetic CaF_2 by crystallization in a fluidized bed reactor working with standard fluoride solutions at laboratory scale [1-3], and the pilot plant scale operated with industrial wastewaters [4].

A model of crystal growth of calcium fluoride was reported by Aldaco et al. [5-7], from the fitting of growth rate data to the variables: supersaturation, seed particle size, and superficial velocity in the fluidized bed. The crystal growth model was based on the aggregation and molecular growth mechanims, while the nucleation process related to fines formation was described by a nucleation rate equation as a function of the supersaturation [7].

As fines formation leads to a reduction of the process efficiency in terms of the amount of crystallization product recovered in the reactor, it is important to focus on the undestanding of the mechanims of fines formation in order to minimize this effect, mainly by means of the control of supersaturation.

Using the concept of distribution of local supersaturation along the reactor, achieved by multiple feed points, Costodes et al. [8] reported results of crystallization efficiencies up to 94 % for the nickel hydroxy-carbonate recovery. The efforts to undestanding of the mechanisms involved in the fluidized bed were also referenced for the removal of phosphorous [9, 10].

Taking into account these previous studies on crystallization processes in fluidized bed reactors, this work was involved in the fluoride recovery as solid product CaF_2 with the objectives of (i) the improvement of process efficiency by means of the reduction of fines formation with multiple feed points of Calcium into the reactor, and (ii) the simulation of the fluidized bed reactor to describe the effect of the distribution of the supersaturation, with the introduction of the product growth model and the fines formation equation in order to predict the process efficiencies in terms of fluoride removal and recovery as solid product and.

The experimental results of process efficiency at laboratory scale indicated a significant increase of 20 % when three feed points of Calcium where used in comparison to one point at the bottom of the reactor, working with fluoride concentration of 500 mg/l at the inlet of the reactor. The process simulation also provided the estimation of the benefits on the consumption of raw materials and waste disposal, and it is used as an important tool to scale up the process for its integration into the production lines.

Acknowledgments

This research is financially supported by the Spanish Ministry of Science and Technology (Project CONSOLIDER CTM2006-00317).

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DYNAMIC SIMULATION OF A COMPLETE MICROSTRUCTURED NATURAL GAS FUEL PROCESSOR FOR FUEL CELL APPLICATIONS

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Introduction

Fuel Processing for future energy systems based upon fuel cell technology attends widespread attention currently as alternative to hydrogen storage options. The fuel processor is a complex system of chemical reactors and balance-of-plant components [1], the dynamic behaviour of which is crucial during start-up and load changes. Few examples of dynamic simulations of fuel processors are published in open literature yet [2-5].

Specific issues of natural gas fuel processing

Natural gas, composed of methane and small amounts of light hydrocarbons has the unique feature, that the main feed molecule is stable and thermodynamically favoured by low temperature of the reforming process as well as by high pressure [1]. On the other hand methane is known to be neither harmful for the carbon monoxide clean-up catalysts of the fuel processor nor for the catalyst of the fuel cell anode itself. Coke formation is also less an issue for methane compared to long chain hydrocarbons. Compared to other fuels, kinetic data are easier available in case of methane, which makes results of the process simulation more reliable.

System under investigation

The system, which was investigated applying ASPEN software is shown in Fig. 1. The core components of the fuel processor are namely a combined microstructured reformer/ catalytic burner (REF and BURN 2), an air-cooled water-gas shift reactor [6] (WGS and HX3), and a methanation reactor for the selective methanation of carbon dioxide [7] (METH and HX6). The steam generation is performed by two evaporators. One of them (EVAP 2) is supplied with energy from the burner off-gases of the reformer burner. Energy supply of the second evaporator (EVAP 1) comes from a coupled catalytic burner (BURN 1), which utilizes the unconverted hydrogen from the fuel cell anode (AFC) off-gas. The heat of the fuel cell cathode (CFC) air is not further utilized. Another four heat-exchangers (HX1, HX2, HX4 and HX5) completes the fuel processor set-up. Results from simulation of the start-up and load change behaviour will be presented.

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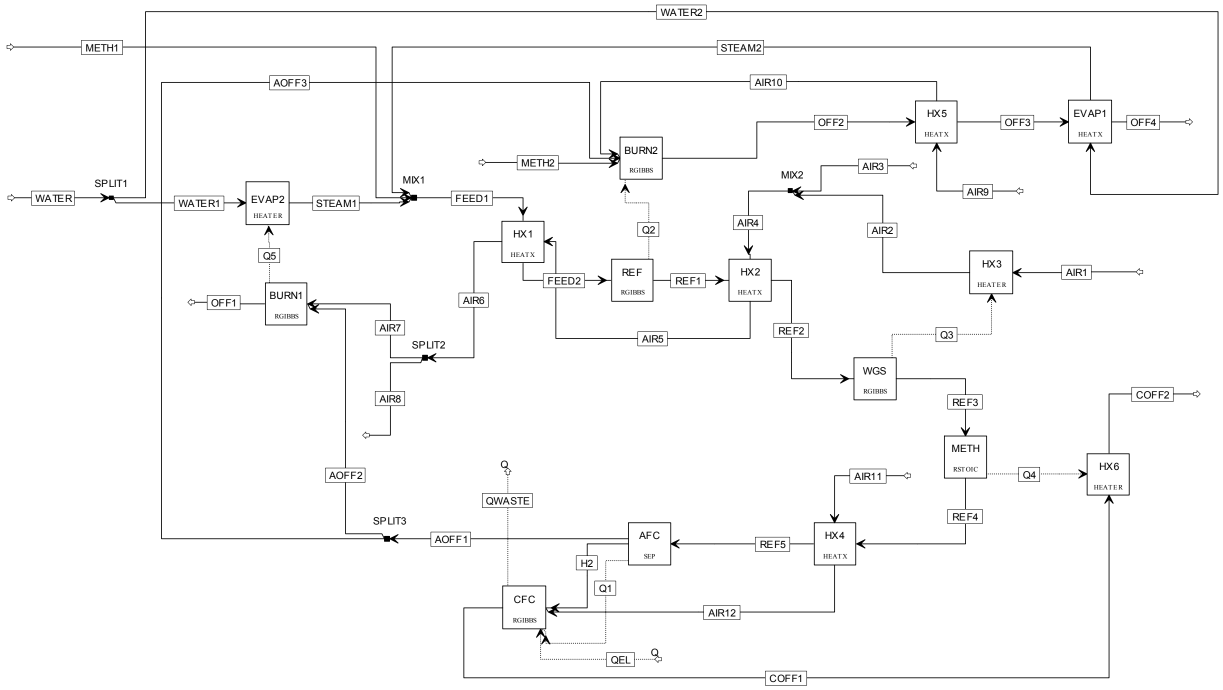

Fig. 1. ASPEN model of the integrated methane fuel processor.

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MONITORING OF THE PROGRESS OF AN EXOTHERMIC CATALYTIC REACTION IN A TRICKLE BED REACTOR: AN NMR IMAGING STUDY

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Trickle bed reactors (TBRs) are generally fixed bed catalytic reactors with the cocurrent flow of gas and liquid. The main application of TBRs lies in the petroleum refining industry. The different hydrodynamics, mass transfer and heat transfer parameters influence the performance of TBR. The experimental data concerning the bed structure, the peculiarities of gas and liquid flows, the reagent and product concentrations, temperatures, liquid hold-up, mass and heat transfer, wetting efficiency, etc., necessary for modeling of TBRs and enhancing of their performance can be obtained by a modern technique – NMR imaging (MRI).

In this work MRI was applied to monitor the progress of an exothermic catalytic reaction carried out in the TBR. It was shown that the occurrence of the exothermic catalytic reaction influenced the distribution of the liquid phase inside an individual catalyst pellet. Moreover, under certain conditions the oscillations of the liquid phase content inside the individual catalyst pellet and the reciprocating motion of the front of the liquid phase propagation into the pellet were observed and modeled. The experimental results showed a good agreement with the results of the mathematical modeling and confirmed that the differences in the rates of the heat and mass transfer processes and catalytic reaction are responsible for the observed oscillatory behavior of the individual catalyst pellet operation.

A special set of the MRI experiments performed on the catalyst bed during the progress of the hydrogenation reaction showed that the proceeding of the hydrogenation reaction influenced very much the distribution of the liquid phase in the catalyst bed as well. It was shown that in the absence of the hydrogenation reaction the distribution of the liquid phase in the bed was uniform at the very low rates of the liquid reagent supply and even under conditions of the total absence of the liquid reagent supply. When the flow of hydrogen was supplied to the catalyst bed, the bed started drying, when the rate of the liquid reagent supply was still sufficiently high, and the distribution of the liquid phase in the catalyst bed became non-uniform. At the lower rate of the liquid reagent supply the catalyst bed became completely dry, at the same time showing the highest degree of conversion and the highest productivity of the catalyst bed, apparently, due to the gas-phase hydrogenation reaction taking place in the dry catalyst bed.

Recently it has been demonstrated that the reactor performance can be improved, when the TBR operates under forced time-varying liquid flow rates. In this mode of operation, the bed is periodically flushed with the liquid during the continuous feeding with the gas phase. In our work, the operation of TBR under conditions of the periodical supply of the liquid reagent to the catalyst bed was studied by MRI and the comparison of the stationary and periodical operation of the TBR was done. It has been found that the degree of conversion of 1-octene into octane in the model hydrogenation reaction really increased, when the liquid reagent started to be periodically supplied to the catalyst bed. The degree of conversion in the regimes under forced time-varying liquid flow rates is dependent on the duration of the pulse of the liquid reagent supply. The comparison of the images detected by MRI in the course of the stationary and periodical operation of the TBR showed, that under conditions of the continuous supply of the liquid reagent to the catalyst bed the bed was filled sufficiently with the liquid phase and was characterized by the uniform and stationary distribution of the liquid phase, whereas under conditions of the periodical supply of the liquid reagent to the catalyst bed with the same liquid reagent flow rate, as in the previous case, the bed was sufficiently dry and was characterized by the non-stationary distribution of the liquid phase. The increase of the duration of the pulse of the liquid reagent supply lead to the increase of the liquid phase content in the catalyst bed, whereas the increase of the duration of the period of the absence of the liquid reagent supply to the catalyst bed resulted in the complete drying of the bed. It has been shown that the internal wetting efficiency under conditions of the periodical supply of the liquid reagent to the catalyst bed is lower than under conditions of the continuous supply of the liquid reagent to the bed. Based on this observation, the intensification of the process under forced time-varying liquid flow rates can be explained by the reduction of the transport resistance for the gaseous reagent (hydrogen) and better performance of the gas-phase hydrogenation reaction.

Acknowledgements: A.A. Lysova and I.V. Koptyug thank RAS (grants 5.2.3, 5.1.1), SB RAS (integration grant 11), RFBR (07-03-12147) and RSSF. A.A. Lysova acknowledges the Council on Grants of the President of the Russian Federation (MK-5135.2007.3).

THE USE OF IONIC LIQUIDS AS EFFICIENT EXTRACTION MEDIUM IN THE REACTIVE SEPARATION OF CYCLOOLEFINES FROM CYCLOHEXANE

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Cyclohexane (CH) is the commonly used solvent in the manufacture of styrene-based synthetic rubber by anionic polymerization; n-butyl lithium is used as initiator. The presence of certain impurities (e.g. water, cyclopentadiene, etc.) in the raw materials or in the solvent used in polymerization may have a poisonous effect on the catalyst. In the manufacture of hydrogenated synthetic rubber, during the hydrogenation process (after the anionic polymerization) small quantities of cyclopentadiene (CP) are formed by degradation of the titanocene compounds, which are used as hydrogenation homogeneous catalyst [1]. Additionally, cyclopentadiene easily dimerizes at room temperature to form dicyclopentadiene (DCP) that must be also removed. In order to recycle and reuse cyclohexane to the reaction process, the cyclopentadiene and dicyclopentadiene contents must be reduced to less than several parts per million. Because the low concentrations of the former compounds in the cyclohexane stream, separation based on conventional distillation is difficult and energy intensive [2].

The separation of condensed olefins from the mixtures with the corresponding paraffins has been investigated widely in literature [3]; the most promising alternative appears to be π-complexation with silver ions. Separation by π-complexation is a subgroup of reactive separations where the mixture is contacted with a second phase, containing the complexing agent (Ag^+).

Reliable data on the solubility of the olefins in a compatible solvent are required for the proper design of extraction systems. In this work, the ionic liquid $BMImBF_4$ has been selected for experiments because it is essentially immiscible with cyclohexane and it is able to dissolve a suitable silver salt ($AgBF_4$), allowing to absorb both CP and DCP due to reversible complexation of silver ions with unsaturated olefinic double bonds. Experimental results were obtained working at different concentrations (100-1000 ppm) of both dienes in the organic phase. The influence of temperature and silver concentration on the solubility of the dienes in the $BMImBF_4$ -Ag^+ solution was assessed and the enthalpy (ΔH^o) for the complex formation reaction was estimated.

Many factors have been found to influence the equilibrium extraction characteristics of these systems. Three important variables are the nature of the olefin extracted, the concentration of silver salt, and the type of diluent. In Figure 1 the results of partition of CP and DCP between organic and ionic liquid phases are given at 293 K; as shown, both solutes are selectively extracted from cyclohexane.

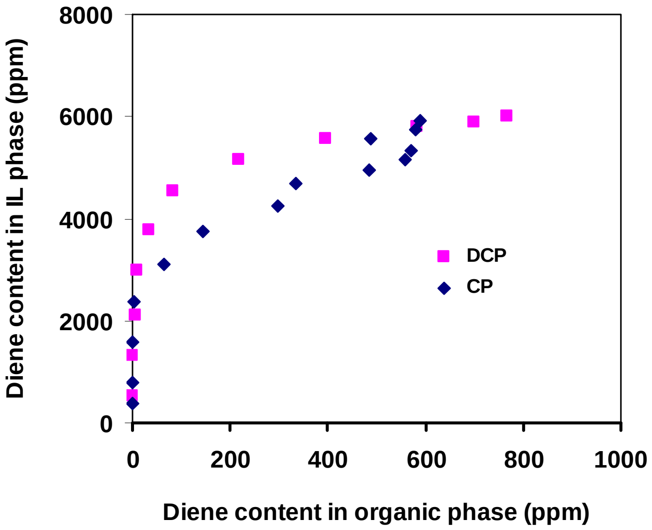

Figure 1: Partition equilibrium of cyclopentadiene and dicyclopentadiene between organic and ionic liquid phases ([$AgBF_4$] =0.1 M in ionic liquid solution; 293 K)

As conclusions, in our work it was found that the selective extraction of the dienes (CP and DCP) via silver complexation can be carried out in an ionic liquid media. The solubility of dienes in extractive mixtures increases with increasing silver concentration, and it decreases at higher temperatures due to a decreasing complexation constant as π-complexation reactions are exothermic.

Acknowledgements

The Ministry of Education and Science (Spain) financially supported this research under projects CTQ2005-02583/PPQ and CTM2006-00317.

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MULTINUCLEAR NMR IMAGING IN CATALYTIC RESEARCH

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The development of very efficient and environmentally safe technological processes relies more and more on the detailed knowledge of their fundamental aspects, which requires the development and application of novel instrumental techniques in scientific research. A unique feature of NMR imaging (MRI) is its ability to provide, in a spatially resolved mode, a broad range of useful information about an object and the dynamics of its evolution, which can be further combined with the chemical specificity of NMR spectroscopy. This makes MRI one of the most versatile toolkits for a broad range of applications. While significant progress has been achieved in this field lately, the potential of the technique for applications in chemical engineering and catalysis is far from being exhausted, and novel applications continue to emerge.

In an ongoing study, ^{1}H MRI technique is employed to characterize *in situ* the hydrogenation of unsaturated compounds on Pt/γ-Al_2O_3 or Pd/γ-Al_2O_3 catalysts in an operating gas-liquid-solid trickle bed reactor [1] with continuous or modulated reactant feed. These studies allow one to map the distribution of the liquid phase within the catalyst bed, to visualize directly various dynamic processes, and to evaluate local reactant-to-product conversion. At the same time, we have recently developed approaches for multinuclear MRI studies of a number of solid materials. Since one of the issues of paramount importance in exothermic processes is that of heat transport, we are developing an approach for the spatially resolved NMR thermometry of operating catalytic reactors. It is currently based on the direct imaging of the ^{27}Al nuclei of the Pd/Al_2O_3 catalyst bed. A pronounced temperature dependence of the ^{27}Al NMR signal was used to reveal the variations of temperature along the catalyst bed in the course of hydrogenation of propylene into propane. Future extensions to two and three spatial dimensions should allow one to characterize heat transport in operating catalytic reactors and to visualize hot spots formation and evolution.

Furthermore, the MRI studies of heterogeneous catalytic reactions can be brought to an entirely new level of sophistication and information content. It is well established that homogeneous catalytic hydrogenations of unsaturated compounds with parahydrogen can be utilized to enhance NMR sensitivity by several orders of magnitude and to perform detailed mechanistic and kinetic studies of such reactions. We have demonstrated for the first time [2] that parahydrogen-induced polarization (PHIP) can be observed in heterogeneous hydrogenations as well, with the use of transition metal complexes immobilized on suitable solid supports. Furthermore, we have shown [3] that PHIP can be observed with supported metal catalysts (e.g., Pt/Al_2O_3, Pd/Al_2O_3) as well. These demonstrations can be employed to develop new advanced MRI-based approaches to study operating heterogeneous catalytic reactors [4], to visualize active regions of the catalyst bed, and to address in detail the reaction mechanism.

To address the fundamental principles that govern the interplay of mass transport and non-linear chemical reactions, we have studied the effect of liquid flow (advection) and convection on the propagation of reaction fronts in a number of homogeneous autocatalytic reactions including non-oscillatory autocatalytic processes. In particular, convective motion of a fluid induced by the propagating concentration front was visualized and the quantitative spatially-resolved maps of convection flow velocities were detected for oxidation of thiosulfate with chlorite carried out in a glass tube. Advection of reaction fronts in a porous medium was studied for the same reaction carried out in a packed bed of glass beads. It was demonstrated for the first time [5] that under appropriate experimental conditions, stationary wavefronts can be observed for a wide range of velocities of the reactive medium flowing through the bead pack. These results are rationalized in terms of the reaction-diffusion-advection model and imply the «wide gap» limit behavior and the effective quenching of the axial diffusion of an autocatalyst by advection in a porous medium.

Acknowledgments

This work was partially supported by RFBR (grants 07-03-12147, 08-03-00661), RAS (grants 5.2.3, 5.1.1), and SB RAS (integration grant 11). IVK thanks Russian Science Support Foundation for financial support. AAL acknowledges the Council on Grants of the President of Russian Federation (MK-5135.2007.3).

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MODELING OF DIESEL FILTERS FOR PARTICULATE REMOVAL

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A diesel particulate filter(DPF) is regarded as the most hopeful technology to reduce particulate matter or soot from exhaust gas of a diesel engine with filtration efficiencies frequently excessing 90%. It is constructed from a square cell monolith structure and the channels are plugged at alternate ends. Exhaust gas entering the channel is forced to exit through the ceramic porous wall into the adjoining cells and thus leaving behind the particulates. The collected particulate matter inside the trap has to be periodically oxidized to reduce the pressure drop. The burning of the collected particle matter inside the trap represents DPF regeneration. The deposition of particles and the regeneration of filters are subject of modeling. We have developed an advanced mathematical nonstationary spatially 2D model of the filter and its regeneration. The momentum, mass and enthalpy balances of the gas and the solid phase were employed in the model including the description of heat conduction, diffusion in the solid phase and complex soot combustion kinetics. The description of kinetics of two types of combustion by O_2 – both the thermal initiated one and the catalyzed one (e.g. Ce oxides based catalyst is added to the fuel) and the oxidation by NO_2 is used in the reaction-diffusion equations for each gaseous component. The results of simulations include the prediction of development of concentrations, temperature, pressure and flow pattern, soot layer thickness along the filter. Contribution presents parametric studies, simulations review and detailed discussion of the kinetics of NO_2-assisted soot oxidation coupled with NO/NO_2 equilibrium reaction and also a filtration model. The filtration model includes cake and deep-bed filtrations and thus predicts porosity, permeability, filtration efficiency of the soot layer and the wall. Main advantage of the developed numerical model for simulations is fast computing of both the regeneration process and the DPF loading. Software for the solution of the above mentioned models will be described and results for various operation conditions will be presented.

OP-II-9

MODELLING OF DIESEL PARTICULATE FILTRATION IN WALL-FLOW TRAPS

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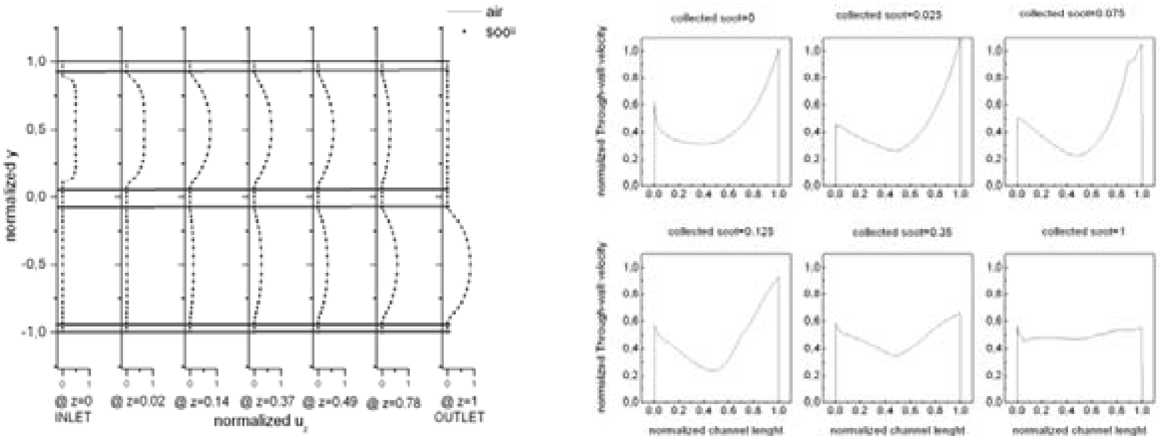
Nowadays, soot emissions from Diesel engines can be reduced by physically trapping the particles with on-board diesel particulate filters (DPFs). The investigation of soot filtration via DPFs, and their regeneration, can be split into four sub-problems: i) the computation of the multi-phase flow field inside the DPF; ii) the description of the evolution of the filter characteristics as soot is deposited and filtered; iii) the formation of a soot cake in the DPF channels; iv) the modeling of regeneration dynamics. Hence, the aim of this work is to develop a mathematical model able to accurately describe each of these four mentioned steps.

Two and three dimensional CFD simulations of the multiphase flow inside the filter channels are carried out by resorting to an Eulerian-Eulerian approach. The interaction between the main phase and the soot particles is taken into account through the drag force, calculated according to Schiller and Naumann [1]. The influence of Brownian forces on the drag force via the Stokes-Cunningham coefficient, and on particles trajectories in the channels, is proven to be negligible.

Fig. 1 shows the gas and soot velocity axial profiles inside the DPF channels at the beginning of filtration (Fig 1-a), and the evolution of the gas velocity across the filter wall with respect to the total amount of collected soot (Fig. 1-b). The accumulation of soot particles into the filter pores modifies its characteristics: the porosity and the permeability of the filter decrease until a maximum value of deposited soot volume fraction is reached into the porous media, thus making these regions impermeable to the dispersed phase and entailing the formation of a soot layer onto the filter surface. A parameter of major importance in particle interstitial filtration is the local efficiency, namely the probability of successful collections of soot particles onto fictitious spherical collectors constituting the channel walls, largely due to deposition from Brownian motions and interception. In the evaluation of the efficiency, calculated as indicated in literature [2], the size of the soot particles has a strong impact. In the light of this consideration, our Eulerian-Eulerian approach is particularly interesting because it can be easily coupled with a population balance equation (PBE) for the description of poly-disperse solid-gas flows, resulting in a much lower computational time when compared with alternative Lagrangian-Eulerian approaches. The real soot distribution



(a) ***Particle size 100nm*** **(b)**

Fig. 1. (a) Profiles of axial velocity at different axial positions in the channel for gas (solid line) and soot particles (dots). **(b)** Through-wall gas velocity for different amounts of collected soot.

was substituted by a series of mono-dispersed particle distributions, whose size and volume fraction was calculated by means of the so-called direct quadrature method of moments [3].

The cake resistance coefficient is generally higher than that of the filter, thus entailing that the soot cake immediately becomes the only considerable resistance, and the soot through-wall velocity profile evolves towards an «iso-permeability» constant profile (Fig. 1-b), characterized by a constant thickness of the soot layer. However, the ever-changing driving conditions generate a variable cake thickness along the axial coordinate, which influence the dynamics of the regeneration process, modelled by inclusion in the code of soot combustion kinetics determined experimentally.

A wide range of operating conditions are considered in this work, for which a large amount of experimental data within our research group are available for comparison and validation. The developed model represents a unique design tool for diesel particulate traps with minimum space occupancy and maximum filtration efficiency and is being exploited on a specific contract with a major car manufacturer.

Acknowledgements

The European Community financial support for the ATLANTIS project is gratefully acknowledged.

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Section 3.

Catalytic processes′ development and reactors design: modeling, optimization, new catalyst application

CATALYTIC REACTOR FOR N_2O ABATEMENT IN ADIPIC ACID PRODUCTION

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Commercial processes currently employed for the production of adipic acid (AA) are based on oxidation of a mixture of cyclohexanone and cyclohexanol (KA oil) in excess of strong nitric acid. Nitric acid is reduced mainly to nitrous oxide, but also to nitrogen, to nitric oxide, and to nitrogen dioxide. Effluents of NO_x are recovered as nitric acid or removed in all AA plants. However, N_2O emission has not been regulated for many years.

In 1991 it was pointed out in [1] that N_2O from AA production is harmful to the environment and should be strictly controlled. The only commercial process in use for N_2O removal is non-catalytic incineration of effluents with added fuel under reducing conditions at 1200-1500°C, which results in nitrous oxide decomposition to nitrogen and oxygen. Due to the high worldwide prices for natural gas, this process is rather expensive; specific NG consumption reaches as much as 500 m^3 per 1 ton of N_2O.

Very limited information is available on catalytic methods for N_2O decomposition. Led by DuPont, chemical companies BASF, Asahi, Bayer, ICI and Rhone-Poulenc in cooperation with catalyst companies are searching for an economical way of N_2O catalytic removal. Two options are usually considered: (1) selective oxidation of nitrous oxide to higher nitrogen oxides followed by its recovering as nitric acid; and (2) decomposing of nitrous oxide to molecular nitrogen and oxygen. Up to present, no commercial implementation of catalytic technologies has been reported.

The 1997 Kyoto Protocol declared nitrous oxide as one of the main greenhouse gases with global warming potential equal to 310. New catalysts and catalytic processes for N_2O removal at moderate temperatures are expected to solve this serious environmental challenge.

In this work, a catalytic technology for N_2O abatement from AA tail-gases is proposed. Typical composition of tail-gases after NO_x absorption tower in AA production plant is (in vol. %): 11-13 N_2O; 0.1-0.3 NO_x; 0.06-0.12 CO; 14-15 O_2; 3-5 H_2O; N_2 – balance. We consider a two-stage technological system. At the 1st stage, nitrous oxide is converted to nitrogen and oxygen over BIC proprietary cobalt-zeolite catalyst. At the 2nd stage nitrogen oxides are selectively reduced by ammonia over commercial vanadium-alumina catalyst.

BIC's catalyst for N_2O decomposition meets requirements of activity and stability within a wide temperature range of 450-700°C at above mentioned conditions. Tests conducted in a small-scale reactor demonstrated acceptable activity during long-term run at normal conditions and high stability at extreme hydro-thermal treatment conditions. Kinetic parameters of the reaction of nitrous oxide decomposition were determined for catalyst granules of commercial size.

Much attention has been paid to the optimal design of the reactor unit, because the catalytic reactor must meet mandatory emissions regulations for AA plants. The adiabatic heat release at total conversion of 12% N_2O is over 400°C, therefore adiabatic reactor with 2 beds of catalyst and intermediate heat exchange was developed. Mathematical and hydrodynamic modeling of the catalytic process has been carried out, and basic technological parameters have been found. This study resulted in determination of an optimal residence time in each catalyst bed, optimal temperature strategy, and reactor design at lowest pressure drop. In Fig.1, temperature profiles are plotted along each catalyst bed length, as well as N_2O conversion curves. Concentration of N_2O at the reactor outlet is lower than 500 ppm, which comply with environmental protection demands.

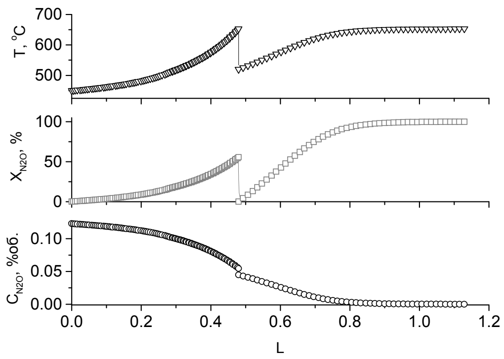

Fig.1.

To ensure uniform gas flowing and perfect mixing before the catalyst bed, special internal devices were developed. Using computer program Fluent 6.1, hydrodynamic features of reactor were simulated for all reasonable process space velocities, and temperature ranges. Built-in gas flow distributors and internal mixer secured homogeneous inlet flow with respect to velocity, temperature and composition of the reactants. Non-uniformity of axial velocity was found to be within ±10% which ensures normal reactor performance.

Methods of catalytic removal of nitrous oxide at moderate temperatures 450-650°C prove out to be far more efficient for treatment of tail-gases from AA production plants than the existing thermal decomposition technology, and are expected to replace it in the future.

Authors are pleased to thank Prof. A. Kharitonov and Dr. L. Pirutko for their efforts in development and preparation of the catalyst samples.

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Cu-ZSM5 BASED MONOLITH REACTORS FOR NO DECOMPOSITION

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Introduction

Monolith catalysts are widely used in environmental applications due to the several advantages they offer like low pressure drop even at high space velocity, high geometric surface area, good mechanical strength and durability [1-3]. In particular, monolith catalysts are used in DeNOx catalysis both for mobile and stationary source.

The catalytic decomposition of NO into N_2 and O_2 would be a very attractive solution for NOx abatement since no addition of reducing agent is required [4]. Cu-ZSM5 provides the best performances for this reaction. Although widely investigated as powder catalyst, Cu-ZSM5 dispersion on a structured support has been poorly studied.

Results

Deposition of a zeolite on ceramic monoliths can be made by in-situ hydrothermal synthesis or by deposition from a slurry of fine pre-synthesized zeolite powder (dip-coating) [5]. The advantage of the first method is the stronger adhesion of the coating to the support. Nevertheless, it is more complex and diffusion limitations can occur through the dense layer with small intercrystalline pores. On the other hand, the main advantage of the dip-coating method are the shorter diffusion distances.

In this paper a ZSM5 (Si/Al = 25) powder sample has been deposited on cordierite monoliths by dip-coating using colloidal alumina or silica as binders in aqueous suspension. After a preliminary study to determine the best binder and the best zeolite/binder ratio to obtain a ZSM5 washcoat with a good mechanical resistance, monolith catalysts have been prepared according to two different procedures: i) deposition of a Cu exchanged ZSM5 ii) deposition of a H-ZSM5 followed by copper exchange of the structured catalyst.

The monolith catalysts have been investigated by morphological (SEM/EDX), physical (BET and porosity), chemical (ICP/MS, H_2 TPR) and catalytic (NO decomposition tests in a flow reactor) analysis. Results have been compared with those obtained on a Cu-ZSM5 powder sample with the same total copper content in order to define the best preparation procedure.

A very good adhesion of uniform zeolite washcoat layer (Fig. 1) has been obtained by dip-coating technique using a low amount of silica binder. The preparation method strongly affects the nature of copper in the monolith catalyst determining different catalytic properties of the structured reactors and suggesting that the copper exchange represents a crucial step for these systems. Release of active copper cations from the zeolite powder suspended in the solvent during the coating step or a bad control of the exchange of the zeolite layer deposited on the structured support, due to the complexity of the system ceramic monolith/binder/zeolite, are the possible phenomena occurring during the preparation procedure.

Activity in the presence of water vapour, strongly deactivating Cu-ZSM5 powder, has been studied for monoliths as well, determining the effect of zeolite dispersion on the hydrothermal stability. A surprisingly better hydrothermal resistance was found for monolith catalysts, whatever the preparation procedure used, likely due to a buffer effect of the ceramic support.

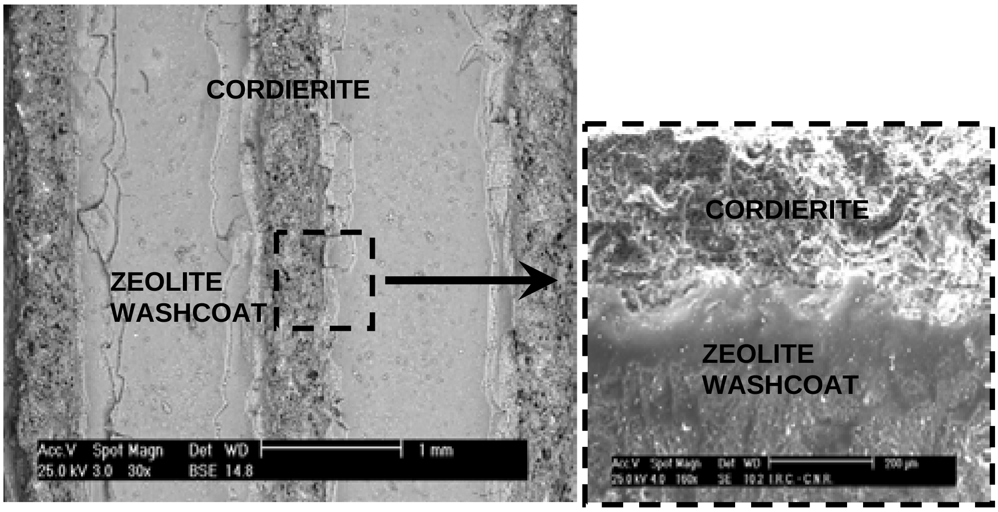

Figure 1 – SEM image of the ZSM5 monolith cross section and magnification of the selected area (90° rotated).

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NH_3 SCR MODELLING FOR Fe ZEOLITE CATALYSTS MODEL-SETUP AND VALIDATION

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Introduction

Upcoming stringent legislation will require NOx exhaust treatment of Diesel vehicles. One alternative for the removal of NOx from lean exhaust gas is ammonia SCR where the ammonia is produced from urea in the exhaust system. Fe exchanged zeolites are attractive materials for automotive exhaust ammonia-SCR since they show a high selectivity towards the desired products N_2 and H_2O, particularly at elevated temperatures [1,2].

The application potential of a dynamic SCR-catalyst model for the layout of exhaust system and for an improved urea dosing system has been recently demonstrated by Chatterjee and co-workers [3] for vanadium based catalysts. It is the objective of the current contribution to characterize the dynamic operation of Fe zeolite catalysts experimentally and to set up a model describing the observed behaviour.

Materials and Methods

The catalyst tests were performed at a model gas test bench. Gas mixtures containing NO, NO_2, NH_3, O_2, N_2, and H_2O were prepared using a standard flow controller setup and conversion was measured over a coated monolith sample. Reactor temperatures were in the range of 150 - 400 °C and hourly space velocities in the range 12500 h^{-1} to 25000 h^{-1}. Gas concentrations were measured by an FTIR analyzer. One transient test procedure consists of step changes in NH_3, NO and NO_2 concentration at isothermal conditions. This sequence is designed for the gain of all relevant information for the characterization of steady state and transient performance of the catalyst within 24 hours. Another test procedure consists of a transient temperature program performed at fixed gas feed conditions and serves as a very useful tool for validation of the model at conditions similar to operational conditions in the vehicle.

Results and Discussion

A kinetic model is set up that takes into account the storage and release of NH_3 on the zeolite catalyst and the different reactions of NH_3 with NO alone, NO_2 alone and combined NO/NO_2. NH_3 oxidation by O_2 is found to be negligible in the observed temperature window.

Analysis of the results shows that ammonia storage/release and inhibition of the SCR reactions by NH_3 are the key processes for an understanding of the transient performance of the SCR catalyst [4]. The dynamic behaviour of the Fe zeolite catalyst proves surprisingly similar to the vanadium based catalyst.

The model was validated successfully by a transient temperature sequence including steep temperature rises. Figure 1 shows the temperature program together with the emissions and the model output of NH_3.

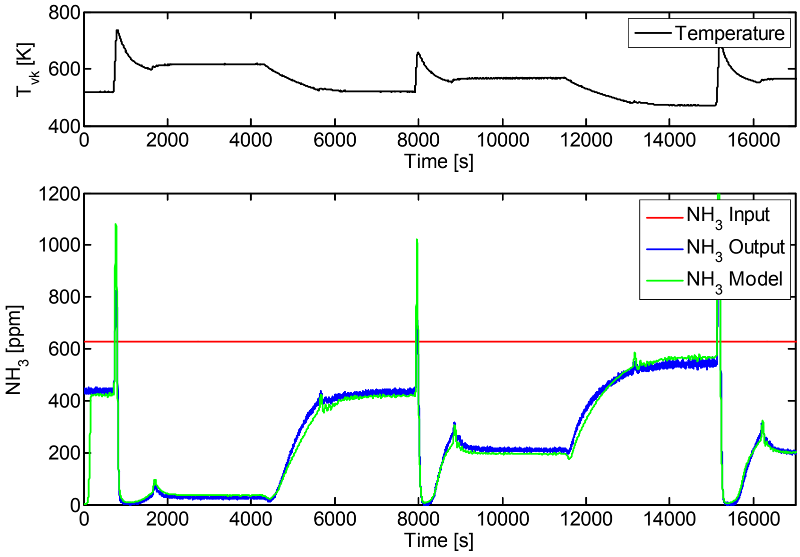

Figure 1: Temperature validation sequence carried out with fixed feedgas concentrations (600 ppm NO, 600 ppm NH_3, 6 % O_2, 5 % H_2O, GHSV 25000 h^{-1}).

The model is able to reproduce the emissions of the catalyst under transient and constant temperature conditions. The ammonia peaks evolving during the heating phases and the ammonia storage during cooling times are as well mapped as the steady state conversion levels.

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SCR OF NO_x IN DIESEL EXHAUST WITH ONBOARD PRODUCED SYNGAS AS REDUCTANT

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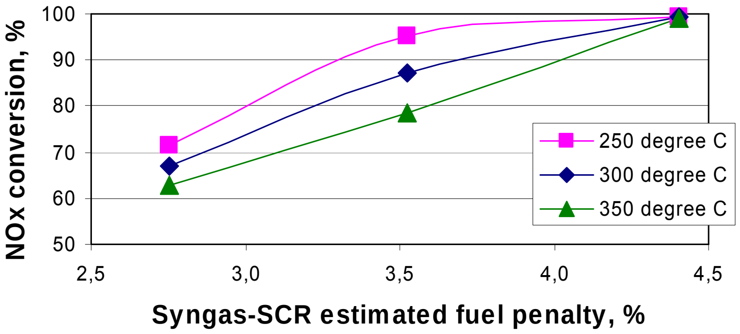
At the present state of the art, diesel engines have the best potential for low fuel consumption out of all existing internal combustion engines. At the same time the using of diesel engines for vehicle propulsion will require a continuous development of exhaust aftertreatment systems [1, 2].

Today, a high concentration of NO_x in diesel engine exhaust is the most important ecological problem. Because of inevitable enforcement of vehicle NO_x emission standards in the future, the promising solution of the NO_x emission problem is the application of catalytic systems for exhaust aftertreatment. A number of such systems were developed [3]. Today two most competitive methods are: Selective Catalytic Reduction of NO_x with urea as reducing agent (Urea-SCR) and Lean NO_x Trapping (LNT).

The recent results obtained in a number of research centers, including the BIC, have shown that hydrogen is an efficient reducing agent of nitrogen oxides on Ag/Al_2O_3 catalyst at lean conditions and temperatures from 150 °C [4-7].

In the presenting work it was shown that the application of synthesis gas with a high H_2 concentration for NO_x reduction on Ag/Al_2O_3 catalyst is very promising method (Syngas-SCR). Synthesis gas can be onboard generated via autothermal reforming of the diesel fuel, thus there appears a possibility to develop efficient catalytic system for NO_x neutralization (see the figure below).



In the table below we compared the suggested method (Syngas-SCR) with the existing on the market technologies of diesel engine exhaust aftertreatment:

OP-III-4

Exhaust aftertreatment technology	**Additional reducing agent**	**Temperature range where NO_x conversion is > 80%**	**Fuel penalty, weight % from engine consumption**	**Content of platinum group metals in catalysts**
Urea-SCR	Urea	200 – 500°C	about 1% urea	None
LNT	None	250 – 450°C	3 – 4% diesel fuel	≥ 2 g/l
Syngas-SCR	None	180 – 400°C	estimated 3 – 4% diesel fuel	None

The obtained results permit an optimistic forecast concerning the possibility of development of an efficient catalytic system for diesel engine exhaust aftertreatment. The technology of NO_x reduction by synthesis gas, generated via autothermal reforming of diesel fuel, can provide high efficiency of the cleaning system within the wide temperature range.

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CATALYTIC DENSE BIMEVOX MEMBRANE REACTOR: A REVIEW

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BIMEVOX materials based on $Bi_4V_2O_{11}$ structure are known as highly oxide ion conducting materials at low temperatures (400-700°C). BIMEVOX membranes which behave as Mixed Ionic Electronic Conductors were used in the oxidation of alkanes in a catalytic dense membrane reactor (CDMR). This device allows to carry out the redox mechanism of oxidation in two separate steps, the dense ceramic membrane separating two compartments, one containing the oxidant (air), the other containing the (diluted) hydrocarbon to be oxidized. The driving force is the difference between the oxygen chemical potentials in each compartment. The paper presents the last developments when an electric current is applied to a gold/BIMEVOX cermet deposited on the BIMEVOX membrane in order to fasten the transfer of specie across the membrane during the catalytic oxidation of methane or of higher alkanes to syngas, and the conclusions on a series of experiments.

SOME PROPERTIES OF PEROVSKITE-LIKE FERRITES AND THEIR PERFORMANCE IN MEMBRANE CATALYTIC REACTORS FOR PARTIAL OXIDATION OF NATURAL GAS

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At the present time, the technology based on use of mixed-conducting membranes is considered as the most promising approach for syngas production from natural gas. However, the application is still considerably hindered by absence of membrane materials, which would satisfy special requirements. In addition to high mixed oxygen ion and electron conductivity, the oxygen semi-permeable ceramics should maintain thermodynamic and dimensional stability under harsh operation conditions, mechanical strength and compatibility with other components of electrochemical reactors, moderate costs, etc. In order to develop better materials one may either try to enhance the ion mobility in stable materials by taking into account structure-mobility relations, defect ordering, etc. or to study the thermodynamics and stability limitations in highly defective oxide materials with the pursuit of improving their stability. The search requires experimental efforts aimed at evaluation of ion and electron conductivities, mobility and concentration of charge carriers, with emphasis on strongly reducing conditions. Moreover, a correct evaluation of changes in oxygen stoichiometry with working conditions is very important to confirm estimates of defect concentrations and the defect chemistry models. In order to identify the effects of doping upon structural stability and transport properties a number of ferrites with perovskite related structure were appraised employing dilatometry, oxygen permeation studies, total conductivity and thermopower measurements in a wide oxygen partial pressure range at temperatures within 650-1000 °C. It is shown that some ferrites exhibit advantageous combination of properties, and may be considered as viable candidate materials for oxygen separating membranes. In support of these findings bench scale prototype reactors with the yield of syngas up to 100 L/h demonstrate stable parameters during several months of operation.

SIMULATION STUDIES OF A MEMBRANE WATER-GAS SHIFT REACTOR UNDER NON-ISOTHERMAL CONDITIONS

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Introduction: Hydrogen production processes and their subsequent purification steps have been extensively studied in the last two decades for fuel-cell feeding. Reforming or partial oxidation of hydrocarbons or alcohols have been reported as the main routes to obtain the required hydrogen. In most cases, the CO content also evolving from the production reactor has to be reduced to avoid the poisoning of the fuel-cell anode catalyst. The water-gas shift reaction (WGSR) is selected to accomplish this task, with the additional effect of increasing the H_2 production. This moderately exothermic reaction is strongly controlled by chemical equilibrium. An attractive alternative to increase the CO conversion is the use of membrane reactors (MR) to provoke an equilibrium displacement by the selective permeation of hydrogen from the reaction medium [1-2].

Many studies have been reported concerning water-gas shift membrane reactors (WGS-MR) [3]. In the vast majority of them isothermal operation has been considered. This assumption is reasonable in low-scale (laboratory) equipment due to the high relations transfer area / reaction volume under use. Nevertheless, when several membrane tubes are installed in parallel inside a shell through where the sweep gas flows, the hypothesis of isothermal-operation could be no more realistic. In a previous publication, a theoretical study of the influence of thermal effects on a WGS-MR performance is carried out for different configurations of the sweep-gas flow on the reactor shell (co and counter-current) [4]. The present contribution presents results regarding the effect of the operating pressure and the sweep-gas flowrate on the performance of the WGS-MR. A 1-D, pseudohomogeneous mathematical model has been selected to represent the reactor operation under adiabatic conditions (energy transfer between process and permeate streams only due to the permeation flow). A comparison with a conventional fixed-bed reactor (CR, without H_2 permeation) is also reported.

Results and discussion: The operation of a WGS-MR to process the outlet of a $1kW_{th}$ methanol reformer was analyzed. 30 membrane tubes of 8mm I.D. and 150 mm length, located in parallel, have been selected. Simulations show a strong influence of the operating pressure (P) for a constant sweep gas pressure of 1 atm, flowing co-currently with the process gas. In fact, higher pressures lead to an appreciable increase of the CO conversion (X_{CO}) due to higher H_2 permeation flows and enhanced equilibrium displacement. This increase in X_{CO} is also associated to higher thermal effects. To show this phenomenon, Figure 1 reports conversion-temperature trajectories for both the membrane reactor and the conventional fixed-bed reactor. The increment of temperature in the membrane reactor when comparing with the conventional reactor is due to both the increase in CO conversion and the diminution of the molar flowrate of the process gas [5]. The reduction of the catalyst volume (reactor length) to reach a required X_{CO} level was also analyzed for increasing operating pressures (results not shown). Medium pressures of around 5 atm appear favorable to achieve a noticeable diminution of the reactor length with moderate increase on compression and manufacture costs.

The performance of the non-isothermal WGS-MR for operation without sweep-gas has been also studied. This alternative arises as highly attractive since no separation / purification steps are required for the pure H_2 permeated gas. Figure 2 presents a comparison of H_2-partial pressure (P_{H2}) axial profiles for operation with and without sweep gas, for both process gas and permeate sides ($P_{H2,R}$ and $P_{H2,P}$, respectively). The increase in operating pressure results also beneficial for the operation without sweep gas but in a lower extent when compared with the operation with sweep gas. This behavior obeys to the elimination of the dilution effect provided by the sweep gas. The operation without sweep gas leads to lightly lower CO conversions but a pure H_2 stream is attained in the reactor shell. Besides, an improved utilization of the catalyst in the reactor length is achieved.

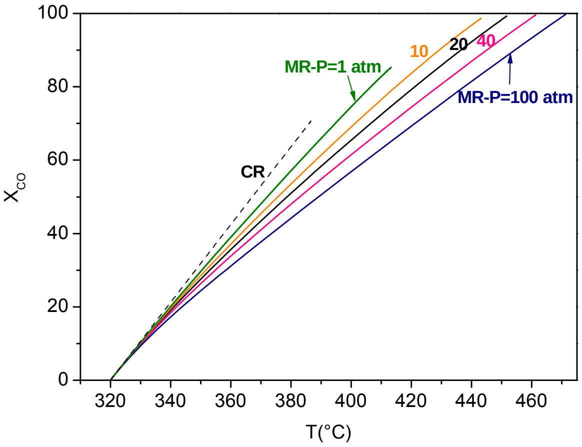

Figure 1: influence of the operating pressure on the MR performance (for CR the performance is unaltered by increasing pressures). Process gas inlet flowrate: 9.58 10^{-3} mol/s. Inlet dry basis concentrations: H_2: 43.5%, CO: 8%. Sweep gas flowrate at inlet conditions ($F_{SG,i}$): 50 l/min.

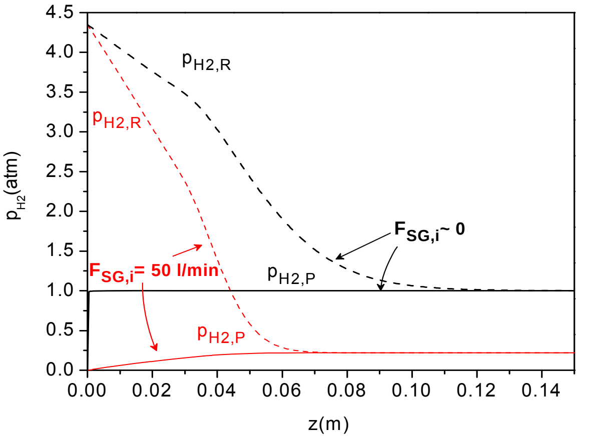

Figure 2: H_2 partial pressures in the process gas side (dotted lines) and permeate side (solid lines), for operation of MR with and without sweep gas ($F_{SG,i}$ = 50 l/min and $F_{SG,i}$ = 0, respectively). Operating conditions as in Figure 1.

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Acknowledgments: Support of this work through *Universidad Nacional del Sur (UNS)*, *Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICET)* and *Agencia Nacional de Promoción de Ciencia y Tecnología (ANPCyT)* is gratefully acknowledged.

MODELLING OF NON-DISPERSIVE SO_2 ABSORPTION PROCESS

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Introduction

Non-dispersive absorption based on membranes has demonstrated a number of widespread advantages: controlled interfacial area, independent control of gas and liquid flow rates and it avoids solvent losses due to drops dragging (Karoor and Sirkar, 1993; Gabelman and Hwang, 1999). However, the resistance of the membrane to mass transfer leads to the need for a equipment optimization (Qi and Cussler, 1985). Most studies emphasize that the best operating mode is the non-wetted mode (Luis et al., 2007; Yan et al., 2007) where membrane pores are filled by gas leading to a high diffusion coefficient in comparison with that if pores were filled by a liquid. N,N-dimethylaniline is a hydrophobic compound commonly used as absorbent due to its affinity with SO_2 (Basu and Dutta, 1987; Bhattacharya et al., 1996). Thus, hydrophilic membranes should be used to achieve a non-wetted contact.

Methods

A hollow fibre hydrophilic membrane module made of alumina is studied as gas-liquid contactor. In designing hollow fibre membrane modules for soluble gas removal, the mass transfer process into a fibre can be mathematically described by three flow models: gas-phase laminar model, gas-phase plug flow model and gas-phase mixing model. A numerical analysis based on previous works (Luis et al., 2007) was carried out to describe the performance of the hollow fibre membrane contactor for the removal of sulfur dioxide considering diffusion-controlled mass transfer and an instantaneous reaction between SO_2 and the liquid. Experimental validation was also carried out in order to confirm the applicability of the models.

Results and discussion

According to the mathematical modelling, the non-wetted operating mode shows higher process efficiency due to higher values of the mass transfer coefficient. The laminar and plug flow models estimate the same values of efficiency in the evaluated range of parameters. This range is in good agreement with the operation conditions of the experimental system used to validate the model. The behaviour of both models can be explained because the main resistance is the membrane and the diffusion of the SO_2 molecules through the gas can be neglected. Thus, the parabolic profile in the gas phase can be ignored.

In order to validate the applicability of the models, some experimental runs have been carried out. The process efficiency is about 50% which is close to the efficiency obtained with the models: 56% with laminar and plug flow models and 45% with a mixing model.

Conclusions

A mathematical modelling considering diffusion-controlled mass transport and instantaneous reaction has been applied to the non-dispersive absorption process using a hollow fibre membrane module. Experimental results show a good correlation with the model, showing that the membrane is the main resistance to the mass transfer as it could be expected.

Acknowledgments

This research is financially supported by the Spanish Ministry of Science and Technology (Project CONSOLIDER CTM2006-00317).

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FRONT VELOCITY AND CRITERION OF TRANSVERSAL PATTERNS IN PACKED-BED REACTORS

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Introduction

Predicting hot zones in catalytic reactors is the focal point of design criteria aimed to avoid severe safety hazards. Thermal fronts are known to exist in such reactors and some experiments indicate that they may undergo symmetry breaking in the transversal direction under certain conditions. Note, that the linear stability analysis of the 1-D front solution is a rather complex problem as the basic (steady or moving) front state is not known, a priori. Reported studies employ numerical simulations[1], which are very time consuming and are difficult to analyze. To simplify the full 3-D problem analysis several reduced models yielding a 2-D presentation have been proposed[2-3]. Linear stability analysis can be applied then after a single, or multiple steady state (SS) solutions have been determined. The only analytical result obtained with such reduced models, in the case of a single stable SS is that the necessary condition for emergence of ***stationary*** transversal patterns is: $Pe_{Ctrans} < Pe_{Ttrans}$[2]. This is exactly a condition of the Turing activator-inhibitor mechanism and can be applied for a stationary front, but it is considered to be unrealistic for fixed beds.

A new criterion of transversal symmetry breaking of ***moving*** fronts have been recently proposed by us[4]. Using both a learning two-tube model exchanging heat and mass, and a thin cylindrical annular 2-D bed model we obtained for a first order activated reaction the critical condition to be:

$$\alpha=\Delta T_{ad} Pe_T/\Delta T_m\, Pe_C > 1, \tag{1}$$

where ΔT_{ad} and ΔT_m are the adiabatic and the maximal temperature rises. This condition coincides with the previous condition for stationary fronts ($\Delta T_{ad}=\Delta T_m$) when ratios of transversal to axial dispersions of heat and mass are consistent ($Pe_{Ctrans}/Pe_C=Pe_{Ttrans}/Pe_T$). The novel condition (1) can be satisfied in an upstream propagating front ($\Delta T_{ad}/\Delta T_m<1$) for feasible operating conditions ($Pe_C>Pe_T$) as was verified by direct numerical simulations of a 2-D shell PBR model[4]. To implement condition (1) we need to know relation $\Delta T_m=\Delta T_m(\Delta T_{ad},Pe_C,Pe_T)$, which to the best of our knowledge is not available yet.

The purpose of this study is to derive the approximate relations for the propagation velocity and the maximal temperature rise of a planar front in a PBR, accounting for a finite mass dispersion and to analyze transversal symmetry breaking of moving and stationary fronts using the relation between the velocity (V_f) and the local curvature (K) of the front.

Analysis

As a first stage we derived for a planar front two algebraic equations with two unknowns ($\Delta T_m, V_f$), which and in the limiting case of $Pe_C \rightarrow \infty$ can be reduced to the approximate relations known for a 1-D «ideal» front in the case of negligible mass dispersion[5]. Numerical simulations of a 1-D PBR show a good agreement between the simulated and approximated values for moderate and large Pe_C.

At the next stage we considered a curvilinear front propagation in a local polar coordinate system and derived approximate relations for the propagation velocity (V_f^C) and the maximal temperature rise for the case of a finite curvature. Applying the condition $dV_f^C/dK|_{K=0}=0$ we obtained a necessary condition for symmetry breaking in the following form:

$$C(\alpha,\Delta T_{ad},Da,Pe_T,Pe_C,\Delta T_m^C,V_f^C,\gamma)[1-\alpha]<0, \qquad (2)$$

where C is a certain algebraic expression. In the limiting case $\alpha \rightarrow 0$ ($Pe_C \rightarrow \infty$) we have $C>0$ and the planar 1-D front is stable. Analysis of simplified Eq. (2) with $\alpha > 1-\delta$ ($\delta>0$, small) shows that $C>0$ at least for $1< \alpha <2.4$ and thus a planar front is unstable within this domain. Note, that condition $\alpha>1$ coincides with the previously obtained criterion (1), while refined condition (2) can define the upper α boundary of transversal patterns to emerge.

Simulations

The derived criterion was verified by direct numerical simulations of the 2-D cylindrical shell and a full 3-D PBR models showing various types of moving transversal patterns in upstream propagating fronts (Fig. 1).

In conclusion we would like to point that transversal three-dimensional patterns were predicted and simulated in PBR's with a first order activated kinetics within the feasible domain of parameters for the first time.

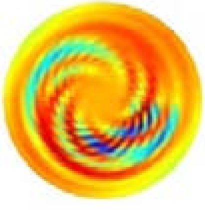

Fig. 1. Typical quasi-«frozen» spiral structure of a front propagating in a 3-D PBR showing the temperature pattern in a cross-section normal to the flow (behind the front).

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REACTOR FOR CARBON NANOFIBERS SYNTHESYS

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The constructions of the reactors, proposed for the synthesis of carbon nanofibers by thermocatalytic decomposition of hydrocarbons or disproportionation of CO are discussed. The most typical deficiencies in their constructions are the narrow range of a change in the characteristics of the obtained product, the low degree of the conversion of raw material, the difficulty for separation of product from catalyst and separation of solid and vapor phases, the increased requirements for the utilized equipment. The original construction of reactor for this purpose is proposed. This reactor makes possible to carry out the synthesis of carbon nanofibers, to divide solid and vapor phases, to separate the formed product from the catalyst in one apparatus. The possibility of obtaining the product with different characteristics is the merit of the proposed reactor. The catalyst block, located along the axis of apparatus is the basic element of reactor. The form of it is the inverted, truncated cone. The maximum contact of reagent is reached as a result of the filtration of the gas through the situated in the block catalyst. The process of the carbon nanofibers formes on the upper catalyst layers is most effective. The product is derived through radial clearance between the reactor vessel and catalyst block. Separation of solid and vapor phases and separation of product from catalyst as a result occurs. It is possible to change the time of an increase in carbon nanofibers varying distance from the catalyst surface area to the upper edge of catalyst block. The result of this changing is the possibility of obtaining the product with different concentration of mineral part in nanofibers and specific adsorptive surface. The diameter of the fibers and their graphitization degree are determined by the temperature of process, by composition and flow of reaction gas, by nature of catalyst. The results of studies carried out at the department of petrochemical synthesis and synthetic liquid fuel of M.V. Lomonosov Moscow state academy of fine chemical technology are represented. They confirm the possibility of synthesis in the reactor of the proposed construction the product with different characteristics.

OP-III-11

PROCESS INTENSIFICATION USING A CONTINUOUS HIGHLY INTEGRATED REACTOR-SEPARATOR DEVICE

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Introduction

Process intensification is a powerful concept to replace large, energy intensive equipment or processes with smaller plants that combine multiple operations in single, highly integrated devices. Our research activities in this area involve the use of continuous, highly integrated reactor-separation devices (CCS) to perform biphasic catalytic reactions in a continuous mode (Figure 1). In the CCS, intense mixing in an annular zone is combined with rapid separation using centrifugal forces. The CCS has been used successfully for oil-water separation (e.g. for cleaning oil spills), for the continuous extraction of fermentation products and in the atomic waste industry for the purpose of extraction and purification of radioactive waste[1)], however, its use for combined catalytic reaction-separation has not been reported to date.

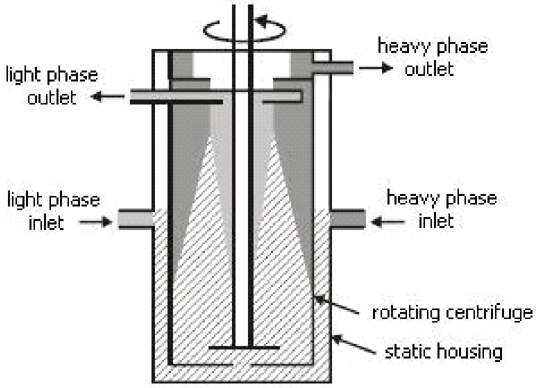

Fig. 1. Cross-sectional view of the CCS.
Hatched: dispersion, light grey: light phase, darker grey: heavy phase

Results and discussion

In this presentation, the application of the CCS for the synthesis of biofuels and (fine-) chemicals will be reported. The use of the CCS for the continuous production of biodiesel (FAME) from methanol and a plant oil was tested for sunflower oil[2]. At 60°C, an average yield of 96% of FAME was obtained, demonstrating the potential of the CCS for biodiesel production (Figure 2).

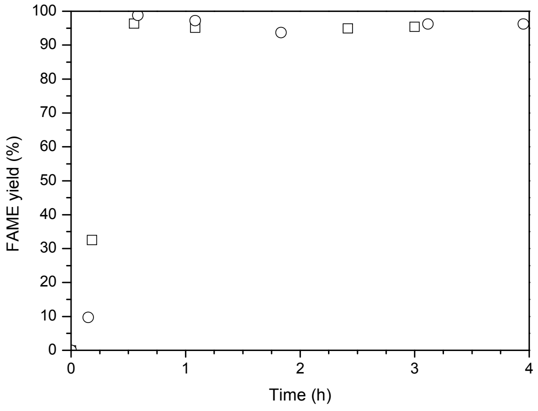

Fig. 2. FAME yield from sunflower oil at 60°C

The CCS is also very well suited for chiral separation of amino-acid derivatives using liquid-liquid extraction. Excellent results were obtained using a chiral cinchona alkaloid extractant[3] in a water-dichloro-ethane system.

Biphasic enzymatic reactions may also be performed conveniently in the CCS. The biphasic *Rhizomucor miehei* lipase catalysed esterification of oleic acid with n-butanol to the corresponding ester in a heptane/water mixture was shown to proceed with oleic acid conversions of up to 70%.

Conclusions

We have demonstrated the applicability of a highly integrated reactor/separator device for interesting biphasic chemical reactions. Details about the systems including optimization studies (kinetic- and reactor modeling) will be reported in the presentation.

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OP-III-12

ETHYL ACETATE SYNTHESIS BY COUPLING OF FIXED BED REACTOR AND REACTIVE DISTILLATION COLUMN – PROCESS INTEGRATION ASPECTS

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1 Introduction

The esterification of acetic acid (AA) and ethanol (EtOH) is known and proven process. The most common production strategy consists of simple esterification of both reaction components in a presence of acidic catalyst. The reaction is limited by chemical equilibrium and formed product mixture with rest of reactants should be separated and raw ethyl acetate (EtAc) purified. This issue is complicated by the formation of heterogeneous azeotrope, which amounts less water than produced by chemical reaction. Thus, an integrated esterification process with selective separation of EtAc was demanded, combining chemical reaction and efficient purification. This process can be reactive distillation[1].

The main objective of this paper is the description of the reaction system of EtAc in both pre-reactor and reactive-distillation column. The lab scale experiments will be fitted by process simulation and the most important results can serve for a scale up of that complicated reaction system[2].

2 Experimental

The experiments were performed in lab scale ethyl acetate unit, consisting of standard one pass packed bed reactor (with partial evaporation of liquid reaction mixture), filled by strong acidic ion-exchanger catalyst and coupled with reactive-distillation column. The reactive-distillation column was compiled from three sections of overall efficiency 13 theoretical stages (TS), see the scheme in Figure 1. Reaction zone of efficiency 1 TS was sandwiched between symmetrical stripping and rectification. The distillate was cooled down in the condenser and both organic (OP) and water (WP) phases were separated in a decanter, which was additionally tempered.

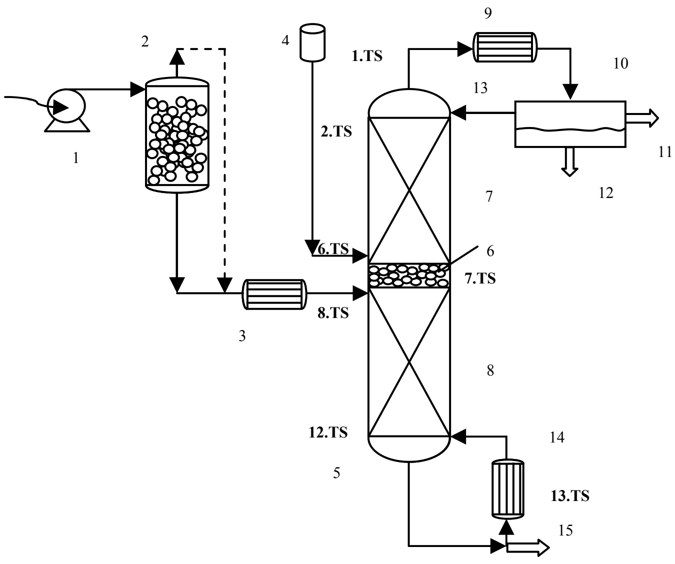

Figure 1: Schematic description of experimental reactive-distillation system with integrated fixed-bed reactor
1 – pump for equimolar EtOH/AA mixture, 2 – fixed-bed pre-reactor, 3 – pre-heater, 4 – additional feed of acetic acid surplus, 5 – reactive distillation column, 6 – reaction zone, 7 – rectification section, 8 – stripping section, 9 – condenser, 10 – decanter, 11 – organic phase, 12 – water phase, 13 – reflux stream, 14 – reboiler, 15 – bottom product

3 Results and discussion

The results consist of utilization of fixed-bed experimental runs for the catalyst activity evaluation, determination of mass transfer limitation of the chemical reaction and also for adjustment parameters for process simulation. The data were used as an input for a design of reactive-distillation column and finally, the complex system including pre-reactor and reactive distillation column has been adopted for process scale up[2].

3.1 Fixed-bed reactor

The reaction mixture was fed at atmospheric pressure to the fixed-bed reactor, filled by ion-exchanger. The outlet was analyzed by GC and/or by acetic acid determination using titration method. The results for catalyst loading between 2 and 10 g_{cat}.h/mol at different reaction temperatures are given in Fig. 2.

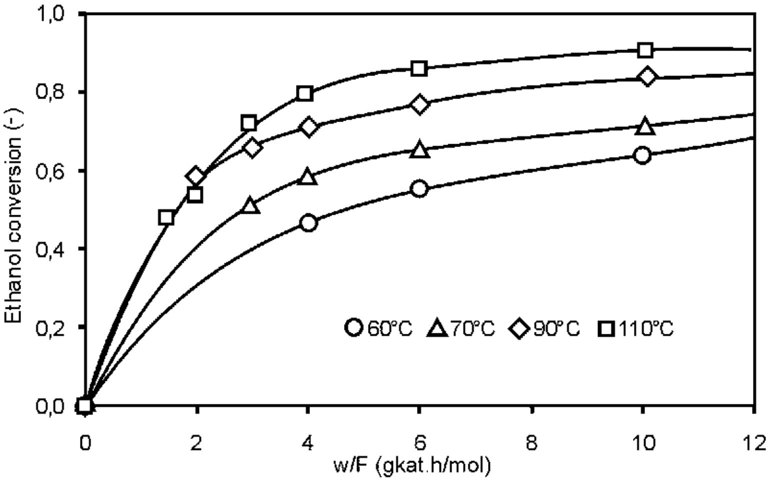

Figure 2: Ethanol conversion for equimolar feed at different reaction temperatures as a function of catalyst loading

For lower temperatures of 60 and 70 °C, ethanol conversion is attacking its equilibrium limitation of 78 mass %. Recalculated to equilibrium feed composition, the equilibrium EtAc concentration in the product equals to 64 mass %. For temperature above 76 °C, the reaction products are vaporized and thus, by evaporating a part of reaction mixture is separated from the catalyst. Therefore much higher conversion of esterification can be achieved, compared to chemical equilibrium conversion. At temperatures above 100 °C, the EtOH conversion >90 % was reached, see Figure 2. Similar reactor performance was already reported for carrying out esterification of acetic acid by butanol in trickle-bed reactor[3]. Such process can be advantageously used for simple and very cheap overcoming of chemical equilibrium limitation of studied reaction system.

3.2 Reactive distillation column

A series of reactive distillation experiments were performed and the process parameters were used as an input for process simulation. Achieved results show that in the organic phase, EtAc can be selectively separated from the organic distillate with purity higher than 92 wt. %. EtOH concentration in the product of only 2-3 % represents the additional separation effort to be putted into the final purification of EtAc. Despite the problems with additional separation, a presence of EtOH is much less disadvantageous compared for presence of AA. The reboiler product is formed by almost pure AA, which after dehydration (e.g. by distillation or by adding defined amount of acetanhydride) can be recycled back to the pre-reactor. The details about all achieved results and process simulation will be given in our full paper.

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PREPARATION AND PERFORMANCE OF WALL TUBE REACTOR IN THE REFORMING OF METHANOL

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Introduction

The steam-reforming reaction of methanol (SRM) has attracted much attention as a promising method for a compact hydrogen production system for a fuel cell. Due to the large endothermicity of this type of reaction,[1] use of a wall tube reactor is proposed.[2] The formation of a porous alumina thin layer on an aluminum plate by anodic oxidation is an established technique.[3] However, until now, there have been no reports on the anodic oxidation of the inner wall of a thin aluminum tube. This paper provides a first report on the anodic oxidation of a thin aluminum tube and its application to the SMR.

Experimental

Anodic oxidation of the inner wall of the pretreated tube was carried out by inserting a Teflon-coated 0.56-mm copper wire, with the Teflon coat partially stripped off, into the tube, and this was used as a cathode electrode (fig. 1). The anodic oxidation was carried out by following the literature.[4] Pre-oxidation was achieved by circulating the electrolyte (0.6 M oxalic acid) inside the tube at a flow rate of 25 ml/min, and an electric potential of 30 V DC was applied between the cathode and aluminum tube. After the first oxidation, the inner surface was exposed to a mixture of 6.0 wt% H_3PO_4 and 1.8 wt% H_2CrO_4 at 60 °C for 15 min to remove the oxidized alumina layer The second anodic oxidation was carried out under the same condition as above for 1-9 h. The obtained tube was washed with distilled water, and calcined at 350 °C under flowing air.

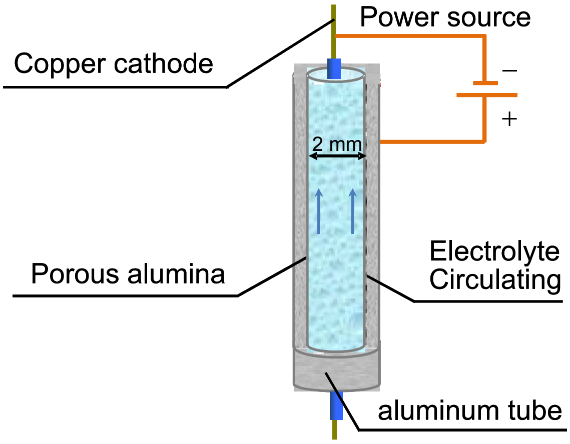

Fig. 1. New method for anodic oxidation of aluminum tube of inner diameter of 2.0 mm.

Results

Figure 2 shows scanning electron micrograph (SEM) images of the cross section and the inner surface of the oxidized aluminum tube. Relatively uniform pores sized 20 to 30 nm were observed, and the surface area (BET, N_2) of oxidized inner wall was ca. 20 m^2/ m-tube.

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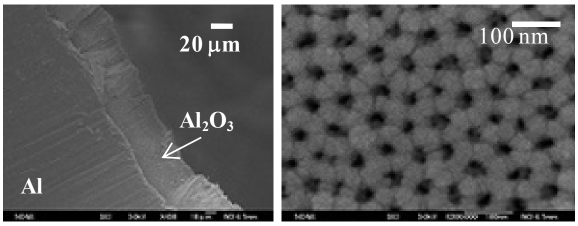
The reforming reaction was carried out by feeding CH_3OH together with Ar as a sweep gas at 200-300 °C, using an effective tube length of 0.8 m (heated zone). As shown in Table 1, with the bare alumina tube (Run 1), CH_4 conversion was nil.



(a) Cross section (b) Inner surface

Fig. 2. SEM images of anode oxidized of aluminum.

With a loading level of 2.8 mg/m-tube combined weight of Cu and Zn oxides, methanol conversion of 23.9% was observed. If the catalyst adsorption time was prolonged from 2 to 12 h, the loading level increased from 2.8 to 4.5 mg/ m-tube at 8 h, with an increase in CH_3OH conversion to 60.2% (Run 5). Since elongation of the catalyst loading time did not significantly increase the amount of loading, catalyst loading process was repeated as shown in Runs 6-9. With increasing repetition number, catalyst loading increased. When impregnation procedures were repeated four times, the loading level reached to 12.4 mg/m-tube, leading to methanol conversion of 45.5% and 98.8% at 200 °C and 250 °C, respectively, with a very low CO selectivity at 200 °C (Runs 9, 10).

Table1 Results of SRM using wall tube reactor[a]

Run	Catalyst preparation: Impreg-nation time h	Catalyst preparation: Impreg-nation repe-tition	Catalyst preparation: Catalyst weight mg/m[b]	W/F[c] g.h/mol	CH_3OH conv. %	H_2 mmol /h	selectivity % CO	selectivity % CO_2
1 [d]	0	0	0	0	0.2	0	0.0	0
2 [d]	2	1	2.8	0.10	23.9	28.3	3.2	91.5
3 [d]	4	1	3.3	0.12	38.7	36.8	2.1	96.5
4 [d]	8	1	4.5	0.17	58.7	70.1	2.0	96.5
5 [d]	12	1	4.5	0.17	60.2	70.1	2.2	97.3
6	8	1	4.5	0.17	28.2	22.7	0.3	99.6
7	8	2	6.2	0.23	78.1	62.9	0.8	99.2
8	8	3	8.3	0.31	89.8	72.3	1.3	98.6
9 [e]	8	4	12.4	0.46	45.5	36.2	0.0	99.9
10	8	4	12.4	0.46	98.8	75.8	2.0	97.9
11	8	4	12.4	0.28	97.2	126	2.1	97.9
12	8	4	12.4	0.20	82.7	151	1.6	98.3
13	8	4	12.4	0.15	73.3	187	1.1	98.8
14	8	4	12.4	0.12	61.3	213	1.3	98.6

a: Reaction temperature: 250 °C, time: 1h, Ar: 30 ml/min, Steam/Carbon = 1.0

b: Total weight of CuO and ZnO,

c: W/F: catlyst weight(g) / feed methanol (mol/h)

d: Reaction temperature: 300 °C

e: Reaction temperature: 200 °C

Thus wall tube reactor was found to exhibit an excellent performance in the SRM.

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MICRO-REACTORS FOR THE COMBUSTION OF METHANE

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Despite the large use, the low energy density of conventional batteries is a limit in the miniaturization of the electronic devices induced by the advances in the fabrication techniques in the area of MEMS [1]. Any fossil fuel shows an energy density at least 50 times higher than a typical Li battery, so rendering the development of innovative processes of in-situ electricity generation via fuel combustion a very intriguing alternative for portable applications, once an effective and relatively integrated efficient conversion system from thermal to electrical power is applicable. Practical considerations related to fast and simple recharge and low cost of liquid fuels render the required efficiency values not extremely high (i.e. 1-5%) to be successful. Thermoelectric (TE) or Thermo-photovoltaic (TPV) systems, based on the direct generation of electricity from fuel chemical potential rather than thermodynamic cycles (and, consequently, moving parts) are showing very promising results [2]. Even if TE or TPV elements need high temperature to work efficiently, a high durability is exhibited by most common fabrication materials provided temperature does not exceed 800 °C and even much lower in the case of thermoelectric conversion systems. Such temperatures are too low for a homogeneous combustion flame to be sustained, especially considering that the scales of interest in the field of the MEMS (1000-100 μm) approach the quenching distance for most possible fuels; so the application of a catalytic system appears the most attractive option. Actually, the use of a catalyst should guarantee a stable exercise of the process even in strongly diluted conditions, allowing a very uniform thermal profile too, with consequent improvements of conversion system efficiency.

Micro-scale catalytic combustion has been receiving a lot of attention. In most cases, ceramic flat substrates supporting noble metals based catalysts have been investigated, mainly in the combustion of hydrogen or very volatile liquid hydrocarbons, such as propane and butane [3]. High volatility and low chemical and thermal stability does not render noble metal catalysts very suitable for high temperature applications driving the research interests towards less expensive transition metal mixed oxide based catalysts [4]. Despite its large diffusion, availability and consolidated distribution systems, few attentions have been devoted to the combustion of methane, whose low reactivity requires higher temperatures for the complete conversion. Particular attention has been recently devoted to the study of the hydrogen-methane mixture providing high methane combustion rate, notwithstanding its relatively low reactivity (compared to other hydrocarbons), and high H/C ratio with favourable consequence on global warming [5].

In this work, we have investigated the properties of a series of catalysts obtained from inert substrates in the shape of plates of different materials characterized by variable thermo-conductibility (SiC, α-Al_2O_3, FeCrAlloy), that have been coated with a γ-Al_2O_3 washcoat and a perovskite-type active phase constituted by $LaMnO_3$ (supported onto alumina pores). The effect of doping the active phase with small amounts of Pt (0.2-1% wt.) has been tested too. All catalysts have been investigated in the combustion of methane, hydrogen and H_2-CH_4 mixtures. A stainless steel reactor has been accomplished in order to house the catalytic system and carry out combustion tests. The reactor design allows to modulate the height of the combustion chamber so to change the S/V (catalyst surface/reactor volume) ratio. The results show that a little amount of Pt into the perovskite structure is very effective in enhancing the catalytic activity towards H_2 oxidation, significantly diminishing ignition temperature, while high temperature CH_4 combustion rate is determined by perovskite content (the activity towards methane combustion seems to be not affected at all by the presence of Pt). Particular attention has been devoted to the combustion of the H_2-CH_4 mixtures. H_2 enrichment of the fuel is effective to enhance CH_4 combustion rate by means of the activation of radical paths in the homogenous phase. Fig. 1 shows that methane conversion increases with increasing H_2 content in the fuel (at constant calorific power of the entire mixture). The results obtained at two S/V ratio are reported; as shown in the figure, increasing the volume available for the homogeneous reaction, CH_4 total conversion is obtained at a lower H_2/CH_4.

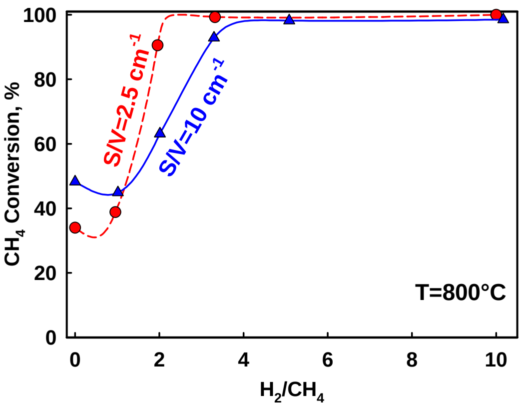

Fig. 1. CH_4-H_2 combustion on FeCrAlloy slab coated with $LaMnO_3/Al_2O_3$ catalyst at two surface-to-volume ratios

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OP-III-15

MICROWAVES AND ULTRASOUND TOWARD PROCESS INTENSIFICATION

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Introduction

Process intensification is an important tool in chemical engineering, transforming current practices and bringing forth new developments in equipment, processing techniques and operational methods. Several unconventional processing techniques rely on alternative forms of energy. In recent years, chemical application of acoustic and microwave irradiation has received increasing attention and widespread research is in progress in these areas.

Acoustic irradiation

The effects of ultrasound on the catalyst activity and selectivity were investigated in several hydrogenation reaction and esterification of propionic acid with ethanol. Enhancement of catalyst activity and enantioselectivity was observed in enantioselective hydrogenation of 1-phenyl-1,2-propanedione over Pt/SF (silica fibre) catalyst. Furthermore, significant suppression of catalyst deactivation was obtained in hydrogenation of D-fructose over Ni sponge catalyst (Intensification factor: 1.54) and Cu/SiO_2 catalyst (Intensification factor: 1.6) as well as in esterification of propionic acid with ethanol over Smopex-101 (polymer fibre catalyst) (Fig. 1). One of the explanations for improvement of the catalyst performance is ultrasonic surface cleaning during the course of reaction (Figs. 2 and 3).

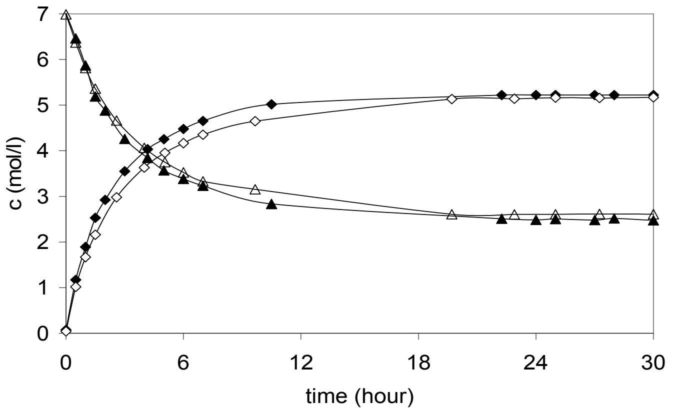

Fig. 1 Esterification of propionic acid with ethanol (◇ – ethyl propionate, Silent; ◆ – ethyl propionate, Sono; Δ – ethanol, Silent; ▲ – ethanol, Sono).

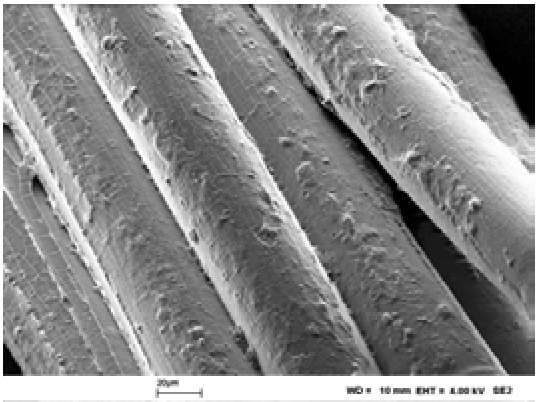

Fig. 2. The spent Smopex-101 catalyst treated in the absence of ultrasound (SEM image).

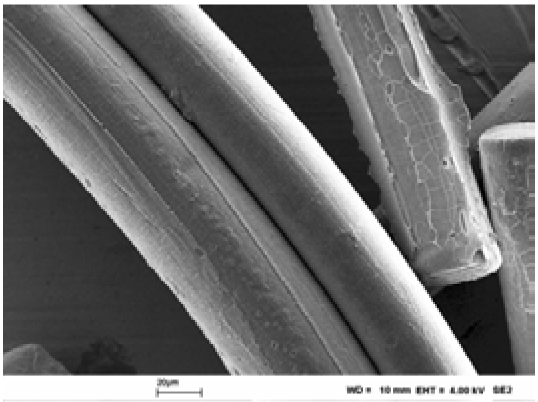

Fig. 3. Ultrasonic treated spent Smopex-101 catalyst (SEM image).

Microwave irradiation

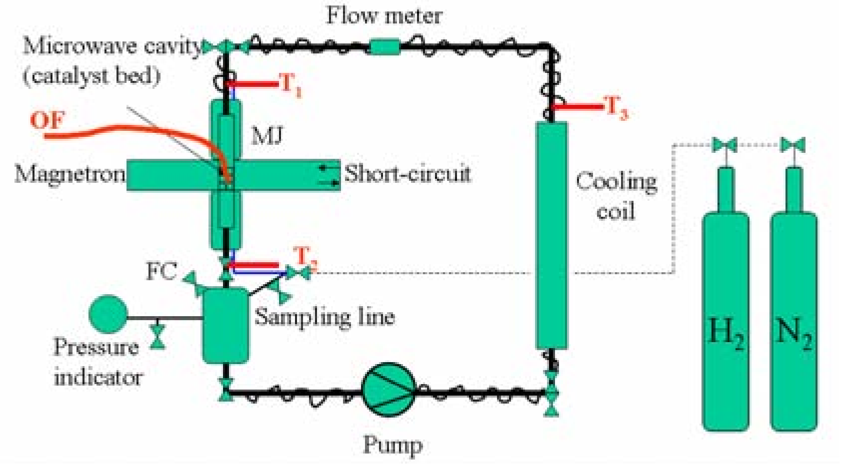

Fig. 4. Schematic drawing of single-mode microwave loop reactor set-up (MJ: metal jacket with N2 flow, FC: loop filling cup, OF: optic fibre).

Esterification of propionic acid with ethanol as well as ethyl pyruvate hydrogenation were carried out in a single-mode microwave loop reactor (Fig. 4), equipped with a conventional heating band as well, to directly compare the efficiency of microwave dielectric and conventional heating. The microwave dielectric heating allowed selective heating of the catalyst bed and of the solvents and reactants as well as instantaneous heating of the chemicals in use. However, the reaction kinetics was not primarily influenced by the mode of the heating.

Conclusion

The alternative energy sources, acoustic and microwave irradiation, were found to be prominent tools of process intensification. The results are, however, very dependent on the chemical system.

OP-III-16

FLOW IN THE HONEYCOMB CATALYST WITH POROUS WALLS

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Honeycomb catalysts are widely adopted for many applications such as chemical industry, car engine emission control, fuel cells etc. Most of previous studies are used assumption that catalytic monolith is a impermeable media and catalytic reactions are held on the monolith surface [1,2]. Volume-averiged transport equation in the porous media by Darcy's law were accounted for [3] to specify heat and mass transfer between catalyst monolith walls and reaction gas in monolith channels. Moreover it is known that diffusivity in washcoat catalyst layer of honeycomb particles played a significant part in exothermic processes, for example in catalytic combustion [4]. In this processes considerable overheating take place on a inlet part of monolith that can lead to thermal destruction of catalyst particles.

The objective of this investigation is to study the 3D flow on a monolith inlet taken into account a permeability of monolith walls. In order to obtain a velocity field the incompressible 3D Navier-Stokes equation and Darcy's law was solved for monolith channels and monolith walls respectively. The computational fluid dynamics (CFD) code Fluent was used for the computation of flow.

The Darcy's law coefficients was described experimentally for catalyst monolith with different shape and size. Air flow was passed through monolith walls at a normal conditions and pressure drop was measured using special set-up. Samples of monolith is shown in Figure 1. The experiment results are shown in Figure 2 where pressure drop ΔP/L through honeycomb walls is plotted as a function of superficial velocity W. L is the wall thickness.

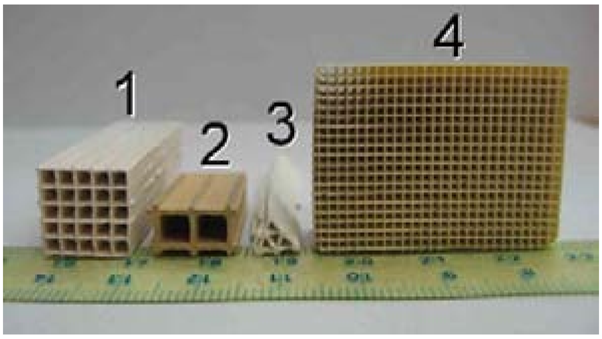

Fig. 1. Samples of monolith examined

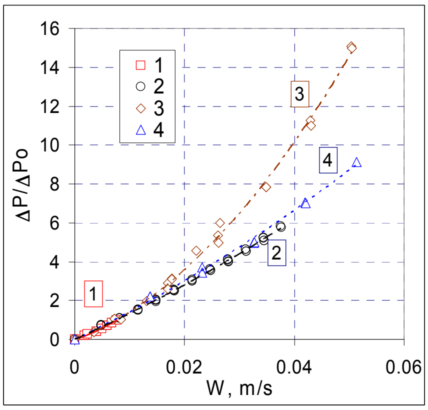

Fig. 2. Pressure drop through honeycomb walls as a function of superficial velocity.

Numbers of curves are according to samples on Figure 1. It is shown the pressure drop function ΔP/L has a square-law dependence on superficial velocity W, $\Delta P/L = A \cdot W + B \cdot W^2$. At used experiment conditions it is significance that flow regime into porous walls is a Fick diffusion or a transition region between Fick and Knudsen diffusion [5]. This fact confirms an accuracy to use momentum transport equation by Darcy's law for porous media.

Velocity fields were calculated on inlet part of monolith in various flow regimes with both porous and impermeable monolith walls. On Figure 3 the example of velocity distribution in porous wall was shown by colours according colour scale in the figure center and equal sise vectors. As a result of this simulations there are two main features at least. Firstly comparatively intensive flow is in frontal part of monolith increasing flux of reaction gases into catalyst wall. In case of exothermic catalytic reactions it can made for catalyst overheating. Secondly a comparison of velocity fields for porous and impermeable monolith show a important differences. For example vortex placed on inlet edges of monolith channels have various intensity. There was changed a heat and mass transfer processes in inlet part of monolith.

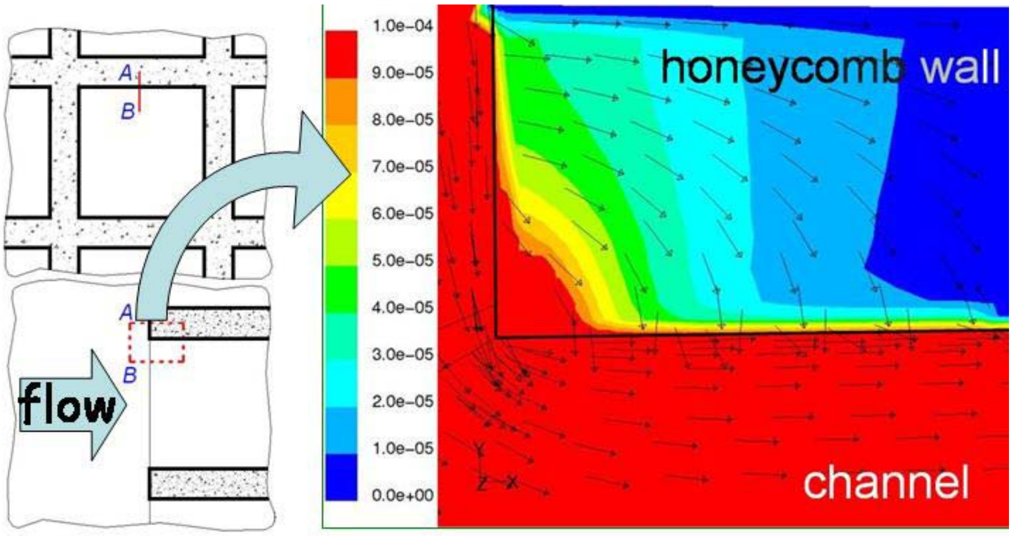

Fig. 3. Flow distribution in frontal part of monolith with porous walls. Velocity was shown by colours according colour scale in the figure center and equal sise vectors.

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HONEYCOMB CATALYSTS WITH POROUS WALLS: CFD MODELING OF INTERACTION OF MASS TRANSFER PROCESSES WITH CATALYTIC REACTION

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Introduction

Structured catalyst systems are promising for new applications, in particular, intensive studies are carrying out for development of compact syngas generators from natural gas and/or other hydrocarbons feedstock. To find a new design solution the detailed data concerning mass transfer effects on the reaction rates are necessary. The use of the boundary-layer models does not always allow us to reveal all features of hydrodynamic processes in such a catalyst system, more precise consideration becomes possible on the basis of CFD modeling [1].

This study is a continuation of [2]. The results of the theoretical investigation of the interaction of mass transfer processes with catalytic reaction in a porous honeycomb catalyst are presented. The impact of operation conditions on the reaction rates distribution at the catalyst surface and in the volume was studied.

Theoretical

CFD modeling approach was used to obtain the spatial distribution of laminar reacting flow in the honeycomb catalyst with triangular channels. The complete system of Navier-Stokes equations for multi-component gas flow was solved by using the software FLUENT 6.3. The catalytic tube reactor was considered with a fragment containing single channel of the honeycomb monolith. The walls of the channel have a porous structure and are permeable for the reacting gas flow; the feed gas mixture contains methane and oxygen. Model kinetic schemes for two reactions are considered: catalytic methane oxidation and methane steam reforming. The operation conditions and fragment geometry were close to those of the process of selective methane oxidation on LaNiPt-catalysts [3]. In the simulations, the inlet feed rate, catalyst activity, and porous structure parameters were varied for temperature of 700-800°C.

Results and discussion

The local mass transfer rates over the channel surface were studied varying inlet feed rate at the contact times in the range of 4-15 ms. At each given feed consumption, the distributions of gas velocity and mass transfer coefficient along the channel length and around the perimeter were determined. The highest values of the transfer coefficient are observed in the middle parts of the triangle sides; the reduced values in the regions near the edges of the channel are related to the formation of boundary layers. Maximum intensity of mass transfer was observed near the channel inlet, which was higher comparing to the case of an impermeable monolith due to the gas flow penetration through the catalyst surface.

The local rates of the catalytic reactions proceeding were determined both at the outer surface and inside the porous catalyst structure. The reaction rate distribution over the channel surface along the monolith length follows the local mass transfer coefficient. The peculiarity of the distribution of the volume reaction rate consists in a high peak at a short initial part caused by a rather high penetration rate of feed components into the volume through the frontal surface of the catalyst. The relative value of this peak is considerably higher comparing to the surface reaction rate and goes down with decrease of the catalyst activity. The dependencies obtained are similar for both reactions under study.

The profile of the effectiveness factor η of the catalyst along the channel looks similar to the volume reaction rate distribution. For all considered cases with variation of the feed rate, η is above unity at the initial part; further, η decreases because the reagents come into the volume only through the channel wall with a low velocity, and finally the reaction rate is higher on the catalyst surface.

Conclusions

The spatial distributions of the gas velocities and local rates of mass transfer along the monolith channel as well as the interaction of mass transfer processes with catalytic reaction in a porous honeycomb catalyst were studied by CFD modeling for two reactions.

It was shown that, for all conditions under study, the distribution of the surface reaction rate along the channel is defined by the local mass transfer from the gas phase to the catalyst, while, because of the gas penetration through the frontal surface, the distribution of the volume reaction rate along the channel has a sharp peak near the channel inlet. Thus, owing to such a difference of the impact of mass transfer processes onto the local reaction rates at the catalyst surface and in the volume, the effectiveness factor of the catalyst has a high maximum above unity near the channel inlet.

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METHANE STEAM REFORMING IN A MICROCHANNEL REACTOR FOR GTL INTENSIFICATION: A COMPUTATIONAL FLUID DYNAMICS SIMULATION STUDY

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Introduction

Gas-to-Liquid (GTL) processes allow monetizing the vast natural gas reserves existing in remote areas around the world as well as fulfilling the flaring constraints imposed on associated gas from oil fields. GTL technology is based on the conversion of natural gas to high quality liquid synfuels in several stages: syngas generation, production of long-chain hydrocarbons by Fischer-Tropsch (FT) synthesis, and hydrocracking of the heavy fractions for naphta, diesel and lubricants production [1]. Steam reforming of natural gas over nickel catalysts is the preferred technology for syngas production. This route is highly efficient but strongly endothermic (ΔH^o_{298} = 206 kJ/mol). On the other hand the FT synthesis is very exothermic (ΔH^o_{298} = -165 kJ/mol). Therefore, heat transfer issues are of the greatest importance for these processes which for this reason are capital intensive. One of the outstanding characteristics of microreactors is heat transfer enhancement; then, microreactor technology provides an opportunity for the intensification of the GTL processes [2].

Results and Discussion

In this work, a Computational Fluid Dynamics (CFD) study with ANSYS CFX software of heat transfer in microchannel catalytic reactors for methane steam reforming (MSR) and FT synthesis is presented. The simulated microreactor is a steel block 17 mm high, 21 mm width, and 21 mm long containing 80 microchannels 1 mm high, 1 mm width, and 21 mm long. Simulations have been conducted under operating conditions relevant for the intensification of the GTL processes. It has been assumed that a very thin layer of an active catalyst has been uniformly deposited onto the walls of the microchannels. As concerns the MSR reaction, first order kinetics with respect to CH_4 according to the rate expression for Ni of Bodrov et al. [3] has been considered whereas the water gas shift reaction has been assumed to be at equilibrium. Gas hourly pace velocities (GHSV) were of the order of 27,550 h^{-1} with H_2O/CH_4 molar ratio of 2. MSR has been coupled with CH_4 combustion for heating purposes. The rate expression proposed by Kolaczkowski et al. [4] for CH_4 combustion in excess air at atmospheric pressure over PdO was adopted. Complete CH_4 combustion (1wt. % in air) is guaranteed in the microchannels at GHSV as high as 214,290 h^{-1} with negligible pressure drop. In the case of the FT synthesis microreactor GHSV in the 5,000-10,000 h^{-1} range have been considered for the syngas stream (H_2/CO molar ratio of 2). The synthesis reaction has been modelled as a heat source on the walls, coupled with the partial boiling of water in neighbour microchannels for heat removal.

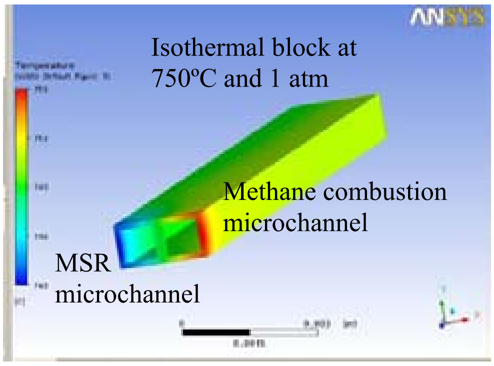

Figure 1. MSR and CH_4 combustion in two neighbour microchannels in parallel arrangement

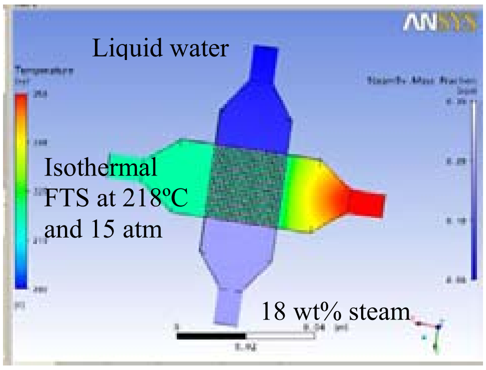

Figure 2. FTS coupled with partial boiling of water at 15 atm in the micoreactor (crossed flow).

It has been found that for both MSR (Figure 1) and FT synthesis (Figure 2) reactions isothermal operation can be achieved at temperatures in the 750-900 °C and 200-250 °C range, respectively. Methane conversions close to the equilibrium values are obtained at the MSR microchannels outlet. Isothermal MSR operation can be achieved by adjusting the space velocity and/or concentration of the CH_4-air mixture although a sufficiently high inlet temperature is required. A great influence of the microchannels arrangement has been found in this case. As concerns the FT synthesis, isothermicity can be achieved by setting the operating pressure at a value (10-39 atm) at which the boiling point of water is slightly below the temperature at which the synthesis reaction has to be carried out.

Acknowledgements

We gratefully acknowledge financial support of this work by Petróleo Brasileiro S.A. – PETROBRAS and Spanish Ministry of Education and Science (MAT2006-12386-C05-01, -02 and -04).

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OP-III-19

COMPUTER MODELING OF CATALYTIC REFORMING PROCESS IN MOVING-BED REACTOR WITH CONTINUOUS CATALYST REGENERATION

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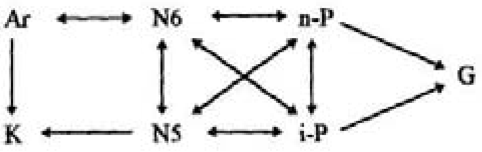
The model for computer prediction of the catalytic activity dependence on service life and technological conditions for bifunctional Pt-catalysts has been proposed. The proposed model is based on physical and chemical laws of multicomponent hydrocarbon transformations on polymetallic catalysts and takes into account deactivation of acidic (Al) and metallic (Pt) sites. It allows calculating the product composition and catalytic activity level for real industrial units as a function of their technological parameters and raw material characteristics. Petrochemical processes are very complex for the computer simulation as they include a number of parallel and successive stages. Industrial realization of these processes requires the determination of optimal unit parameters. Our task was to analyze systematically physical and chemical information. In this case, mathematical modeling is an efficient instrument. Models formed on the basis of hydrocarbon transformation laws permit to compute quantitative process characteristics and predict an optimal work regime for industrial units. A specific feature of petrochemical processes is in the fact that oil and oil refining products have complex hydrocarbon compositions. So, the mathematical description would be very complex if all reactions and substances are considered. On the other hand, a pseudokinetic model can be created for pseudocomponents constructed from hydrocarbons belonging to one homologous group. In this case, kinetic information is lost.

This problem has been solved due to creation of a mathematical description for an industrial reforming process, which includes stages presented in the scheme below:



where Ar are aromatic hydrocarbons, N6 are hexamerous naphthenes (C6-C12), N5 are pentamerous naphthenes (C5-C12), n-P are normal paraffins (C1-C12), i-P are isoparaffins (C4-C12), K is coke, G are gaseous substances, C is the number of carbon atoms in molecules. Relations of hydrocarbon molecular dimension and structure with quantitative and qualitative characteristics of its conversion, such as conversion mechanism, activation energy, chemisorption heat and probability of bond dissociation, have been investigated. The results of this investigation permit to aggregate certain components used during construction of the mathematical model. The proposed model contains material and heat balances equations:

$$G\cdot\frac{\partial C_i}{\partial z} = -u\cdot\frac{\partial C_i}{\partial r} - \vartheta\cdot\frac{\partial C_i}{\partial l} + W$$

$$\rho\cdot C_p^{\text{см}}\cdot G\cdot\frac{\partial T}{\partial z} = -u\cdot C_p^{\text{см}}\cdot\rho\cdot\frac{\partial T}{\partial r} - \vartheta\cdot C_p^{k}\cdot\rho\cdot\frac{\partial T}{\partial l} + \sum Q_j\cdot W_j$$

$t=0$ $T=T_0$; $r=0$ $T=T_{\text{вх}}$; $l=0$ $T=T_{\text{вх}}$

where j is the reaction number according to the process mechanism, i is the number of an individual component or a hydrocarbon group, Z is the quantity of raw material processed after last regeneration, V is the catalyst volume, G is the unit flow rate of crude oil, Ci is the concentration of the i-th individual hydrocarbon or hydrocarbon group, C is the hydrogen concentration, Lj is the hydrogen reaction order of the j-th reaction, T is the reactor temperature, Cp is the mixture heat capacity, Hj is the enthalpy of the j-th reaction, Wj is the rate of the j-th reaction, l is a length of reactor.

Experimental data for an industrial reforming process obtained on the Omsk refinery (Russia) were used for computation. The refinery has three reforming units: L-35-11/1000. Technological schemes contain three reactors for each unit. A block of computer programs based on the proposed model for calculation of the industrial reforming unit works depending on technological conditions.

A REACTOR WITH CO_2 LASER RADIATION FOR DEHYDROGENATION OF LIGHT ALKANES TO ALKENES

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Introduction

Improvement of the process for ethylene production via dehydrogenation of ethane and other light alkanes in tube furnaces is a topical problem. In tubular reactors [1-3] energy is supplied to reactants by burning a part of hydrocarbon feedstock on the external surface of the tubes. Hot walls of the tubes facilitate not only the formation of radicals, but also their coking. Pyrolysis of ethane is performed in the temperature range of 760 – 820°C with the conversion of 32 – 68% [1]. We propose to create a local zone of elevated temperatures in the tube gas with the use of laser radiation introduced in the reaction volume. The radiative power should be two orders of magnitude lower than the heat rate coming to reactants from the walls. The establishment of such zone of elevated temperature creates the conditions for control over the process of pyrolysis. The zone of elevated temperature is a source of radicals for initiating a radical-chain process, which will enable us to reduce temperature of the tube walls and decrease the dilution ratio. The transformation of CO_2 laser energy to thermal power occurs with the use of ethylene, which is the main product. This will enable the control of pyrolysis via the generation of radicals in the gas phase by the reaction $C_2H_4 + C_2H_6 \rightarrow C_3H_7 + CH_3$.

The lecture presents results of the study on ethylene dehydrogenation in a lab-scale model reactor with the laser input of energy, and a solution of basic engineering problems arising at heating the reaction mixture components by the laser energy flux delivered directly into the gas.

Results

A particular engineering task is to supply the radiation into reactor with a high power density and prevent its absorption by gas near the windows. Such protection can be provided by a gas flow not absorbing the energy of laser radiation. The FLUENT software program tested with the experimental data of laboratory setup will allow using the numerical methods to search for the reactor design, which will be further implemented in a prototype reactor.

In the experiments, total consumption of argon was set at 3L/h, consumption of the ethane-ethylene mixture was specified as 1.7L/h at a 30% content of ethylene. The distribution of gas flows in the reactor was studied at their temperature of 20 °C and atmospheric pressure. The results of numerical modeling with the FLUENT program were obtained by solving the Navier-Stokes equations for the dynamics of gas flow mixing. Thus, this software can be used for calculations taking into account chemical processes and radiation.

Dehydrogenation of ethane was performed at atmospheric pressure and temperatures below 1000 °C with the main reaction products: C_2H_4, CH_4 and H_2. Propylene and C_2H_2 accounted for no more than 1 and 4% vol., respectively. Ethane conversion is close to zero in the region of 600 °C, gradually increasing to 80-90% as the temperature was raised up to 850 °C.

Thus, it was demonstrated that reactions in the zone of laser radiation absorption proceed with high efficiency.

Conclusions

The proposed line of improving the alkane pyrolysis processes is based on the use of a ‘control element’. Such elements include lasers with power up to 1 kW. This may decrease the length of pyrolytic tubes, which is a beneficial effect diminishing the overall dimensions of pyrolytic furnaces.

Our work showed that the problems of energy input to the reactor with a high power density are solvable. Ethane pyrolysis in the reactor with laser input of energy has been implemented successfully with conversion exceeding 80% and ethylene yield of ca. 55 mol % per a mole of feedstock. Ethylene was found to be an efficient converter of laser energy to heat power.

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THE WAY OF METHANOL PRODUCTION: NEW TRENDS TOWARD INCREASING PROCESS PROFITABILITY

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In Russia, there is currently a significant demand for high-octane environmentally clean motor fuels [1-2]. Natural gas conversion to motor fuels and the key products of chemical synthesis is usually performed by two processes, namely, the Fischer–Tropsch synthesis and the Mobil process. In both processes, hydrocarbon products are obtained from synthesis gas. However, the selectivity of the Mobil process with respect to hydrocarbon components of gasolines is higher. These components are synthesized in the Mobil process by synthesis gas conversion to methanol and/or dimethyl ether conversion to motor fuel hydrocarbons. Consequently, it is of prime importance to improve technologies for methanol production from natural gas [3]. Methanol production will occupy a key place in industry if the cost of produced methanol can be reduced by 15–20%.

Known industrial technologies for methanol production from natural gas are analyzed. Their main advantages and disadvantages are determined, and a new methanol synthesis technology without feed circulation is proposed, which, in particular, is also applicable at a significant nitrogen content of the synthesis gas feed.

To predict the operation of equipment with high energy and resource savings, it is necessary to construct new models that would allow one to calculate the concentrations of the desired products and the byproducts in individual stages of methanol production with high accuracy. The purpose of this work is to analyze and model the process of natural gas conversion to methanol in order to enhance this process for reducing the product cost. The development of new highly profitable industrial processes for synthesizing methanol from natural gas could provide a way to use the fields of natural gas in which the gas is at various stratum pressures for the production of oxygenated diesel and hydrocarbon motor fuels.

The results of the experimental investigation of the kinetics of methanol synthesis and the modeling of this process in catalytic reactors revealed a region in which methanol synthesis is highly selective. In the crude methanol obtained by the new technology the concentration of byproduct water is several times lower than that in currently produced industrial crude methanol. It is experimentally shown that regions of highly selective synthesis gas conversion can be formed in catalytic reactors by regularizing the catalyst beds, adding inert heat-transfer media to the feed, and externally heating the catalyst beds. Note that the crude methanol obtained by the new technology has high purity; therefore, for a number of industries, this can be either a marketable product, e.g., for the gas industry, or a raw material for producing dimethyl ether, ethylene, propylene, and motor fuels. For the highly purified methanol obtained, the number and volume of industrial distillation columns are much smaller, which reduces the specific metal content of the process equipment and the energy consumption. Moreover, the absence of feed circulation in the methanol production by the new technology results in additional energy savings. This also increases the methanol production profitability. Last, since methanol is synthesized under mild operating conditions, the service life of industrial catalysts is also prolonged.

The experimental data are processed by the nonlinear least squares method to estimate the constants of all kinetic models. It is shown that all the models are in agreement with the experimental data. The goodness of fit of the kinetic model of methanol synthesis to the experimental data is tested by Bartlett's criterion. This criterion is used for testing the hypothesis of equality of two variance–covariance matrices, one of which is calculated from the results of a replicate experiment and the other of which is computed from the residual vector calculated from the model constructed.

The final step of modeling of a catalytic process is to calculate the designs of the reactor unit and its constituent individual reactors and to determine the operating conditions of the reactor unit under which a given output, feed conversion, and energy consumption are ensured. A three-reactor methanol synthesis providing 75-80 % conversion of the synthesis gas feed is calculated. The crude methanol obtained has a high content of the desired product of 94-99 wt.%. The residual synthesis gas should have a calorific value no less than 2400 kJ/m^3 so that it can be used to generate power sufficient for the process to be closed in energy. Low-output methanol synthesis plants can be placed directly at gas production sites for providing immediate transport of the liquid products of gas processing from the north of the Russian Federation to its central regions and abroad.

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MATHEMATICAL MODELLING OF THE ETHYLENE GLYCOL OXIDATION PROCESS

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Heterogeneous catalytic oxidation of alcohols is one of the most important methods of synthesis of such valuable carbonyl compounds as formaldehyde, acetaldehyde, acetone, propionic aldehyde, phtalic aldehyde, etc. Glyoxal, one of the most important products of modern industry, can be synthesized by partial oxidation of ethylene glycol. This aldehyde is used in wood-working, tanning, pharmaceutical, paper and many other industries.

Industrial production of glyoxal is generally carried out by vapor-phase oxidation of ethylene glycol over copper, silver and complex Cu-Ag catalysts [1]. New catalytic systems for this process based on silver nanoparticles were developed at the Laboratory of catalytic researches of Tomsk state university. These catalysts show high activity and thermal stability, and are perspective for using in industry.

The aim of the present work is to develop a mathematical model of the ethylene glycol oxidation process, allowing the optimization of the process conditions, and prediction the behavior of the reaction system.

Experimental data of the process realization, taken for model development, were obtained according to [**Ошибка! Закладка не определена.**]. The investigations were carried out in continued-flow fixed bed reactor (reactor length was 100 mm), the temperature span was 500-650 °C. In each experiment the temperature profile along the reactor under steady operating conditions was measured and recorded. Liquid and gas products of the reaction were analyzed chromatographically. Mathematical processing of the experimental results was performed with using of HYSYS program.

The following statements were used during the development of the mathematical model: (1) the ethylene glycol oxidation process is realized in the external diffusion mode; (2) both oxidation reactions of glyoxal into CO and water, and CO into CO_2, as well as water-gas-shift-reaction take place on the catalyst surface in the kinetic mode.

To calculate the heat balance the time-dependent equation of heat transmission over the solid phase of the catalyst bed was used. General heat exchange coefficient was calculated according to the quasi-homogeneous model of tubular reactor [2-3]. The maximal temperature at the centre of the catalytic bed was estimated by the determination of the heat exchange coefficient as a function of both Bio parameter and coefficient of heat exchange with the reactor wall from the two-dimensional model [**Ошибка! Закладка не определена.**]. Temperature mode optimization within the framework of the developed mathematical model included variation of the following parameters: temperature of the reaction gases incoming flow, reactor wall temperature, temperature in the center of the catalytic bed, catalytic bed porosity, and degree of dilution of the catalyst by inert support.

In *Figure 1* one can see the calculation of the reactor temperature mode, satisfactorily describing the experimental data with respect to the value and position of the «hot zone» of the catalytic bed as well as the main parameters of the process: ethylene glycol conversion, glyoxal yield and selectivity, and CO and CO_2 yields.

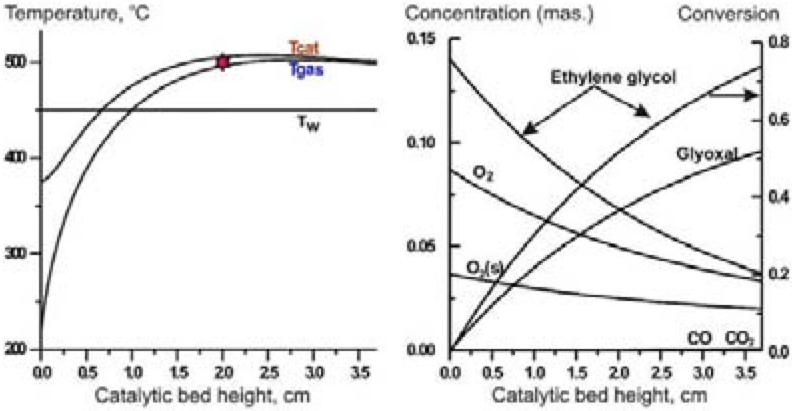

Figure 1: calculation of the reactor temperature mode and main parameters of the process

Predicting calculations were performed for two variants of the organization of the catalytic bed, providing the given productivity of the reactor: (1) variation of the catalyst bed height at constant reactor tube diameter; (2) variation of the reactor diameter at minimal value of the catalyst bed height.

It was shown that the mathematical model developed for both variants allows optimizing the bed height and dilution of the catalyst, providing acceptable temperature mode for the catalyst bed (less than 650 °C at the «hot zone») as well as the given values of the ethylene glycol conversion (100 %), and selectivity with respect to glyoxal (90-92 %). The model developed satisfactorily describes the experimental data obtained with using of the laboratory reactor. This allows predicting the effective temperature modes of the realization of the ethylene glycol oxidation process in the preassembled catalytic reactor.

Acknowledgements

This work was supported by the Grant of the President of the Russian Federation №YD-968.2007.3 and the Grant of Tomsk region Administration № 336.

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NEW ROTOR REACTOR FOR THE SYNTHESIS OF DIFFERENT MORPHOLOGICAL TYPES OF CARBON NANOFIBERS

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Carbon nanofibers (CNFs) and nanotubes (CNTs) are promising to revolutionize several fields in material science and are suggested to open the way into nanotechnology. CNFs and CNTs are well known to have physical properties (strength, tensile modules, high electrical and thermal conductivity) that tend towards single crystal graphite. Due to their extraordinary properties the nanostructured carbon materials can be widely used for many applications. The most developed directions of use are listed below:

- Extenders for conductive coatings and paints;
- Reinforcements for polymer matrix composites and rubbers;
- Conductive structural adhesive for aerospace applications;
- Polymers in automobile industry (bumpers, dash and door panels etc);
- Storage materials for hydrogen energetic;
- Materials for broadband electromagnetic shielding;
- Component for super-capacitors and lithium-ion anodes;
- Enhancement of catalyst utilization in methanol and hydrogen fuel cells;
- Adsorbents and filters.

In the present time there are more then 100 companies in the world that are dealing with production of CNFs and CNTs for diverse applications. The annual production of nanostructured carbon materials has achieved 500 tons per year in 2007 that corresponds to almost 1 billion dollars of summarized world market, which is believed to be doubled in next two years. According to forecast of market specialists, the low-cost light and reinforced composite materials for automobile and aerospace industry would be the most essential in the nearest future.

Further market development is thought to be depending on material availability at reasonable prices as well as an effective manufacturing technology for production of such materials in extended scales. In most cases wide practical application, in particular in the field of composite materials, is not possible yet due to lack of low-cost CNFs in sufficient quantities. Our research was focused on creation of new type of reactor for the synthesis procedure yielding bulk amounts of high purity carbon nanofibers of defined morphology. The original design of rotor reactor for production of CNFs as well as catalyst compositions and parameters of synthesis procedure of carbon nanofibers of desired structure will be reported.

The considerable theoretical and experimental experience collected for today permits one to formulate the basically challenges to be faced while transferring the technology from lab-scale to pilot plant level. In any case when searching for the principle design of reactor for the synthesis of CNFs, the defining peculiarity of this process must by taken into account. The point is that the initial volume of loaded catalyst is supposed to be significantly increasing (in hundreds times fold) during the process of carbon nanofibers deposition which makes impossible the use of conventional reactors with a fixed bed catalyst layer. The carbon nanofibers growing over the stationary layer of catalyst was found to convert into monolith soon, which causes the suppression of further process of synthesis. That is why the fundamentally new design solutions are required while creating the reactors for CNFs manufacturing. It should be also noted that the specificity of this process imposes a limits on realization of synthesis by uninterrupted technology. As soon as the reactor is filled with the product it should be stopped, emptied and then refilled with the next portion of catalyst.

We have considered and compared a several different types of reactor design:

- With the fluidized catalyst bed;
- With the moving catalyst;
- With the moving catalyst countercurrent to gas flow.

Nevertheless, for a variety of reasons we have chosen the type of fully rotating horizontal barrel with the cylinder shape. While the reactor is revolving on its axis it makes catalyst granules to be continuously moving and over-pouring inside the barrel with favors shaking and stirring of carbonated catalyst to intensify the mass exchange with gaseous phase. The nanostructured carbon product depositing on catalyst is to occupy gradually the void volume of rotor reactor that requires further break and overloading.

There are three principle structures of nanoscale carbon fibers that can be distinguished: coaxial-conic, coaxial-cylinder and platelet. The combination of said morphologies allows one to obtain the huge variety of other structures of CNFs. The synthesis conditions for CNFs in extended scale using the prototype rotor reactor will be discussed in the report. The following types of CNFs will be considered:

- Coaxial-conic fibers (herringbone);
- Platelet fibers;
- Featherlike (disordered) fibers.

The morphology of developed samples of CNFs was analyzed and confirmed by scanning (SEM) and transferring (TEM) high resolution electronic microscopy.

LOW-TEMPERATURE DIRECT ROUTE TO ANILINE *VIA* AMINATION OF BENZENE IN THE PRESENCE OF OXYGEN AND HYDROGEN

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Introduction

Aniline is produced from benzene in two-stage routes of (1) nitration of benzene followed by reduction of nitrobenzene, and (2) amination of phenol obtained by hydroxylation of benzene. One-stage vapor-phase amination of benzene with ammonia

$$C_6H_6 + NH_3 = C_6H_5NH_2 + H_2$$

is strongly exothermal reaction [1]. An appreciable equilibrium concentration of aniline can be obtained over metal catalysts at extremely high temperature. Addition of oxidants consuming hydrogen shifts equilibrium to aniline. However, the noble metal catalysts operate at the temperature as higher as 350-500 °C even in the presence of oxidants, such as molecular oxygen [2-3] or reducible metal oxides [4-5].

In the present study, it was found that the temperature of amination can be hundred degrees lower when a mixture of oxygen and hydrogen is used as oxidant.

Experimental

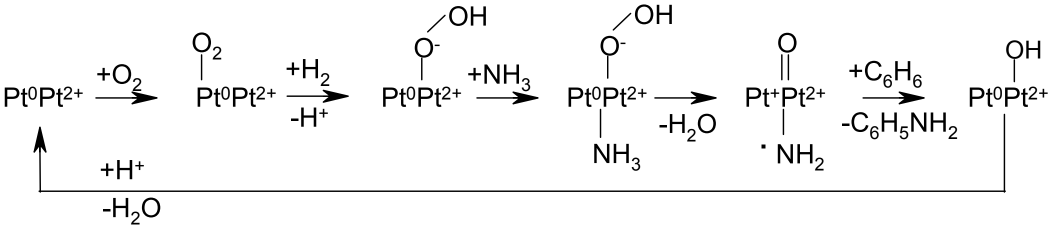
The $Pt/\gamma\text{-}Al_2O_3$ samples were prepared by incipient wetness impregnation of alumina with a solution of H_2PtCL_6, followed by drying in air, calcination at 450 °C and reduction with H_2. X-Ray photoelectron spectra (XPS) of the samples were recorded on ES-300 (KRATOS Analytical) spectrometer.

The amination of benzene with ammonia was performed in a fixed-bed flow reactor at ambient and elevated pressure. Oxygen, hydrogen (or premixed $O_2/H_2/N_2$ gas in experiments at elevated pressure) were controlled by mass-flow controllers, the liquid benzene (and liquid ammonia in experiments at elevated pressure) were introduced by a syringe pump. The reactor was supplied with an on-line GC for an analysis of O_2, H_2 (NaX molecular sieves), CO_2 and NH_3 (Hausep C + 4.5% KOH) and aniline, phenol, benzonitrile and biphenyl (0.4% 1-nitroanilinoanthraquinone on carbon black) in the stream.

Results and discussion

The Pt/γ-Al_2O_3 samples catalyzed amination of benzene with ammonia in the presence of oxygen and hydrogen. Reaction proceeded above 200 °C, maximal rate of conversion of benzene and production of aniline being attained at around 250 °C. Aniline amounted to 60% of the total products. Along with aniline, conversion of benzene produced benzonitrile and diphenyl.

The stream supplied was strongly enriched with ammonia and contained small amounts of oxygen and hydrogen. It was determined that increasing O_2 resulted in a higher conversion of benzene and increase of benzonitrile, not aniline, in the outlet stream. Equimolar contents of O_2 and H_2 in reagents appeared optimal to obtain aniline. Under equal partial pressures of O_2 and H_2, the rate of formation of aniline grew with elevation of the O_2+H_2 percent, and was invariable under variation of C_6H_6 percent from 7 to 27%. At elevated pressure, 5-fold increase in partial pressure of reagents resulted in 2.5 times increase in the rate of formation of aniline and disappearance of benzonitrile.



XPS analysis of the Pt/γ-Al_2O_3 catalysts with Pt content of 2 to 10 wt.% indicated Pt 4d signal to corespond to metal. Oxidative conditions of the process permited partial oxidation of the surface, so that mechanism of amination speculatively represented by the following scheme, included charged Pt species. They were engaged into generation of reactive oxygen and, then, aminating radical species $^{\cdot}NH_2$ which possess reactivity with respect to benzene.

Conclusion

Application of the O_2/H_2 oxidant permitted to carry out amination of benzene below the temperature of intensive decomposition of ammonia. The process was suggested to be realized by the radical intermediates on the surface of platinum catalyst.

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Section 4.

Catalytic technologies in fuel and energy production
– production of hydrogen
– production of environmental friendly fuels
– environmentally friendly engineering

OP-IV-1

DEEP DESULPHURIZATION OF PETROLEUM STREAMS: NOVEL TECHNOLOGIES AND APPROACHES TO CONSTRUCTION NEW PLANTS AND UPGRADING EXISTING FACILITIES

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One of the most important challenges that the refinery industry faces nowadays is the continuous demand on the low sulphur content in transportation and other fuels. Changes in legislative norms enacted by different counties towards both the sulphur concentration and the application of new feedstocks (e.g. plant oils) force the fuel manufacturers over the world to search for the effective ways in processing.

The paper reviews the situation in the development of the new approaches to desulphurization and focuses on the scientific and practical issues important for refineries.

Despite the fact that a great number of new chemical and adsorptive procedures for the sulphur reduction have been developed last time, they are not and, apparently, will not be able to compete with the traditional desulphurization method – hydrotreating, which do and will dominate in industry.

In refinery, the continuous hydrodesulphurization (HDS) process is carried out in the so-called trickle-bed reactors (TBR) where the hydrogen-content gas flows downwards together with liquid through the fixed catalyst.

In order to provide the necessary intensity of mass transfer as well as the demanded temperature control, an enormous quantity of the hydrogen-content gas (sometimes up to 3000 Nm^3gas/m^3oil) should be recycled through the catalyst bed. Since the recycle compressors can only operate under mild temperatures that are significantly less than those in the reactor, the recuperative heat exchangers should be used on the gas loop. That increases the pressure drop and, therefore, leads to considerable requirements of energy for compressing. It is not surprising that 20% of energy consumption in a refinery is spent in hydrotreating processes. The detailed analysis of energy expenditures in an operating HDS plant shows that, due to the nature inherent in two phase gas-liquid flow, TBR units have very low energy efficiency for the process purposes and have no potential for the process improvement.

Our paper introduces the possibility of revamping the existing HDS units and constructing the new HDS facilities on the basis of the next generation of the POLF technology, according to which the reaction is brought about in the presence of the single liquid phase, but this liquid is previously saturated with gas.

Our estimations show that the implementation of the POLF technology allows a refinery to save: (i) 15% of heat energy in a burner, (ii) more than 70% of the total electrical energy spent for gas compressing and feed pumping as well as (iii) to decrease the consumption of make-up gas by 17%. It is expected that the application of the POLF process not only increases the reactor productivity (or desulphurization grade), but also decelerates the catalyst aging, improves the performance in a burn heater and simplifies the next stripping stage.

One of the main advantages of the POLF technology is the possibility of the comparatively simple upgrading of the existing TBR units. In this case, nearly all equipment and control systems can be utilized. Moreover, the old technological scheme will not be destroyed and every time can take over the process if necessary.

OP-IV-2

LACTIC ACID AS A BACKGROUND CHEMICAL FOR A «WHITE CHEMICAL INDUSTRY» DEVELOPMENT

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The growing oil demand, high oil prices and lack of perspectives of substantial increasing of oil production were the main reasons for the development of new industry of motor fuel production from renewable sources based on carbohydrates and vegetable oils. Progress in the development of new technologies of renewable raw materials transformations to fuels makes it possible to displace now up to 10% of fossil fuels to biodiesel and bioethanol. Moreover a profitability of a large number of petrochemical manufactures is going down because of the growing oil prices. For many petrochemicals it becomes critically low and for some of them - negative and their production were closed (e.g. glycerol, based on propylene, lactic acid, based on ethylene or propylene, and others). In these situation the same raw materials of vegetable origin, as for biofuels production, becomes competitive with oil for many of commodity chemical intermediate production. So unsaturated acids produced from vegetable oils are good raw materials for manufacture of alfa olefins, dicarboxilic acids and other products. Cheap glycerol, produced from vegetable oils, becomes attractive intermediate for many other chemical products. But the largest raw material source for commodity chemical intermediate production is glucose and sugars which can be isolated from vegetable sources of different kind, or produced by means of biotechnological methods from vegetable carbohydrates of different origin (starch from corn, wheat, potatoes; cellulose from wood, straw, wood dust and so on). Progress in biotechnology, large resources and low and comparatively stable prices of vegetable raw materials permanently make the list of chemicals, produced from sugars and competitive with petrochemicals, longer and longer. Now the list includes ethanol, lactic acid, 1,3-propanediol, polyhydroxyalkanoates, pyruvic acid and some other products. The first two chemicals are the source for production of a huge number of other products many of which are ecologically friendly or biodegradable. So we are witnesses now of the birth of new kind of industrial chemistry which could be called «white chemistry». The «white chemistry» includes biotechnology, is based on sugars, is opposite to «black chemistry», based on oil, and corresponds to a part of «green chemistry», which is based on renewable sources and gives ecologically friendly and biodegradable products.

We consider lactic acid as a background chemical for production of a lot of intermediate and final large scale commodity chemicals many of which are ecologically friendly and biodegradable. The technologies which we are working on at the moment include:

- ammonium lactate production from glucose;
- ammonium lactate transformation to butyl lactate and ammonia;
- production of pure lactic acid and a series of «green solvents» (methyl, ethyl, isopropyl, butyl and other lactic acid esters, which are biodegradable and are able to replace a series of toxic solvents mentioned in REACH);
- production of lactic acid oligomer from lactic acid or butyl lactate, which can be transformed to lactide or to a series of other lactic acid esters;
- lactide polymerization with polylactide formation which is biodegradable polymer with a wide spectrum of application and is able to replace traditional polymers finally transformed to a huge quantity of wastes;
- butyl or methyl lactate or lactic acid hydrogenation with propylene glycol formation which will be able to replace toxic and widely used ethylene glycol;
- butyl or methyl lactate dehydration with corresponding acrylate formation – another large scale petrochemical.

The key process in this list is a micribiological transformation of glucose to ammonium lactate which determines the cost and competitive ability of the other chemicals listed below in comparison with the corresponding petrochemicals. For decreasing of operation cost we used membrane continuous fermenter with thermopilic bacteria. This method makes it possible to increase productivity of the reactor comparatively with usual periodic installation up to 30 times and to exclude the stage of biomass separation which works continuously in the membrane reactor as a catalyst. The other transformations listed above are usual chemical technologies which are needed in active, selective, stable and cheep homogeneous or heterogeneous catalyst, optimal reactor design and reaction conditions. We have found such catalysts, reaction conditions and designed reactor systems for the majority of the processes listed above, which will be presented in this report.

OP-IV-3

CO REMOVAL FROM H_2-rich GAS MIXTURES IN MICROCHANNEL REACTORS WITH Cu/CeO_{2-x} CATALYSTS

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Preferential CO oxidation (PROX) is one of the promising methods for CO removal from hydrogen-rich gas mixtures produced by hydrocarbons conversion processes. Microchannel design of catalytic reactors due to enhanced heat and mass transfer has big advantages for this process. However it requires development of new active components of catalysts able to realize these engineering breakthroughs by operation at short contact times without loss of activity and stability. Besides such engineering arguments, micro-channel reactors demand for new kinds of catalyst formulation also from the system integration side, most prominently being washcoated layers attached to the channels' walls.

Several series of the catalysts for preferential CO oxidation were synthesized. Copper-cerium oxide was used as the main active component. The catalysts were synthesized by various procedures that allowed variation of the textural and morphological characteristics of the samples. The main efforts were focused on the finding of the optimum copper-cerium oxide catalyst composition and development of the most feasible preparation procedure that would provide introduction of the active component into microchannels without activity losses. It was obtained that the procedure for copper-ceria catalyst introduction into microchannels based on the deposition of water suspension of the catalyst with polyvinyl alcohol as a binder was the most promising one. Experiments with the variation of catalyst composition and preparation method of catalyst-binder suspension resulted in reproducible data on the introduction of copper-cerium oxide washcoats into microchannels of stainless steel platelets. The obtained samples demonstrated good impact-resistance, survived contacts with water (that is critically important for microreactor operation in real conditions, as well as in the case of water condensing on fuel processor startup and stop).

Simple sandwiched (two-plate) and laserwelded micro-channel reactors were used for catalyst testing. The catalyst performance for selective CO oxidation in H_2 excess was studied in a flow setup with on-line chromatographic analysis of the reaction products. Catalytic performance of the microchannel reactors were checked using model feeds at WHSV = $5000 \div 120000$ $cm^3/g{\cdot}h$ and temperature $100 \div 300$ °C. For comparative experiments on the activity of copper-cerium oxide catalyst towards the reactions in the microreactor and in conventional flow reactor, the same bulk catalyst was selected as for microreactor preparation (which was prepared with the use of all intermediate procedures for Cu/CeO_{2-x} washcoating into microreactor channels). It was founded that in all cases the CO output concentration initially decreased and then increased with temperature over both packed bed reactor and microreactor with copper-cerium oxide catalyst (Fig. 1). The minimum value of CO concentration in the microreactor was as low as 10 ppm from 180 to 220 °C. The minimum value of CO concentration in the packed bed flow reactor was 800 ppm at 210 °C. Almost 100% selectivity was observed in the microreactor at T = 150 °C. A further increase in the temperature resulted in a dramatic decrease in selectivity to 33%. The same trend was observed for the packed bed reactor, but selectivity was no more than 80% at 180 °C and further increase in the temperature resulted in a dramatic decrease in selectivity to 33%.

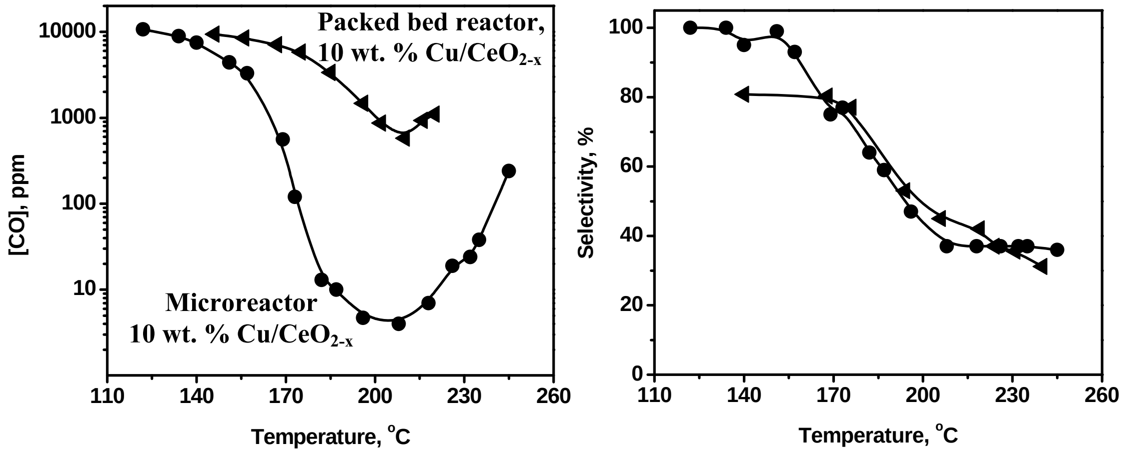

Figure 1. Effect of temperature on the outlet CO concentration and selectivity
Inlet gas composition: 60 vol. % H_2, 1 vol. % CO, 1.5 vol.% O_2, 20 vol. % CO_2, 10 vol. % H_2O, He (N_2) – balance. P = 1 atm; WHSV = 45000 $cm^3/g{\cdot}h$.

The better performance of the microreactor as compared to the packed bed reactor can be explained by the following consideration. At high flow rates, the reaction releases significant amount of heat. In microreactor, the released heat dissipates quite readily over metallic platelet that facilitates the reaching of isothermic state (temperature difference at the microreactor inlet, center and outlet was no more than 1-2 °C). In the packed bed reactor, the catalyst bed was not isothermic at high CO conversion rates (the temperature difference at the reactor inlet, center and outlet was 10-15 °C). In the case of hindered heat removal from the catalyst surface, side reactions tend to proceed. Reverse water gas shift seems to be one of these reactions. Due to RWGS, the outlet CO concentration in the packed bed reactor increases. In the microreactor, no hot spots appear due to prompt dissipation of the released heat that facilitates more efficient CO removal.

The work is supported partially by grants BRHE Y4-C-08-12, INTAS № 06-1000014-5774, «Global Energy» Foundation.

OP-IV-4

REFORMING OF ETHANOL OVER METAL CARBIDES SUPPORTED BY MULTIWALL CARBON NANOTUBES

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Abstract:

Carbides (Ni, W, V, Fe and Mo) have been prepared by the reduction and reaction of partially reduced oxides with multiwall carbon nanotube and carbon Norit. This way of preparation produced carbides in nano size. The formation of carbides was followed by XPS. Metal carbides exhibited different catalytic performances, which are influenced by the preparation of oxides, by the starting compounds, by the nature of carbon support, and by their pretreatment. NiC and Mo_2C were found to be most effective in the production of hydrogen.

Keywords: H_2 production, ethanol, carbides.

1. Introduction

The production of hydrogen from alcohol, particularly from bioethanol gained an increasing attention in recent years. Al_2O_3-supported noble metals are effective catalysts for the decomposition of ethanol, but the reaction required high temperatures. Another drawback is the rapid deactivation of the catalysts. In the light of these features, great efforts are being made: (i) to replace Pt metals with less expensive materials, (ii) to lower the reaction temperature, and (iii) to increase the stability of the catalyst. Potential candidates for the replacement of noble metals are the carbides, which exhibit high catalytic activity in many reactions, but were hardly applied for the production of hydrogen from alcohols. A noteworthy exception is the Mo_2C, which was found to be active in the decomposition of ethanol[1] and methanol[2] to generate hydrogen. In the present work we examine the catalytic performance of various carbides (Ni, V, W, and Fe) in the decomposition and reforming of ethanol. In order to increase the dispersion of carbides we use multiwall carbon nanotube (CNT) and activated carbon (Norit) of high surface area as support materials.

2. Experimental

Catalytic reaction was carried out at 1 atm of pressure in a fixed-bed, continuous flow reactor consisting of a quartz tube (8 mm id)[1,2]. The flow rate was in general 40 ml/min. The carrier gas was Ar, the ethanol content of the reacting gas-mixture was ~9.0%. Carbides were prepared by the reaction of oxides with the surface layer of carbon supports, which results in carbides in nano size. The starting compounds for the preparation of carbides were the corresponding oxides, which were prepared by impregnation of carbon supports into solution of metal nitrates to yield the desired amounts of carbides. The dried suspension was calcined in air at 673 K for 3 h, and then heated in the catalytic reactor in H_2 flow up to 973-1173 K with a temperature ramp of 5 K/min. The reduction of oxides and their reaction with carbons have been followed by X-ray photoelectron spectroscopy (XPS).

3. Results and discussion

XPS measurements revealed the reduction oxides started at 475-573 K, followed by the reaction of partially reduced oxides with carbon supports. The complete transformation of oxides into carbide was observed at the lowest temperature in the case of nickel, and the highest temperature, >1173 K, in the case of vanadium. The decomposition of ethanol started at the lowest temperature, 473 K, on V_xO-VC followed by W_2C, NiC and Fe_2C. The temperature dependence of the reaction varied with the catalysts. Total conversion was approached at 673-723 K. With the exception of vanadium the main process was the dehydrogenation of ethanol to produce hydrogen and acetaldehyde, which decomposed to CH_4 and CO. As regards the production of hydrogen we obtained the highest values (%, selectivity) on Ni_3C and W_2C, where the yield (selectivity x conversion) of H_2 was 30% and 27%, respectively. This value is somewhat lower than that determined for Mo_2C/C catalyst[1]. These carbides exhibited a remarkable stability even at 723 K. Adding water to ethanol changed the product distribution and enhanced the content of hydrogen in the products. In search for a promoter we found that the addition of potassium to Ni_3C/carbon improved its catalytic performance: increased the formation of hydrogen both in the decomposition and in the reforming of ethanol by facilitating the water gas shift reaction.

In order to obtain a deeper insight in the interaction of ethanol with carbides, we studied the adsorption of ethanol Ni_3C/Ni(111) and Mo_2C/Mo(100) under UHV condition. By means of HREELS spectroscopy we found that the primary step of the activation of ethanol is the rupture of O-H bond to give ethoxy (C_2H_5O) species. In addition, the cleavage C-O bond on the carbon deficient sites also occurs resulting in the formation of ethyl (C_2H_5) species.

4. Conclusions

Carbides, prepared by the reaction of oxides with the surface layer of carbon supports, catalyzed mainly the dehydrogenation of ethanol. Adding water to ethanol enhanced the formation of hydrogen. Comparing the catalytic efficiency of various carbides determined under similar conditions the most effective catalyst to produce hydrogen is still Mo_2C/C followed by NiC. Their catalytic performance in the generation of hydrogen can be increased by potassium promoter.

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MODELING OF HYDROGEN PRODUCTION BY STEAM REFORMING OF ETHANOL IN PACKED BED AND WALL-COATED REACTORS

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Introduction

Nowadays, it is of reach interest the accomplishment of research activities to find alternative fuels and develop more efficient equipment for energy production because of the extended use of fossil fuels has been a determinant factor on several environmental pollution problems. The hydrogen is a promissory fuel by its clean and efficient combustion. Its problems of handling and storage can be solved using ethanol as a chemical source. Moreover, ethanol is possible to produce in large quantities from biomass, which does a renewable fuel. In recent years, many researchers have devoted their efforts to develop catalysts for steam reforming of ethanol to produce hydrogen for use in fuel cells [1-6]. Also, it has been developed kinetic models for some catalysts [7-11] and simulated its behavior in packed bed reactors [12]. In this work, with the aim of to find a kind of reactor more efficient for hydrogen production, a comparison between packed bed and wall-coated reactors by mathematical simulation was made.

Model description

Kinetic model

The catalyst selected in this case was a Ni(II)-Al(III) lamellar double hydroxide developed by Mas V. et al. [13] for which a preliminary kinetic model was developed. In this model was taken into account a reaction scheme of two reactions for ethanol steam reforming and used a power-law-type rate expression.

Phenomenological model

The software FEMLAB® 2.3 was used to simulate packed bed and wall-coated reactors with diameter of 4 mm and catalyst coating thickness of 0,1 mm (for wall-coated reactor) by means of a 2D heterogeneous axisymmetric model. Energy and mass balances for each component both in gaseous and catalyst phase were made. The operational conditions for the simulation at reactor inlet were: temperature 923 K and volumetric flow 0.2 ml/h (which was a mixture 1:6 molar ethanol/water) at atmospheric pressure. The reactor wall temperature was assumed constant and equal to inlet value in both cases.

Simulation results and conclusions

The temperature profiles for packed bed and wall-coated reactors are shown in the Figures 1 and 2. The simulation was run for a reactor longitude where total conversion was achieved. Thus, for packed bed reactor this distance was 0.92 cm and for wall coated reactor it was 2 cm. Total conversion is reached at low reactor longitude with a packed bed but, a high temperature gradient was found (40 K). However, the wall-coated reactor showed a almost isothermal profile, in spite of the high endothermic nature of ethanol reforming reaction. Therefore, the wall-coated reactor is a better choice for this process, because its thermal behavior lets to reduce operational problems such as catalyst deactivation by coking at low temperatures, and many others.

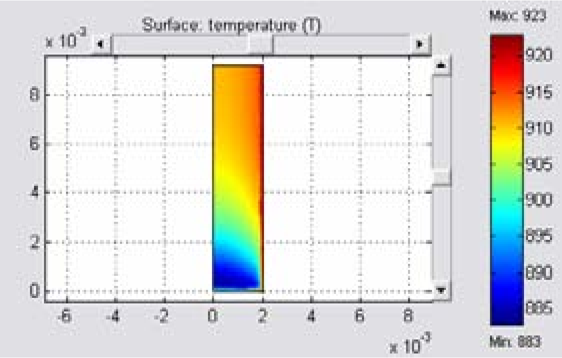

Fig. 1. Temperature profile for packed bed reactor.

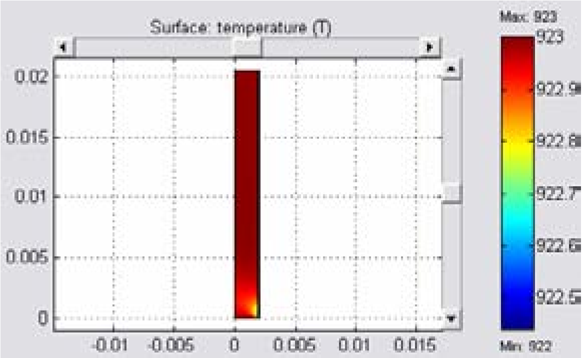

Fig. 2. Temperature profile for wall coated reactor.

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PRODUCTION OF HYDROGEN FROM THERMO-CATALYTIC DECOMPOSITION OF METHANE IN A FLUIDIZED BED REACTOR

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The Thermo-Catalytic Decomposition (TCD) of CH_4 is an attractive process for the production of H_2 with reduced CO_2 emissions. Main advantages of the TCD process compared to the conventional technique, i.e. CH_4 steam reforming, are: i) the energy requirement is less (37.3 kJ/mol_{H2}) than steam reforming (68.6 kJ/mol_{H2}); ii) due to the absence of oxidants, no carbon oxides are formed, so CO_x-free H_2 is produced; iii) the process is very simple (no water gas shift, CO_2 separation and CO-PROX units). A catalyst would be necessary since the thermal decomposition would require elevated temperatures (above 1200°C) [1], even if it deactivates due to produced carbon deposition on its surface.

Fluidized bed reactors (FBRs) have been recently indicated [2-5] as an efficient reactor solution for TCD process to overcome the limits linked to the use of fixed bed reactors, proposed in the past [1]: i) relatively high pressure drops, increased by the accumulation of carbon in the bed; ii) impossibility of a continuous operation due to the necessity to unload carbon and in turn to regenerate the catalyst. Consequently, new criteria have to be taken into account for catalyst design. In particular, a suitable catalyst should be characterized by a low propensity to attrition in addition to the requirements of high thermal stability and conversion efficiency [6]. Ammendola et al. [7] have proposed a suitable copper dispersed on γ-alumina catalyst in terms of: i) relatively high activity (between that of carbon and Ni catalysts, mainly studied in literature); ii) high operative temperature (up to 1000°C); iii) relatively high mechanical resistance to attrition.

In the present study the TCD of CH_4 has been investigated in a laboratory scale bubbling FBR. The experimental apparatus is reported in the Figure. It consists of a 2.6 cm ID stainless steel reactor, equipped with a gauze type gas distributor, an electrical oven surrounding the reactor employed to heat up the reactor at the reaction temperature and to provide enough heat for CH_4 decomposition, a device for collecting fine particles (> 300nm) escaping from the reactor in the exit gases. Temperature and pressure drops were measured by means of thermocouples horizontally inserted in the reactor and pressure transducers respectively. The inlet and outlet streams were analyzed by on line continuous analyzers for CO, CO_2, CH_4 and H_2.

A home-made copper dispersed on γ-alumina catalyst has been used. Details on catalyst preparation and characterization are reported elsewhere [7]. The Table reports its main characteristics.

The effects of both superficial gas velocity and amount of catalyst, i.e. contact time, as well as of reaction temperature, CH_4 inlet concentration and catalyst particle size on CH_4 to H_2 conversion, amount of carbon accumulated on the catalyst and deactivation time have been investigated. The fate of carbon produced during these CH_4 decomposition tests carried out in a FBR has been analyzed in order to evaluate the necessity of a catalyst regeneration stage on the basis of effectiveness of attrition to remove carbon deposited on the external surface of catalytic particles.

Figure. Experimental apparatus.

Table. Catalyst properties.

Active phase	Surface spinel $CuAl_2O_4$
Copper content (%wt)	8.4
Surface area (m^2/g)	156
Activation energy (kJ/mol)	155
Frequency factor ($cm^3/g/s$)	$1.8 \cdot 10^8$

Samples of bed catalytic particles after TCD tests and elutriated fines have been characterized by means of different techniques: i) elemental analysis to obtain the amount of carbon deposited on the catalyst and that elutriated in the exit gas; ii) SEM/EDS analysis to determine the morphology of carbon deposited on the catalyst surface; iii) BET analysis to obtain the surface areas of deactivated catalyst.

Experimental results have been used to highlight the relative role and relevance of elementary processes concurring during TCD of methane in FBRs (CH_4 catalytic decomposition, catalyst deactivation due to carbon deposition and catalyst reactivation by means of carbon attrition) as well as to individuate the more favourable operating conditions to maximize CH_4 conversion to H_2.

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SYNTHESIS GAS PRODUCTION FROM BIO-OIL: STEAM REFORMING OF ETHANOL AS A MODEL COMPOUND

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Currently, biomass via the fast pyrolysis converts to bio-oil typically being a complex mixture of oxygenates. Catalytic steam reforming (SR) of such bio-oil is an attractive route to produce hydrogen and so-called bio-synthesis gas which could be used as a potential source for production of renewable liquid fuels (dimethyl ether or hydrocarbons by Fisher-Tropsh process) and valuable chemicals [1]. Ethanol is one of the major components presents in bio-oil, therefore, steam reforming of ethanol (ESR) as a model bio-oil compound has been studied for the development of an efficient bio-oil processing via SR. Realization of bio-oil SR in structured reactors promotes the increase of syngas output that demands the study of the reaction at short contact times over relevant catalysts of a high activity [2].

In previous study, we reported that among a large number of catalysts, Ru- and Ni-Cu-Cr-containing samples based on doped Ce-ZrO_x are the most active and coking stable in ESR [3]. In the present work, the influence of such process parameters as a feed composition, contact time, temperature on the ESR proceeding is studied to obtain a high yield of syngas with a given composition.

Experimental

The catalysts 10%Cu-Ni-Cr/$Ce_{0.45}Zr_{0.45}Sm_{0.1}/\gamma$-$Al_2O_3$(CNC/CZS1) and 1.4%Ru/ $Ce_{0.4}Zr_{0.4}Sm_{0.2}/\gamma$-$Al_2O_3$ (RuCZS2) were synthesized via impregnation of La-stabilized γ-Al_2O_3 with corresponding solutions followed by calcination at 800°C.

ESR was conducted over the 0.25-0.5 mm catalyst fraction in a U-shaped tubular flow reactor at atmospheric pressure, 3300-50000 h^{-1} GHSV (0.07-1s contact time) and 300-800°C. Before testing the catalysts were reduced at 400°C in the flow of 10 % H_2 in N_2 and then exposed to a feeding gas mixture ($C_2H_5OH:H_2O:N_2$:=10:30-60:30-70%vol.). Three on-line gas chromatographs (GC) «LHM-8» were used for the analysis of reactants and products.

Results and discussion

Effect of the temperature and contact time on ESR. The testing of the catalysts in SRM shows that, at short contact times, the complete ethanol conversion over CNC/CZS1 was obtained only at 800°C. For RuCZS2, it reaches 100% at temperatures 400-700°C at all contact times in the feed $C_2H_5OH:H_2O:N_2$=10:40:60% but concentrations and selectivity of desired- and by-products strongly depend on the contact time. At decreasing contact time, the formation of H_2 and CO is hampered at temperatures below 700°C and C_2H_4 formed via ethanol dehydration is mainly present (Fig.1). At contact times < ~0.5 s, further temperature increase up to 800°C leads to the rise of syngas concentration up to ~35vol.%.

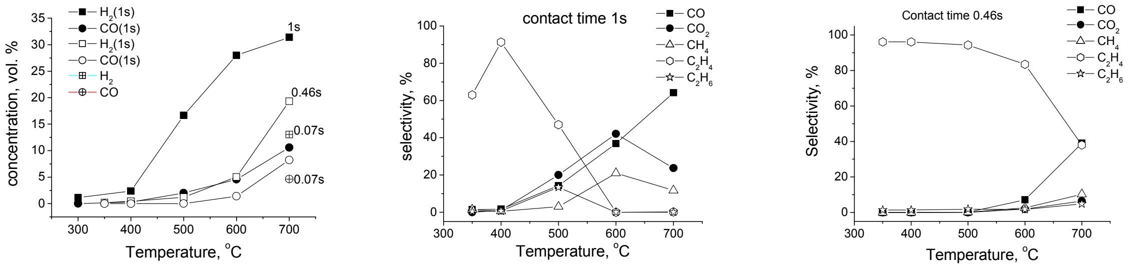

Fig. 1. Temperature dependence of H_2 and CO concentration (A) and product selectivities (B,C) on the contact time over RuCZS2 catalyst. $H_2O:C_2H_5OH=4:1$.

Effect of the feed composition. For RuCZS2, at contact time 0.07-0.1 s and H_2O:EtOH < 6, some decrease of ethanol conversion is observed at temperatures below 800°C. Variation of H_2O concentration in the feed strongly influences the product selectivities that allows tuning of syngas composition (Fig. 2). At temperatures above 700°C, for the same contact time, the reduction of H_2O:EtOH ratio leads to a lower yield of syngas and favours the formation of C-containing products. The temperature dependence of H_2/CO ratio varies with the value of H_2O:EtOH and contact time. The highest syngas yield (~45vol.%) is achieved at H_2O:EtOH=5-6 and temperature 750-800°C.

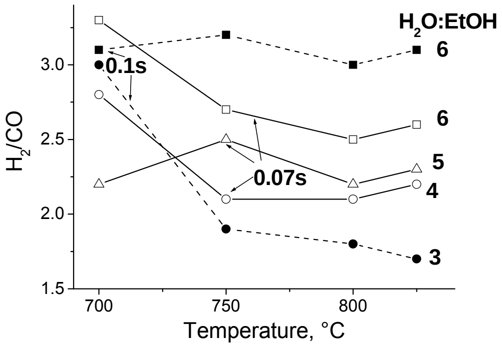

Fig. 2. Temperature dependence of H_2/CO at the contact time 0.07 and 0.1s. Catalyst RuCZS2.

Conclusion

ESR is realized with a high yield of syngas at contact times 0.07-0.1 s over developed Ru- and Ni-Cu-Cr-containing catalysts based on doped Ce-ZrO_x which is suitable as active components for production of structured catalytic systems. Preliminary data on ESR carried out over monolith supported RuCZS2 have shown a syngas yield up to 50vol.%.

The authors acknowledge the financial support of INTAS 05-1000005-7663 project.

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OP-IV-8

HYDROGEN PRODUCTION FROM METHANOL OVER COMBUSTION-SYNTHESIZED NOBLE METAL/CERIA CATALYSTS

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1. Introduction

H_2 can be catalytically produced from methanol via decomposition (MD), partial oxidation (POM) and steam reforming (SRM) [1]. Commercially Cu-based catalysts (e.g. Cu-ZnO-(Al_2O_3)) have been widely used for generating H_2 from methanol [2,3]. However, several drawbacks limit their application in small mobile fuel processors: slow start-up response due to the slow kinetics, pyrophoricity and poor thermal stability above 300^{o}C. Catalyst formulations based on noble metals seem to be promising alternatives, exhibiting activity comparable to that of $Cu/ZnO/Al_2O_3$ catalysts [4,5]. In the present study, we report on the MD activity/selectivity of combustion-synthesized (Pt, Pd, Rh)/ceria catalysts.

2. Experimental

The urea-nitrate combustion method was used for the synthesis of Me/CeO_2 (Me = Pt, Pd, Rh) catalysts [1]. A mixed solution of urea with noble metal and cerium nitrates (Me/(Me+Ce) = 0.0266, 75% excess of urea) was autoignited in an open muffle furnace (~450°C). All the produced powders were sieved to obtain the desired fraction ($90<d_p<180$ μm). The samples were characterized by N_2 physisorption, XRD, SEM and XPS.

The catalytic performance for the decomposition of methanol was investigated at 1 atm, in the temperature range 180-325°C, in a fixed-bed reactor system [1]. The catalyst weight was 0.3 g and the total flow rate of the reaction mixture (5% CH_3OH/He) was 70 $cm^3\ min^{-1}$ (W/F = 0.257 g s cm^{-3}). The samples were reduced by exposure to the feed stream for 1h at 325°C, after which measurements were made by stepwise decrease of reaction temperature. Product and reactant analysis was carried out by a Shimadzu GC-14B equipped with TCD and FID.

3. Results and discussion

For all samples, the isotherms of N_2 adsorption/desorption were of type II and had type B hysteresis loops, which closed at P/P_0 values in the range of 0.40-0.45. The pore size distribution (BJH method), was very broad, starting from ~4 nm and extending well into the macropore region. The surface area (S_{BET}) of the catalysts increased in the order Pd<Pt<Rh (Table 1). The fluorite oxide-type diffraction pattern of CeO_2 was observed in all samples. No

detectable diffractions of noble metals crystallites could be distinguished, suggesting that noble metals were highly dispersed and/or a surface solid solution was formed. SEM micrographs reflected the foamy and agglomerated nature of the material, which has to do only with ceria, since it was impossible to detect any separate noble metal particles, as well with XRD. XPS measurements suggested the presence of oxidized states of noble metals in the as-prepared samples, while in-situ reduction with H_2 at 300°C for 1h led to metallic states.

The activity-selectivity values -measured at 225 and 275°C- for the decomposition of methanol to CO and H_2 over the noble metal/ceria catalysts are given in Table 1. The Pd/ceria catalyst appeared to be the most active and selective, while the Rh/ceria catalyst was significantly less active. The major products of the reaction were H_2 and CO. Other byproducts, such as CH_4 and CO_2, were also detected at temperatures higher than 225°C. At temperatures lower than 225°C, where methanol conversion was low, formaldehyde and methyl formate were detected in trace amounts. Ethylene, ethane and propylene were identified at temperatures higher than 275°C, only in the case of Rh/ceria catalyst.

Table 1. *Methanol decomposition measurements.*

Catalyst	S_{BET} (m^2 g^{-1})	$T_{reaction}$ (°C)	MeOH conversion (%)	CO selectivity (%)	H_2 selectivity (%)
Pt/CeO_2	37.8	275	100	93.4	96.7
		225	53.6	97.6	100
Rh/CeO_2	43.6	275	54.8	95.2	97.2
		225	13.4	96.1	98.3
Pd/CeO_2	32.6	275	100	98.5	99.2
		225	82.4	98.9	100

4. Conclusions

Methanol was decomposed to CO and H_2 on combustion-synthesized noble metal/ceria catalysts. Their activity increased in the order Rh<Pt<Pd, while selectivity towards H_2 production remained higher than 97%.

Acknowledgment

The work was carried out in the framework of postdoctoral research fellowships of State Scholarship Foundation.

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OP-IV-9

A NEW GENERATION OF SUPER-THIN HYDROGEN FILTERING PALLADIUM MEMBRANES (CREATING OF TECHNOLOGY AND DEVELOPMENT OF PRODUCTION)

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In this report we inform on the program that is represented by the above science, technology and commerce corporation. The aim of this program is the fastest application of the industrial production of the equipment to prepare super pure hydrogen from gaseous mixtures by the method of diffusion through membranes from palladium alloys.

The actual importance of this task due to the orientation of the mankind to the hydrogen technologies does not cause any doubt. The general assignment of hydrogen permeable materials based on palladium alloys is directed to their application in various technologies of the hydrogen energy: the production of hydrogen by conversion of different hydrocarbons as alternative ecologically pure fuel in the auto industry and in the wide spectrum of equipments with fuel cells, in the metallurgy (the production of protective atmospheres), as well as in a number of technologies in the chemical industry which transfers their schemes to «membrane» reactors (the preparation of ethylene, propylene, benzene, etc.).

The main component of the developed composite membrane with the super thin diffusive layer from the palladium alloy is the foil with thickness of 10 microns and lower. One of the key elements of the developed technology providing to it the principal novelty and high competitive ability is the introduction to the process of stages, taken from the industrial technology for the production of tinsel gold in that the authors occupy the monopole positions.

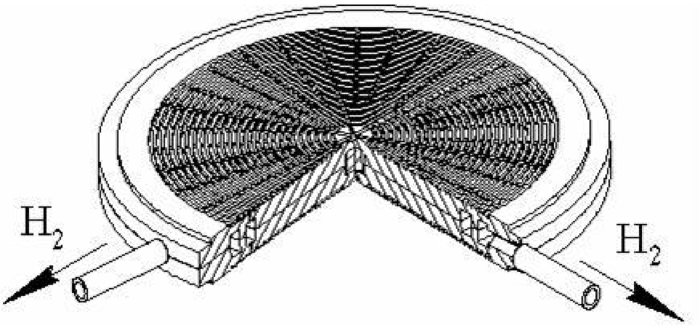
The main task of the program is the forced development of the production of mentioned hydrogen filtering membranes which must provide the implementation leading positions for the science technology corporation both on the forming Russian market and on the foreign markets for such items.

The creation of selective hydrogen-filtering material with small thickness is the main but not single task in the development and industrial production of hydrogen diffusive elements for the separation of super pure hydrogen from gaseous mixture. The program also includes search effective new diffusive alloys and the development of optimal construction of the devices.

Here are some characteristics of developed diffusive elements on base of composite membranes including a selective filtering hydrogen membranes with 10 micron thickness.

The special hydrogen filtering composite membrane at temperature of 550 °C, partial hydrogen pressure in the mixture of.0.6 MPa and the pressure of evolved hydrogen 0.15MPa s is equal to ~100 nm^3 H_2/m^2 hour. For the developed diffusive elements the work temperature is in the interval 400-700 °C.

Presented below photos illustrated first construction decision of a composite filtering element and also scheme for their testing in a laboratory reactor for production of sin-gas from methane.



OP-IV-10

EXERGY ANALYSIS OF ENZYMATIC HYDROLYSIS REACTORS FOR TRANSFORMATION OF LIGNOCELLULOSIC BIOMASS TO BIOETHANOL

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Introduction

The use of lignocellulosic biomass is going to be one of the best ways to increase yields in the production of environmental friendly fuels from renewable sources. The biomass treatment processes with several alternatives such as acid hydrolysis, saccharification, acid dehydration, and especially enzymatic hydrolysis, have shown promising results and have generated great expectations and investigations with the objective of develop this field. In recent years, research has been focused on improving various stages of production of bioethanol and other added-value products through enzymatic hydrolysis, however, the costs of this technology have generated great interest to find out optimal type of enzyme catalytic reactors to get an increase in performance, productivity and energy efficiency, while reducing the costs of the process[1].

In this work the concept of exergy analysis has been applied to choose the best type of o enzymatic hydrolysis reactors of lignocellulosic biomass to produced ethanol fuel from renewable resources. An analysis of the efficiency of exergy in tubular and continuous stirred-tank reactors was made in the process simulator PRO II Simsci, in order to analyze the effect of changes in the dead-state in the efficiency of each of these systems to production of environmental friendly fuels.

Enzymatic Hydrolysis:

The enzymatic hydrolysis of cellulosic materials by means of cellulase enzymes is one of the most promising advances in order to obtain products of great economic importance. This is a process catalyzed by a group of enzymes –cellulases– that are a mixture of different enzyme activities whose joint action produces the degradation of cellulose[3-4]. The reaction of degradation of cellulose to glucose by action of enzymes is shown below:

$$\underset{cellulose}{(C_6H_{10}O_5)_{2n}} \xrightarrow{endoglucanase} \underset{celobiose}{nC_{12}H_{22}O_{11}} \xrightarrow{\beta-glu\cos idase} \underset{Glu\cos e}{2nC_6H_{12}O_6}$$

Exergy analysis:

In the present work, the effect of changing the reference temperature between 16°C and 32 °C in reference to reactors units (typical processes condition 45-55°C) was studied. Gas phase composition was defined similar to Baehr and Schmidt[6] N_2: 0.7559, O_2: 0.2035, Ar: 0.0090, H_2O: 0.0313, CO_2: 0.0003 (molar fractions) with a reference pressure of 1 atm. Water was defined in equilibrium to saturated water vapour at pressure and temperature of the proximities, which implies that exergy of pure liquid water is zero.

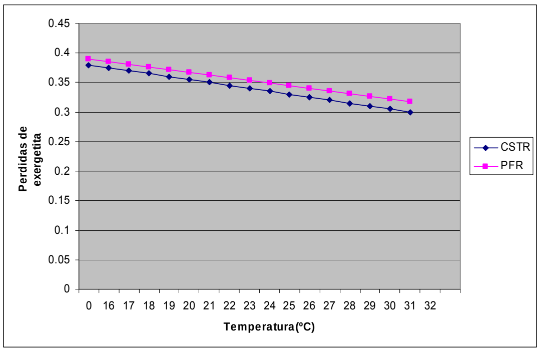

Fig. 1. Efficiency of exergy vs. Reference temperature of reactor CSTR (Δ) and PFR (▪)

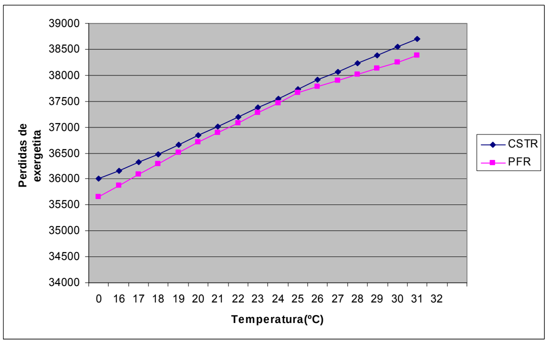

Fig. 2. Losses of exergy vs. Reference temperature of reactor CSTR (Δ) and PFR (▪)

These were the components in the exergy balance: exergy of useful products, exergy losses and exergy of matter that enters the system. The exergetic efficiency of the thermal process as the relationship between actual energy efficiency and the maximum energy efficiency was calculated. PFR was more efficient than CSTR for enzymatic reactions as seen in figure 1 and 2. As reference temperature increases the efficiency decreases and loss-work increases. So the exergy analysis methodology can be useful to determine the energy losses of enzymatic reactors and for the appropriate design of industrial production of environmental friendly fuels from renewable sources.

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OP-IV-11

ADVANCEMENT OF SLURRY BUBBLE COLUMN REACTORS FOR CLEAN LIQUID FUELS PRODUCTION

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Gas to Liquid Fischer Tropsch (FT) synthesis is a acknowledged route for production of clean fuels and chemicals from synthesis gas (a mixture of hydrogen and carbon monoxide) obtained from natural gas, coal or biomass. FT conversions are associated with high exothermic heat for which an efficient mean of heat removal is needed. Therefore, slurry bubble column reactors operated in churn turbulent flow regimes are the reactor of choice for such conversions. Successful commercialization of these reactors needs thorough understanding of prevailing hydrodynamics and transports for proper design, scale up, performance and operation.

To achieve these, 5 companies [ConocoPhillips (USA), Eni (Italy), Johnson Matthey (UK), Sasol (South Africa) and Statoil-GTL-F1 (Norway-South Africa)] have supported an extensive research effort since 1999. For such effort our laboratory at Washington University is collaborating with Ohio State University and with Rensselaer Polytechniq Institute. At Washington University advanced measurement techniques have been used and developed which provide the needed fundamental understanding of these complex reactors. These techniques are: Computer automated radioactive particle tracking (CARPT) techniques for the measurement of 3D flow structure, velocity, turbulent parameters, residence time, etc.; computed tomography (CT) and dual source computed tomography (DSCT) for the measurement of the cross sectional phases distribution along the reactor height; 4-point optical probe for bubble dynamics measurements (bubble size, velocity, local gas holdup and interfacial area); overall gas dynamic tracer technique; optical probe for mass transfer measurement and overall mass transfer coefficient measurement; heat transfer probe that mimicked the heat exchanging internals; dynamics pressure transducers. A number of achievements have been made due to such advanced fundamental understanding of bubble/slurry bubble column. These are: advanced mechanistic reactor scale models; non-invasive technique for flow regime identification, new methodology for scale up bubble column, new methodology to measure FT gases mass transfer coefficients; true and accurate tracer response for the liquid and slurry; accurate characterization of the gas phase extent mixing; detailed flow behavior and transport parameters mapping in a mimicked FT conditions system; advanced neural net work based correlations were developed based on a large size and range of data; reliable benchmark data for evaluating CFD models and closures and development of advanced CFD models and closures.

In the presentation, the consortium and its research effort will be outlined with selected results will be presented. The newly developed methodology for scale up bubble column reactors and identification of the flow regime by the newly developed noninvasive technique will be discussed. Then an brief outline about the research activities that have been undertaken in our laboratory will be mentioned.

OP-IV-12

Pd-DOPED PEROVSKITE CATALYSTS FOR CNG ENGINE'S EMISSION CONTROL

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Advanced compressed natural gas (CNG) engines entail considerable advantages over conventional gasoline and diesel engines. Natural gas (NG) is a largely available fossil fuel and therefore non-renewable. However, NG has some advantages compared to gasoline and diesel from an environmental perspective. Its emissions are lower. The low flame temperature of lean operated CNG engines helps to limit the formation of NO_x. Furthermore, since NG contains only 75 wt% carbon versus 86-88 wt% for gasoline or diesel, it produces less CO_2 per unit of energy released. Furthermore, soot particulate can hardly be formed from methane combustion. Other benefits lie in the fact that NG is neither toxic, carcinogenic, nor caustic. However, unconverted methane in CNG flue gases is much harder to oxidize than gasoline-derived unburned hydrocarbons (UHC). The strong greenhouse effect of methane (more than one order of magnitude higher than that of CO_2) forces a higher and higher concern at a legislation level and, as a consequence, the development of new aftertreatment technologies to abate these emissions. Catalytic combustion of methane on honeycomb converters similar to those used for the treatment of gasoline engine exhaust gases is the way to go. Commercial catalysts are mostly based on gamma-Al_2O_3-supported Pd [1], having a at least three fold higher noble metal loading compared to that of conventional three-way catalysts (up to 300 g/ft^3 against 80 g/ft^3). A research line of ours is aimed at developing nanostructured Pd-perovskite-type-oxide catalysts employing an overall noble metal load significantly smaller than that used in conventional converters, the catalytic performance being the same. Several perovskite-type oxide catalysts ($LaMnO_3$, $LaMn_{0.9}Pd_{0.1}O_3$, $LaFeO_3$, $LaFe_{0.9}Pd_{0.1}O_3$, $LaCrO_3$, $LaCr_{0.9}Pd_{0.1}O_3$) were prepared by Solution Combustion Synthesis (SCS), characterized by B.E.T., SEM (Scanning Electron Microscopy – Fig. 1) and XRD (X-Ray Diffractometer) analyses, and tested as catalysts for methane combustion [2]: a gas mixture (2.5 vol.% CH_4; 7.5 vol.% O_2, He = balance) was fed at the constant rate of 0.83 ml·s^{-1} to a fixed-bed micro reactor constituted of 100 mg of catalyst and 900 mg of SiO_2 (W/F = 0.12 g s/cm^3). Starting from 950 °C, the inlet temperature, measured by a K-type thermocouple placed alongside the quartz tube, was decreased at a 2 °C/min rate and the outlet CO_2, CO, CH_4 and O_2 concentrations were determined by continuous NDIR and paramagnetic analyzers, thus allowing to calculate methane conversion and close the carbon balances.

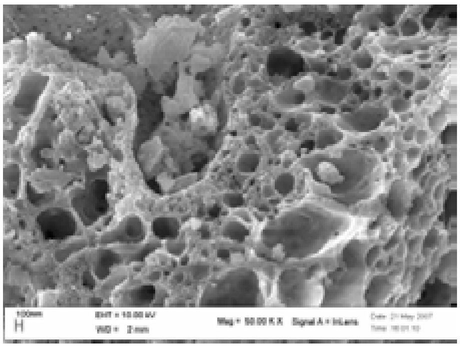

Fig. 1. SEM view of $LaMn_{0.9}Pd_{0.1}O_3$ obtained by Solution Combustion Synthesis.

The comparative analysis of the catalysts activity was carried out with pure perovskites in powder. All catalysts guarantee much lower T_{50} values than the one related to non catalytic combustion (816 °C). By inducing a partial substitution with 10% of Pd at the B site an improvement of the activity was observed for all catalysts. This should entail a reduction of the overall catalyst costs compared to conventional Pd-only catalysts currently employed characterized by high Pd loads. More in detail the methane half conversion temperature (T_{50}) of Pd substituted perovskites was lowered of about 5, 40 and 60 °C for $LaCrO_3$ (T_{50} = 607 °C), $LaFeO_3$ (T_{50} = 535 °C) and $LaMnO_3$ (T_{50} = 485 °C), respectively; the best catalyst was found to be $LaMn_{0.9}Pd_{0.1}O_3$ (T_{50} = 425 °C) and therefore it was selected to be deposited and tested on a cordierite monolith. The catalytic converters (cylindrical cordierite honeycombs by Chauger; cell density: 200 cpsi; length: 25 mm; diameter: 34 mm) were prepared by a preliminary deposition of a layer of γ-alumina by in situ SCS (10 wt% referred to the monolith weight) and then 15 wt% (referred to the γ-alumina weight) of $LaMn_{0.9}Pd_{0.1}O_3$. The adhesion properties between the catalyst and ceramic surface was checked by means of an ultrasonic bath test: a piece of the catalytic monolith was weighted before and after a standard ultrasonic treatment to quantify the catalyst loss. The adhesion between the deposited catalyst and the channel walls of the traps was excellent, as the loss of catalyst by ultrasonic treatment was lower than 1%. Catalytic combustion experiments were performed in a stainless steel reactor heated in a horizontal split tube furnace with a heating length of 60 cm. The catalyzed monolith was sandwiched between two mullite foams to optimize flow distribution. For the temperature control a thermocouple, inserted along one of the central monolith channel, was used to measure the inlet temperature. Lean inlet conditions (0.4% vol.% CH_4, 10% vol.% O_2, N_2 balance) were ensured via mass flow controllers. The methane conversion of the $LaMn_{0.9}Pd_{0.1}O_3$ cordierite monolith at different GHSVs shows that the conversion shifted to lower temperature at lower space velocity. The T_{50} values are 570 °C, 455 °C and 385 °C at the space velocity of 80000 h^{-1}, 40000 h^{-1} and 10000 h^{-1}, respectively.

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OP-IV-13

HYDROGEN PRODUCTION VIA METHANE DECOMPOSITION ON RANEY-TYPE CATALYSTS

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Abstract

Pure hydrogen and filamentous carbon (carbon nanofibres and nanotubes) were produced by catalytic methane decomposition on Raney-type catalysts (Ni, Co and Fe). Conversions near to equilibrium were obtained under well defined operating conditions without any significant catalyst deactivation.

Introduction

Concerns over the environment and depletion of fossil fuels led to the concepts of «hydrogen-energy system» and «hydrogen economy». Hydrogen is a convenient energy carrier which can be used efficiently and without any emissions in fuel cells. Hydrogen is mostly produced by steam reforming of methane, which also yields CO and CO_2. For fuel cell applications, however, very low levels of carbon oxides are tolerated. An interesting alternative process is the catalytic decomposition of methane ($CH_4 \rightleftharpoons C + 2\ H_2$), especially if the carbon by-product can be obtained in suitable form for practical applications [1], such as carbon nanofibres or nanotubes. Thus, there has been an intense research effort on this topic in recent years [2, and references therein]. Supported metal catalysts have been mostly used for this purpose, but in the present work we report promising results obtained with massive catalysts (Raney-type Ni, Co and Fe).

Experimental

The Raney-type catalysts were prepared from Me-Al alloys (Me = Ni, Co or Fe) with nominal active phase content in the alloys of 50 or 30 wt. %. The Ni50 alloy was a Fluka Chemie GmbH product, and the remaining alloys were supplied by H.C. Starck GmbH. The Ni30 and Co30 alloys were prepared by a patented quenching process [3]. The alloys were activated by leaching out Al with a concentrated NaOH solution. The catalysts were tested in a fixed bed reactor either isothermally or under a temperature programme. The original alloys, the resulting catalysts and the carbon deposits were characterized by appropriate techniques.

Results and Discussion

Table 1 collects some properties of the alloys and catalysts. The atomic ratios (R = active metal/total metal) show that residual amounts of Al (in the form of Al_2O_3) are always present on the catalyst upon activation, which may act as a textural promoter to prevent sintering.

Figure 1 shows temperature programmed reaction tests on Ni30 (a), Co30 (b) and Fe50 (c). It is observed that the catalytic activities of Ni and Co start at around 450ºC, negligible traces of CO_x being observed only at lower temperatures. Fe50 starts to be active at higher temperatures, and larger amounts of CO_x are recorded.

Table 1. Characterization of the alloys and catalysts

Sample	Alloy		Catalyst	
	$R_{nominal}$	$R_{experimental}$	$R_{experimental}$	S_{BET} [m^2/g]
Ni30	0,165	0,17 ± 0,02	0,85 ± 0,07	64
Ni50	0,315	0,39 ± 0,06	0,72 ± 0,07	82
Co30	0,164	0,17 ± 0,02	0,94 ± 0,06	26
Fe50	0,326	0,35 ± 0,09	0,95 ± 0,05	62

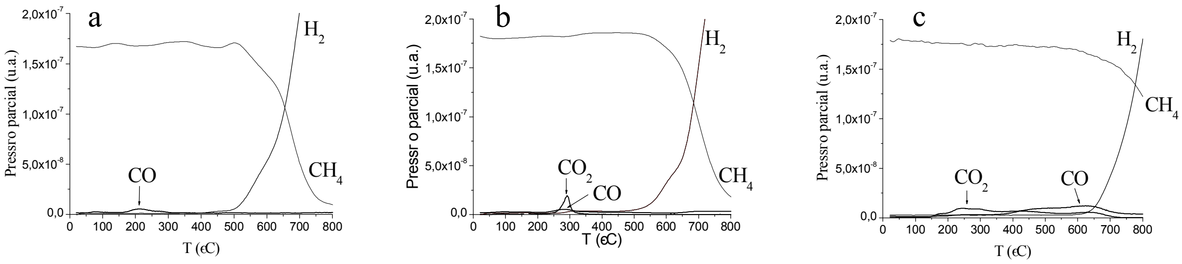

Figure 1. Temperature programmed reaction (a: Ni30, b: Co30, c: Fe50).

Isothermal catalytic tests were subsequently performed in order to study the effects of temperature, contact time, composition and concentration of the feedstream on the conversion of methane and catalyst stability. The results have shown that the best catalysts, Ni30 and Co30, could operate at 600 ºC without significant deactivation, with methane conversions higher than 90% of the equilibrium value. The solid product was found to consist of filamentous carbon, containing both carbon nanofibres and carbon nanotubes.

Acknowledgements

This work was carried out with support from FCT (Portugal) and FEDER (BD/16035/2004 and POCTI/1181).

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Section 5.

Catalytic processing of renewable sources: fuel, energy, chemicals

DEVELOPMENT OF BIOFUELS PRODUCTION PROCESSES VIA CATALYTIC UPGRADING OF BIOLIQIUDS

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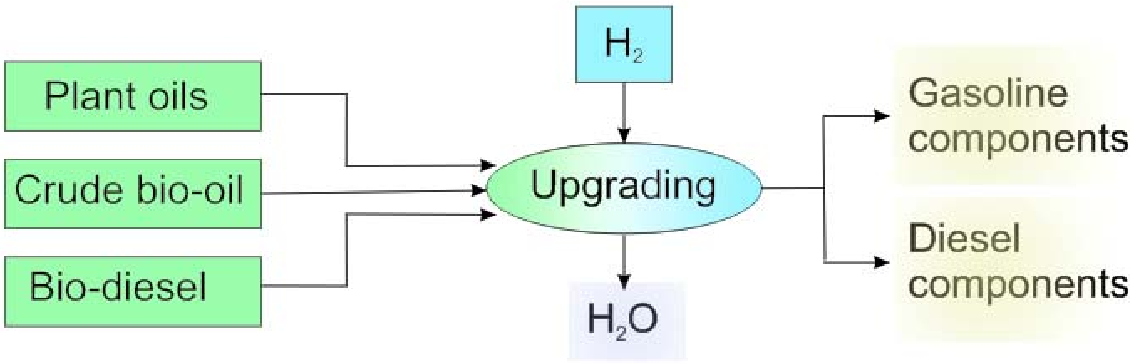
The consumption of petroleum has surged during the 20th century, at least partially because of the rise of the automobile industry. Today, fossil fuels such as coal, oil, and natural gas provide more than three quarters of the world's energy. On the other hand biomass can serve as a source for both energy and motor fuels, and being renewable it is the only sustainable source of energy and hydrocarbons for industry and automobile society. At present the alternate fuels are bioethanol and biodiesel only. The bio-oil, which is a product of flash pyrolysis of grinded wood, is another perspective feedstock for the petrol production. However these bio-liquids cannot substitute traditional gasoline and diesel in the internal-combustion engines on its own owing to their lower operational properties. The main reason is the high oxygen content in above mentioned bio-fuels. Bioethanol and biodiesel can be used as the additive to gasoline and diesel correspondingly while bio-oil requires catalytic elimination of oxygen from it and simultaneous saturation by hydrogen.

It should be pointed out that one cannot use traditional hydrocracking catalysts for oil-refinery at hydrotreatment of bio-fuels because of low sulfur content in original feedstock. The main reason of these phenomena is reduction of the sulfided Co- or Ni- containing active center to the metal state, followed by coke formation and the catalyst deactivation. When so, sulfur is removed from the catalysts and the target products are contaminated by sulfur. Thus, the objective of the present investigation is to develop non-sulfided catalysts for upgraded bio-fuels production. In the work we have used not only bio-oil (BTG Company) and model bio-oil compounds but also biodiesel and vegetable oils as the initial feedstock for the upgrading. The obtained upgraded products can be used as improving additives to gasoline and diesel. As a whole developing processes of upgraded bio-fuels production are shown on Scheme 1.



Scheme 1. The developing pathways of upgraded biofuels production from bioliquids.

It has been suggested during development of bio-fuels upgrading catalysts that the perspective catalyst can be bifunctional catalyst. The oxide form of transitional metal with variable valency is needed for the activation of oxy-groups of compounds – bio-oil components. On the other hand, the presence of transitional metal which is able to activate hydrogen is necessary. One should keep in mind that the process temperature has not to exceed 350-400 °C and hydrogen pressure has not to exceed 8,0-10,0 MPa to prevent the intensive coke formation. Under given conditions Mo, W, Co, Mn, Zr, Ce, Y, Sr, La oxides possess mobile oxygen. Thus, these transitional metals oxides can be used as activators of oxy-organics. As hydrogen activator noble metals (Pt, Pd, Rh) usually are used. However deoxygenating process is considered as large-scale process. So, the application of catalysts based on noble metals would result to higher prime cost of bio-fuels. Thus, according to aforementioned, we believe that the application of nickel based on catalysts which also can activate hydrogen at given conditions is more preferable solution of this challenge.

Indeed preparation and testing in target processes such binary catalytic systems has shown that developed mild hydrocracking catalysts permit not only to obtain alkanes C_{11}–C_{17} in one stage with the yield 100% both from biodiesel and from vegetable oils at mild conditions: 260-350 °C, hydrogen pressure 1,0–2,5 MPa, but also to reduce oxygen content in bio-oils in one stage too from 45 wt% until 5 wt% at 320-350 °C, hydrogen pressure 12–15 MPa.

Acknowledgments

FP6 project № 518312, Russian state contract №02.526.11.6007 in FTP, integration project №2 SB RAS are gratefully acknowledged.

OP-V-2

HYDRODEOXYGENATION OF FAST-PYROLYSIS OIL: A MODEL COMPONENT STUDY

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Fast-pyrolysis oil is a promising energy carrier. It is obtained from biomass by flash-pyrolysis in yields up to 70%-wt [1]. As such, the oil is not suitable for applications in instationary internal combustion engines due to its high oxygen content (ca. 40%-wt) and low pH (ca. 2.5). Various upgrading technologies have been proposed, of which hydrodeoxygenation (HDO) is a very promising option [2]. In this processHere, the pyrolysis oil is treated with hydrogen in the presence of a catalyst with the formation of water and a hydrocarbon-like product. Typically, the reaction requires harsh conditions (> 350°C, > 100 bar pressure) to obtain reasonable conversion rates.

Pyrolysis oil is a dark liquid containing more than 400 components belonging to different compound classes (aldehydes, ketones, organic acids, phenolics, sugars). As a consequencetely it is difficult to gain insights in the molecular processes taking place when hydrotreating the oil. We here report hydrodeoxygenation studies using 10 pyrolysis oil model compounds at temperatures between 250-350°C and pressures of 100-200 bar. The catalyst of choice is Ru/C which in earlier studies in our laboratory showed the highest performance for crude pyrolysis oil with respect to yield and deoxygenation rate.

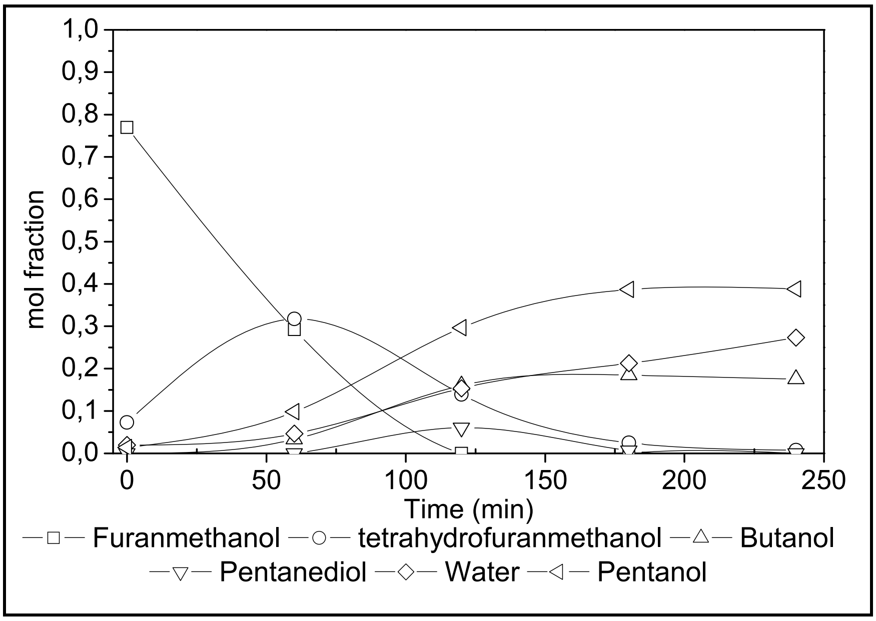

Figure 1. Hydrodeoxygenation profile of furfurylalcohol (furanmethanol) with a Ru/C catalyst at 250 °C and 100 bar for 4 h.

An example of the model compound study is provided in Figure 1. Here, the products formed when hydrodeoxygenating furfurylalcohol at 250°C and 100 bar hydrogen pressure are provided. Furfurylalcohol is fully converted after 2 h reaction time, leading to tetrahydrofuranmethanol, butanol, pentanediol and pentanol. The former is an intermediate product whereas butanol and pentanol reach their maximum values after about 3 h.

The results for all modelcompounds will be presented and discussed. It will be shown that modelcompound studies give valuable insights in reactivity and reaction pathways when hydrotreating fast-pyrolysis oil.

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CATALYTIC HYDRODEOXYGENATION OF ANISOLE AS A MODEL COMPOUND OF BIO-OIL

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Crude bio–oil produced from biomass pyrolysis is the multi-component mixture composed of the various compounds derived from cellulose, hemicellulose and lignin depolymerization and fragmentation. All these aromatic and aliphatic alcohols, ethers, ketones, carboxylic acids and water cause the high oxygen content in bio-oil. The difference between the fossil hydrocarbon fuels and bio-oil is due to such properties of pyrolysis liquid as high viscosity, non-volatility, poor calorific value, corrosiveness, immiscibility with fossil fuels, thermal instability and trend to polymerization on storage and transportation. Therefore bio-oil upgrading is required to reduce oxygen content. Conventional oil – refining hydrocracking catalysts are commonly used for bio-oil deoxygenation. Typical catalysts for this process are Co - Mo and Ni - Mo supported on alumina used in the sulfided form. The main problems of these catalysts are rapid deactivation caused by sulfur loss and coke formation. The use of non-sulfided catalysts for hydrodeoxygenation (HDO) process has been considered to a far lesser extent. The aim of the present work was to develop and to test a non – sulfided and free of noble metals HDO catalyst. At first a number of catalysts based on the various active metals and using various supports were prepared and tested in HDO of model bio-oil compound. In addition the same tests were run with the commercial oil processing sulfided catalysts. The results of the screening showed that the highest yields of hydrogenated products are achieved over the Ni-Cu – based catalysts. Therefore this catalytic system was chosen for the further inquiry. The effect of copper loaded into the Ni-Cu catalysts on selectivity of the HDO reaction was determined by using TPR and XDR techniques as well as the catalytic tests.

Hydrodeoxygenation of anisole was carried out in a flow fixed bed reactor at 300 ^{o}C and 1.0 MPa. Anisole was chosen as a model compound for methoxy functional groups of lignin in pyrolisys oil. HDO reaction over the Ni-Cu catalysts gives both aromatic and aliphatic hydrocarbons, the main reaction products were benzene and cyclohexane, their oxygenated derivatives - phenol, methyl substituted phenols, cyclohexanole and cyclohexanone were obtained in smaller amounts. Products formed via methyl transfer to benzene ring (toluene and methylcyclohexane) were also detected as the reaction products. All the Ni-Cu – based catalysts were shown to be sufficiently active in hydrodeoxygenation. The single Cu supported on alumina shows no HDO activity (anisole is mainly converted to phenols). The results of the hydrodeoxygenation tests showed that Cu loading into nickel on alumina catalysts increases the selectivity of hydrogenated products formation. We suggest that formation of the $Ni_{1-x}Cu_x$ solid solution may cause the difference in selectivity of HDO between Ni and Ni-Cu catalysts. The cyclohexane yield was found to be weakly dependent on the copper content in the catalyst, whereas the selectivity of phenols formation substantially increases with copper content increasing. The experiments on the temperature programmed reduction of bimetallic catalysts clearly showed that the presence of copper promote the nickel reduction at a lower temperatures, i.e. under the reaction conditions of the present study the major part of Ni is already reduced at 300 °C. The main conclusion could be drawn from the present study is that developed Ni-Cu catalytic systems are sufficiently effective for hydrodeoxygenation process under the mild conditions.

The work was financially supported by BIOCUOP project № 518312 (FP6).

KINETICS OF CATALYTIC DEOXYGENATION OF STEARIC ACID OVER Pd CATALYSTS: EFFECT OF METAL DISPERSION

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1. Introduction

Catalytic deoxygenation of triglycerides is of great interest for production of biodiesel in order to decrease the dependence of fossil fuels. Deoxygenation of fatty acids and their derivatives was successfully demonstrated in a semibatch [1, 2] and continuous reactor [3] with one of the most promising catalyst being Pd/C. Several parameters, like pressure, temperature and reaction atmosphere have been optimized previously. The effect of metal particle size has not, however, been systematically studied earlier. In this work a series of Pd catalysts supported on synthetic carbon, Sibunit, were studied with the main emphasis on elucidation of the influence of metal dispersion. Additionally temperature dependence was studied for the most promising catalyst.

2. Experimental

The catalytic deoxygenation of stearic acid was performed in a 300 ml semi-batch reactor. The reaction temperature was kept constant during reaction in the range of temperatures from 260 to 300°C and the reaction pressure was 17 bar. The stirring speed of 1100 rpm was used to prevent external mass transfer limitation. Four different Pd/C catalyst supported on Sibunit were prepared by deposition of palladium hydroxide yielded by hydrolysis of palladium chloride at pH 8-10 [4]. The catalysts were reduced in-situ by hydrogen for 1h prior to the catalytic tests at constant temperature and pressure being 60°C and 3.5 bar, respectively. In a typical reaction, the following catalysts and substrate amounts were used: 0.5–1.0 g of catalyst; 0.1 M stearic acid in 50 ml of dodecane. The reaction temperature was adjusted with a heating ramp 10°C/min to the desired reaction temperature and the reaction commenced. Both gas- and liquid phase samples were analyzed by GC [2]. The catalysts were characterized by CO-chemisorption, SEM and nitrogen adsorption.

3. Results and discussion

The kinetics of the catalytic deoxygenation of stearic acid over four different Pd/C catalyst revealed (Fig. 1a) that there is an optimum Pd dispersion (D=47%, corresponding to the Pd particle size of 2.3 nm), giving the highest reaction rate and conversion. Both with smaller and higher metal dispersions lower reaction rates and conversions were achieved.

Catalyst deactivation was more severe with very small Pd particles, whereas complete conversion of stearic acid was achieved with the catalyst exhibiting optimum dispersion.

The main products were hepta- and pentadecane, which were formed in a parallel fashion up to 45% conversion, thereafter heptadecane reacted further to pentadecane and thus the reaction proceeded both parallelly and consecutively to these two products. Selectivity of heptadecane as a function of stearic acid conversion is shown in Fig. 1b. No other liquid phase products were observed. Analysis of the gas phase products revealed presence of methane, carbon dioxide, carbon monoxide, propene and propane indicating that both decarbonylation and decarboxylation took place.

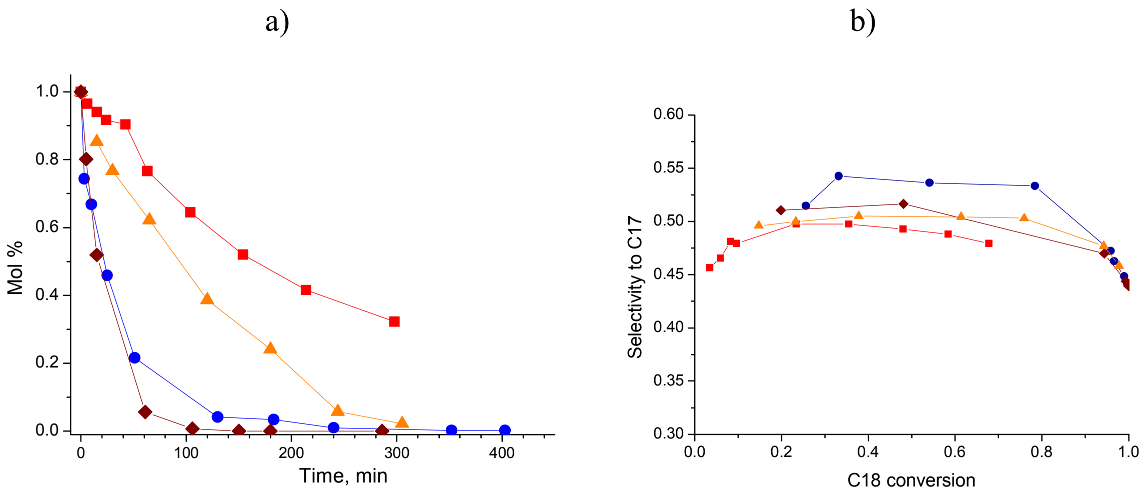

Fig. 1. a) Deoxygenation of stearic acid and b) selectivity to heptadecane as a function of conversion over different Pd/C catalysts at 300°C under 17 bar. Symbols: Pd dispersion 18% (■), 47% (♦), 65% (●) and 72% (▲).

4. Conclusions

Several supported palladium catalysts with varying metal dispersions were tested in stearic acid deoxygenation. Catalyst deactivation was found to be crucial using lower amounts of catalyst. There was an optimum metal dispersion exhibiting the highest reaction rate. The main products were hepta- and pentadecane being formed parallelly. At high conversion levels of stearic acid heptadecane reacted consecutively to pentadecane. The reaction mechanism will be discussed in the final presentation.

Acknowledgments

The part of research work was supported by RFBR Grant № 07-03-12159.

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OP-V-5

KINETICS OF FFAs ESTERIFICATION: BATCH AND LOOP REACTORS MODELLING

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Biodiesel, a fuel derived from a renewable vegetable origin, is object of growing interest in the recent years both as a pure fuel and as blending component to reduce exhaust pollutants of traditional diesel fuel. The production of biodiesel is based on the transesterification reaction of refined/edible vegetable oils or animal fats with methanol using an alkaline catalyst (NaOH, NaOMe) [1] providing that the free acidity of the raw material is below the limit of 0.5% of free fatty acids (FFAs) by weight.

The conventional transesterification technology is not compatible with large amounts of FFAs and water in the feedstocks [5] due to the formation of saponification products that strongly affect the feasibility of catalyst and glycerol purification. For this process a preliminary stage of acidity reduction is therefore necessary [1,4,6,7,8,9]. This can be pursued, as example, by means of an esterification reaction of the FFAs with methanol, catalysed by ionic exchange sulphonic acid resins [8,9,10,11,12] with the following reaction scheme:

$$\mathrm{RCOOH} + \mathrm{CH_3OH} \overset{\text{Cat.}}{\rightleftharpoons} \mathrm{RCOOCH_3} + \mathrm{H_2O}$$

The scope of the present work is the study of the above mentioned reaction in different reactor configurations with the aim to investigate on the optimal operative conditions in terms of catalyst type, reactants ratio, temperature and circulation flow rate. The work has been developed in three different steps:

1) Catalytic screening on different commercial resins at a reference temperature of 100 °C in a batch reactor with the aim to locate the best catalyst in terms of activity, maximum allowable temperature and cost. In these runs, artificially acidified soybean oil has been used as model mixture representative of high acidity waste oils (FFAs content up to 50% by weight).

2) Detailed kinetic study on the selected catalyst from previous step (Amberlyst 15) with different batch runs conducted in the temperature range 80-120 °C with different catalyst concentration. The used reactants are the same as in item 1.

3) Study of the FFAs esterification reaction in a packed bed tubular reactor operated inside a circulation loop with a reservoir tank in which reactants are located. The bed is filled with catalyst particles mixed with small metallic springs [13] that allow stable operation without plugging phenomenon usually encountered in fixed bed of polymeric resins because of the swelling. In the packed bed loop reactor some runs have been performed also on actual raw materials, instead of model mixtures, like palm oil and vegetal FFAs with acidity up to 90% by weight.

The experimental runs in batch conditions have been used to identify the most suitable kinetic law, also by comparing different models and by acquiring information about mass transfer limitation operative in these conditions. A good agreement has been obtained between the experimental batch data and the kinetic model.

The kinetic information have then been employed for the simulation of the runs in packed bed loop reactor by developing a non-stationary PFR model in which external mass transfer limitation has been accounted for by means of a correlation for mass transfer coefficient. Also in this case a satisfactory agreement has been found in the description of experimental data.

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TiO_2/SiO_2 HETEROGENEOUS CATALYST FOR BIODIESEL PRODUCTION: A KINETIC AND MODELLING STUDY AT HIGH TEMPERATURES AND PRESSURES

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Biodiesel is a renewable diesel fuel obtained by transesterification of vegetable oils with methanol. Nowadays, most biodiesel is obtained by transesterification of triglycerides of refined/edible oils with methanol, in the presence of an alkaline catalyst (NaOH, NaOMe) [1].

The recent strong increase in biodiesel production is due to both environmental and technological advantages– i.e. reduction of overall CO_2 emissions; increase of the lubricating properties of modern ultra-low-sulphur diesel by the addition of low amounts of biodiesel (1-2%) [2], but, the greatest driving force is represented by the environmental laws favouring biodiesel use through tax reductions. These incentives are necessary because the higher cost of biodiesel with respect to diesel from petroleum. The main factor determining the cost of biodiesel is the price of the edible oil feedstock, which accounts for 88% of the total estimated production costs. Therefore, great economic advantages could be achieved only by using low price feedstock such as waste or not edible oils [1, 3].

With the conventional technology of transesterification, based on the use of batch plants in which a basic homogeneous catalyst is used, these types of oils cannot directly be used. This is due to the presence of large amounts of free fatty acids (FFA>0.5% w/w) and water [4] that favour the formation of soaps. Soaps emulsify the reaction products (biodiesel+glycerol) and the separation of glycerol becomes difficult. Moreover, alkaline catalyst must be neutralized with mineral acids and recovered glycerol, dirty of the formed salts, is difficult to purify. Therefore, a preliminary stage for free fatty acid elimination is necessary for this process [1,3,5,6,7]. However, the cost of biodiesel could certainly be lowered by using an heterogeneous catalyst instead of an homogeneous one, resulting in a higher quality esters and glycerol that can be obtained, that are more easily separated. It has recently been announced, in France, the construction of a new 160000 t/y biodiesel plant based on the use of an heterogeneous catalyst (a zinc aluminate) developed by the French Institute of Petroleum (IFP) [8]. Unfortunately, this catalyst cannot be used in the presence of moisture and free fatty acids.

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In the present work, a comprehensive study for the development of a new process for the transesterification of vegetable oils with methanol, based on the use of an heterogeneous [9, 10] catalyst, at high pressure and temperature, is proposed. The proposed catalyst can also be used in the presence of free fatty acids (5-10% by weight) and this open the possibility of using directly waste oils as feedstock. The proposed catalyst is a titanium oxide supported on silica, TiO_2/SiO_2, prepared by grafting titanium alkoxide on the surface of silica.

The study has been conducted in three steps:

1) Kinetic runs of the transesterification of refined soybean oil at high temperature (180-220°C) and pressure (15-30 bar) by using different methanol: oil ratio. Tests have then been made also by using soybean oil additioned of oleic acid (up to 10% by weight). The experimental runs have been performed in batch condition using an autoclave (total volume 1 L) equipped with a magnetically driven stirrer.
2) Development of Kinetic Model for the simulation of the experimental batch runs.
3) Modelling of a continuous packed bed reactor by using the kinetic model derived from batch runs and taking into account also the occurring mass transfer phenomena. The experimental runs have been performed at different pressures, temperatures, feed flow rates, methanol: oil ratios and amounts of catalyst.

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CATALYTIC BIOMASS GASIFICATION: CO_2 CAPTURE AND HYDROCARBONS STEAM REFORMING IN FLUIDISED BED AND MICROREACTOR USING M/DOLOMITE CATALYSTS

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It is well known that biomass is one of the important primary and renewable energy sources, with neutral balance in carbon dioxide cycle. Gasification produces a syngas containing tar, from 5 to 75 gr/Nm^3 of product gas in fluidised bed gasifiers. This is a complex mixture of cyclic and polycyclic aromatic hydrocarbons[1] very harmful for toxicity and cancerous properties; moreover, corrosive and pollutant characteristics of tar compounds prohibit direct utilization of gas product stream. Catalytic steam reforming seems to be the best way to eliminate tar compounds, *converting* it in a syngas; however, steam reforming of model tarry compounds other than toluene[2] and naphthalene[3] has not been yet studied to a great extent. In this work, toluene and 1-methylnaphthalene has been used like tar model compounds in fixed bed microreactor and in fluidised bed. Two M/dolomite supported catalysts (M=Ni,Fe) has been developed. Dolomite is known to have a catalytic activity in tar reforming[4], and is a very attracting material to adsorb CO_2 from syngas. Nickel almost completely remove tar, but it is toxic so the disposal is a potential environmental problem. Iron, on the other hand, has been less studied because of the high efficiency of nickel catalyst, but it has several advantages: lower cost which can imply a higher metal concentration in the catalyst (20-40% weight), and harmless behaviour for the environment. In this work, we evaluate catalytic activity related to these materials, making possible tar steam reforming and cyclic CO_2 capture process.

Catalysts was prepared by means of impregnation method, using different preparations conditions (temperature, calcination atmosphere, solvent). The aim of catalyst synthesis is the formation of a solid solution M/dolomite, to form strong interactions that should limit carbon deposition[2] in the catalyst surface. These interactions, highlighted by Mossbauer spectrometry (for iron), temperature-programmed reduction (TPR) and by powder X-ray diffraction (XRD), will be discussed in details. In brief, the most important crystalline phases detected were

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$Ca_2Fe_2O_5$, $MgFe_2O_4$ and FeO-MgO solid solution for iron/dolomite, NiO-MgO solid solution for Ni/dolomite. After reduction by TPR, only free metal (M^0) and metal oxide-magnesium oxide solid solution has been detected, leaving free CaO available for CO_2 capture.

The experiments for catalytic steam reforming of tar components and CO_2 capture were carried out by using fixed bed microreactor and bench scale fluidised bed. The first choice is focused on evaluating catalytic reaction rate data, whereas fluidised bed represent common industrial applications of biomass gasification plants. The aim of this work being to reproduce biomass gasification conditions in the gasifier, reactivity of M/dolomite catalysts has been investigated in a mixture of tar model, steam and syngas, varying mainly steam/hydrocarbons ratio and reaction temperature. The schematic diagram of the experimental setup, for fluidised bed reactor, is shown in Fig.1. Briefly, 1-methylnaphthalene (1-MN) liquid circulates through a heated column. A N_2 constant flow, entering in this column, produces a 1-MN saturated nitrogen stream, circulating into reactor entrance via heated line. To avoid condensation and stabilise the mixture of 1-MN-N_2 in the range 10.000-50.000 ppm of 1-MN, a pre-heated primary nitrogen line has been added to the reactor inlet flow system. The 1-MN concentration has been monitored by a MultiFID 14 analyser before and after reactor. Moreover, H_2, CO, CO_2 and CH_4 concentrations in the product gas has been detected by using gas analyser URAS 14, leading to comprehensive understanding of the process.

Catalytic activity of M/dolomite catalysts will be discussed in details in order to evaluate tar purification and CO_2 adsorption capacity and stability.

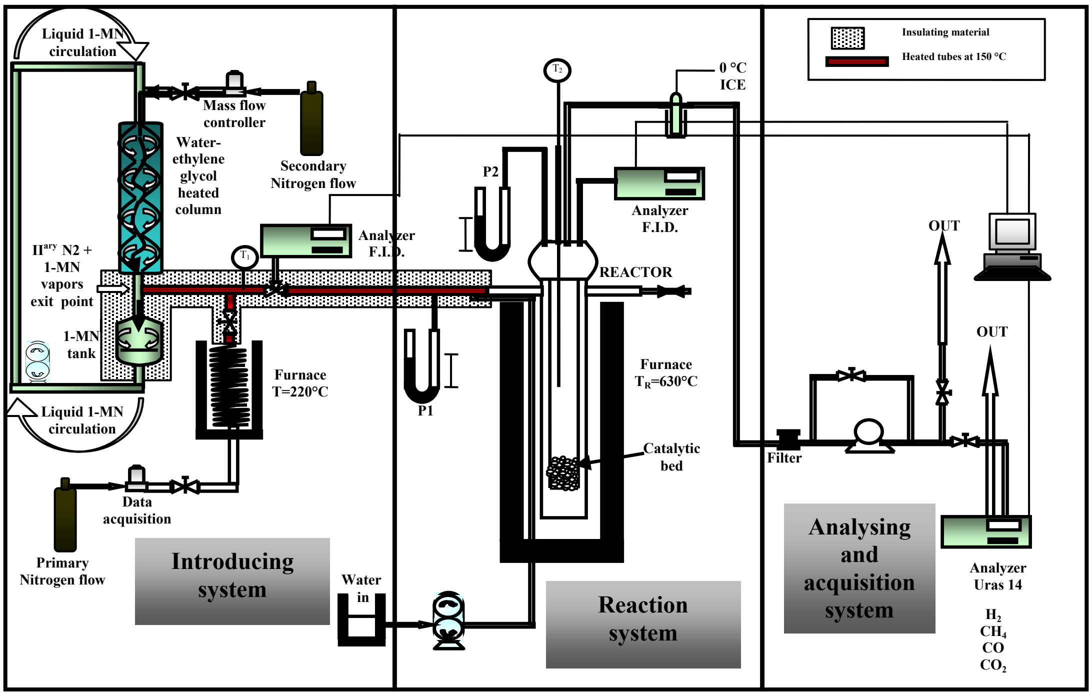

Figure 1: Schematic of the bench-scale fluidised bed reactor system

Rh-PEROVSKITE CATALYSTS FOR BIOMASS GASIFICATION

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Introduction

Biomass conversion to a hydrogen-rich gas is attracting an increasing interest because of depletion of fossil fuel, being an abundant and renewable energy source with a CO_2 neutral effect on the environment [1].

Biomass undergoes an easy decomposition process at quite low temperature producing a wide range of species. A fast heat transfer promotes the production of gas phase with respect to solid and liquid and it is easily performed in a fluidized bed reactor [2]. Nevertheless, formation of tar and char represents a severe limitation and conversion of these products into permanent gases is required to transform biomass into a suitable fuel for internal combustion engines, fuel cells or feedstock for chemical synthesis [1]. Catalytic removal of tar has been widely investigated and use of dolomite, olivine or Ni based catalysts [3] has been proposed as in-bed (primary) or hot gas cleaning (secondary) catalysts, respectively. The use of a catalyst has different goals: enhance gas formation, increase reforming reactions of hydrocarbons contained in the gas and avoid soot-induced deactivation [3].

In this paper kinetics and composition of products deriving from biomass decomposition/gasification were preliminary investigated, then the activity of a Rh-$LaCoO_3$ based catalyst towards conversion of these products into syngas was studied.

Results

A Rh-perovskite catalyst was proposed because of its reforming and oxidation properties, successfully tested in methane partial oxidation [4], which can potentially improve hydrocarbons conversion and avoid coke formation, respectively. Moreover, introduction of the noble metal into the perovskite matrix improves stability and hinders Rh sintering phenomena.

Maple wood chips with low ash content (about 0.5 wt %) were used as biomass. Thermogravimetric analysis of biomass pyrolysis was carried out with a Perkin Elmer TGA7 under N_2 flow. The thermobalance was connected to a FTIR (Perkin Elmer Spectrum GX) gas cell for the analysis of release products. Both FTIR cell and transfer line were heated at 200°C in order to avoid tar condensation. After moisture loss at low temperature, biomass decomposition starts at about 150°C, being completed at about 300°C. Hemicellulose and cellulose components decompose at 180-250°C and 280-330°C respectively, lignine decompositions takes place in a wider range of temperature superimposing to that of the other two components (Fig.1 left). The following species were found according to the semi-quantitative analysis of the main products, except H_2 (not IR detectable): H_2O, CO, CO_2, light hydrocarbons and, in minor concentration, acid and aldehydes (Fig. 1 right).

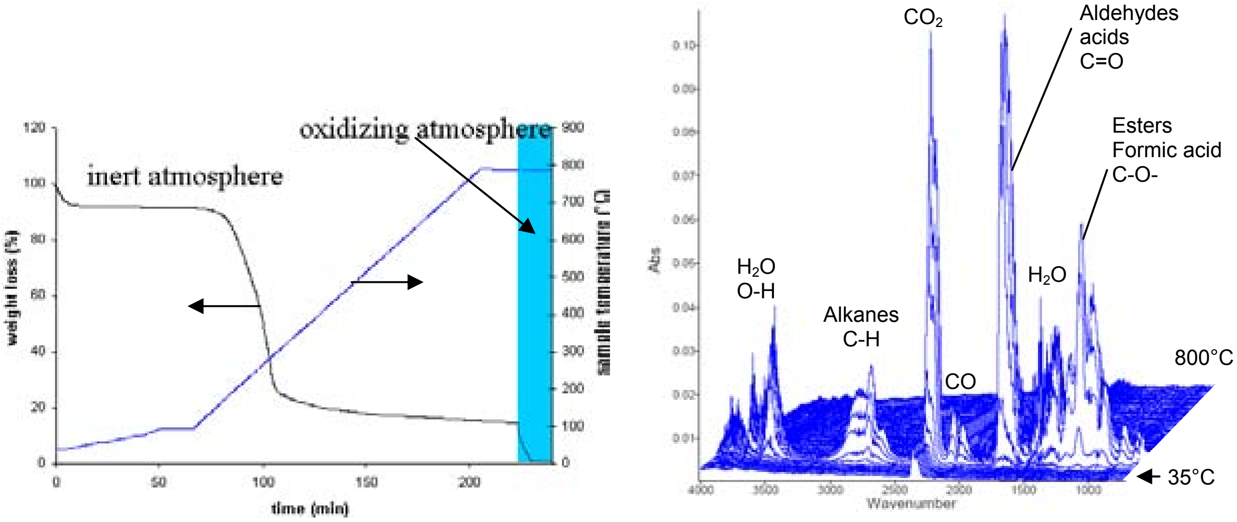

Fig. 1. left: Maple wood weight loss versus time and temperature program (25 mg, size range 125-212 microns); right: Infrared stack plot of wood chip thermal decomposition.

An Al_2O_3 supported Rh-$LaCoO_3$ (Rh 1 wt%) was tested in a fixed bed reactor under isothermal conditions feeding the gas mixture originated from the biomass decomposition carried out in a separate furnace heated up at the same rate as in the thermogravimetric experiments (10°C/min). A micro-GC (HP 6890 Series) was used to analyze the products in order to perform a quick analysis (<1 min) and, therefore, to determine the catalyst activity during the transient evolution of the different species.

The Rh-$LaCoO_3$/Al_2O_3 catalyst was able to convert hydrocarbons and oxygenates at temperature as low as 400°C likely promoting a H_2O or CO_2 reforming. No coke formation was observed on the catalyst surface after the catalytic test due to the good oxidizing properties of the perovskite matrix. These properties, in addition to the high thermal stability of this catalytic system, represent the basis for a potential use of this material as a primary catalyst.

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AUTOTHERMAL REFORMING OF DIESEL FUEL FOR VEHICLES APPLICATION

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Introduction

High concentration of NO_x in diesel engine exhaust emissions is a serious ecological problem, which can be solved using several breakthrough technical solutions being under development. The recent results obtained in a number of research centers [1], including the BIC, have shown that a hydrogen-carbon oxide mixture (3:1) efficiently reduces nitrogen oxides at <200 °C. According to the literature data, the most promising systems are Pd and Pt containing catalysts supported on Al_2O_3, CeO_2, and TiO_2. Thus, there is a possibility for development of new low-temperature systems for neutralization of NO_x and CO generated by diesel engines and other vehicles. First of all, implementation of this method requires solving the following problem: to develop catalysts and equipment for on-board generation of synthesis gas from diesel fuel. Synthesis gas can be generated by autothermal reforming of the preliminary evaporated diesel fuel on the vehicle board equipped with a diesel engine. The key problems arising upon diesel fuel reforming are: catalyst coking and catalyst deactivation caused by interaction with sulfur containing compounds.

Thus, the main goals of the our work are: to specify the composition of catalyst for autothermal reforming of actual diesel fuel into synthesis gas, which will be stable to coke formation and deactivation, and to define the optimal conditions of autothermal reforming.

Results

The lab-scale axial-type syngas reactor for autothermal steam reforming of diesel fuel was made of a stainless steel tube with heat insulation, which encloses monolith reinforced metal porous catalyst. The outer tube diameter is 84 mm, and the reactor length is 160 mm.

The technology of preparation of monolith reinforced metal porous catalysts has been recently developed at the Boreskov Institute of Catalysis for synthesis gas generation from natural gas [2]. This technology was used to prepare a catalyst sample for the autothermal reforming of diesel fuel also. To prepare the catalyst, one used a fechral net formed as a strip covered with Al_2O_3 and SiO_2. Then the support was impregnated with active components. The as-prepared catalytic strips were used to manufacture a multi-channel monolith by sintering a couple of spiraled flat and corrugated strips. The dimensions of the monolith catalyst are: diameter 55 mm, length 55 mm.

Fig. 1 shows a schematic of the setup for tests of catalysts for the autothermal reforming of diesel fuel. The setup contains the following parts: a catalytic synthesis gas generator, an evaporator of a mixture of diesel fuel and water, an autothermal reformer, a catalytic burner, a system of feeding and control and analytical equipment.

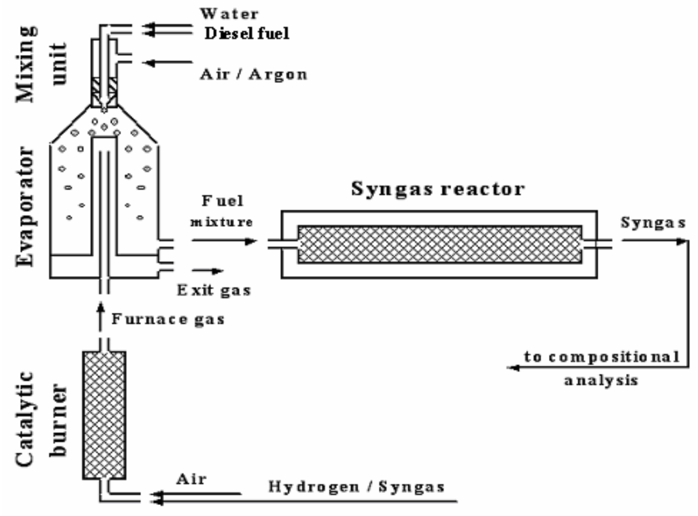

Fig. 1. Scheme of the setup for tests of developed catalysts.

For the autothermal diesel fuel reforming, we developed 6 catalyst composites based on the reinforced gauze support. As follows from the experiments, the samples of monolith reinforced metal porous catalysts containing Ba, Co and Mn as an active component are the most promising for autothermal conversion of diesel fuel. The process of autothermal reforming of diesel fuel into syngas is not accompanied by coke formation for these catalysts. The most promising catalysts provide the yield of synthesis gas (H_2 + CO) in the experimental runs 2.88 l/g of diesel fuel at $H_2/CO=3.5$ with more than 30 vol.% H_2 in the dry reforming products. The optimal conditions of autothermal reforming of diesel fuel are: O_2/C =0.5-0.6, H_2O/C =1.5-1.7, contact time 0.3-0.4 s, temperature of mixture at the reactor inlet 300-400°C.

The obtained solutions will be used in future developments of vehicle versions of the on-board syngas generator in order to provide low pollutants emission in exhaust gas.

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ETHANOL STEAM REFORMING AND WATER GAS SHIFT REACTION OVER Co-Mn/ZnO CATALYSTS

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Introduction

Ethanol steam reforming (ESR) is an attractive route for producing hydrogen from renewable resources (bioethanol). In addition to its high energy density and low toxicity, ethanol is a liquid fuel that may take advantage of the actual fuel distribution network. ESR yields up to 6 mol of hydrogen per mol of reacted ethanol, according to reaction (1). However, other reactions such as ethanol dehydration (2), ethanol decomposition (3), and condensation (4) are commonly observed [1] and, in addition, there is also the water gas shift equilibrium (5) and methanation of CO_x (6,7) reactions that can operate under ESR conditions. For that reason, ESR strongly depends on reaction parameters and the use of appropriate catalysts. So far, catalysts based on Ni, Cu, Co, and noble metals have shown the best catalytic performance [2,3], although issues related to catalyst stability have not been always addressed. Among all catalysts tested, those based on Co show high activity at low temperature (<773 K) for ESR, and values as high as 5.5 mol H_2/mol C_2H_5OH have been reported [4]. Very recently, the addition of Fe and Mn to Co/ZnO catalysts have resulted in even better performance and stability [5]. In this work, we have studied the ESR and WGS reactions addressed to obtain hydrogen over the Co-Mn/ZnO system by varying the Co/Mn ratio from 3 to 20. We have also prepared catalytic monoliths with the best formulation and tested them in the above reactions.

$$C_2H_5OH + 3\ H_2O \rightarrow 6\ H_2 + 2\ CO_2 \qquad \textbf{(1)}$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \qquad \textbf{(2)}$$

$$C_2H_5OH \rightarrow CH_4 + CO + H_2 \qquad \textbf{(3)}$$

$$2\ C_2H_5OH + H_2O \rightarrow (CH_3)_2CO + 4\ H_2 + CO_2 \qquad \textbf{(4)}$$

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad \textbf{(5)}$$

$$CO + 3\ H_2 \rightarrow CH_4 + H_2O \qquad \textbf{(6)}$$

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O \qquad \textbf{(7)}$$

Catalyst preparation

A series of ZnO-supported Co-Mn catalysts have been prepared by co-precipitation and by impregnation in order to study the influence of the preparation method. Samples have been calcined at 673 K and reduced at 673 K with a gaseous stream containing 10% H_2. Catalytic monoliths (cordierite) have been prepared by conventional washcoating methods.

Catalysts characterization

Catalysts have been studied by X-ray diffraction, temperature programmed reduction, high resolution transmission electron microscopy, electron energy loss spectroscopy, and X-ray photoelectron spectroscopy. The existence of bimetallic Co-Mn particles has been evidenced. The adherence of catalyst coatings on cordierite monoliths has been evaluated, and catalyst dispersion and homogeneity inside monolith channels have been studied by scanning electron microscopy and confocal microscopy.

Catalytic tests

ESR has been carried out at atmospheric pressure in a tubular reactor with a $C_2H_5OH:H_2O=1:6$ molar mixture balanced in inert gas. A continuous flow of ethanol (0.33 mL min^{-1} C_2H_5OH) and water were provided separately and mixed before entering the reactor. Reactants and products were analyzed on line either by gas chromatography or by mass spectrometry. WGS has been performed using a $CO:H_2:H_2O=1:2:6$ molar mixture. Co-Mn/ZnO catalysts are active for WGS under ESR conditions, and this affects positively on the hydrogen yield in ESR. Catalytic monoliths coated with a catalyst containing 10%Co and 1%Mn produce 5.7 mol H_2/mol ethanol at 723 K.

Acknowledgments

Financial support from MEC (ENE2006-06925) is acknowledged.

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HYDROGEN PRODUCTION BY STEAM REFORMING OF DIMETHYL ETHER OVER Cu-Zn/CeO_2-ZrO_2 CATALYTIC MONOLITHS

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Introduction

Hydrogen and fuel cells are attracting much attention as potential devices for energy transportation and transformation. Steam reforming and oxidative steam reforming of natural gas and other hydrocarbons as well as alcohols as a route for producing hydrogen in a variety of environments have been addressed extensively in the last decades. Dimethyl ether (DME) has recently become a potential fuel for hydrogen production because provides a high hydrogen to carbon ratio, has a high energy density, and can be easily handled, stored, and transported[1-4].

Steam reforming of DME comprises two consecutive, moderately endothermic reactions: DME hydrolysis and methanol (MeOH) steam reforming. The overall reaction is **(1)**[4]:

$$(CH_3)_2O + 3\ H_2O \rightarrow 6\ H_2 + 2\ CO_2 \quad \Delta H^o = 135\ kJ\ mol^{-1} \qquad \textbf{(1)}$$

The hydrolysis reaction is known to take place actively over acidic catalysts. Since DME hydrolysis provides low equilibrium conversion, an active catalyst to effectively reform methanol is also the key for DME steam reforming. In general, steam reforming of MeOH proceeds over Cu-, Pt- or Pd-based catalysts[4]. As a consequence, catalyst formulations containing both acidic and metal sites are thus preferred.

In this work, DME steam reforming has been performed over several Cu-Zn/CeO_2-ZrO_2 catalysts, which have been used for coating cordierite monolithic structures for practical application[5].

Catalysts preparation

Cordierite monoliths were first coated with 10% w/w of ZrO_2, CeO_2 and $Ce_{0.5}Zr_{0.5}O_2$ supports, using zirconium oxychloride and cerium trichloride as precursors. Monoliths were dried under continuous rotation at 373 K for 2 h and calcined in air at 773 K for 2 h. Cu, or Zn, or a mixture of Cu and Zn were then added to each support by incipient wetness impregnation using copper nitrate and zinc nitrate as precursors. The total metal loading was ca. 10% w/w with respect to the support. The resulting catalytic monoliths were dried under continuous rotation at 373 K for 2 h and calcined in air at 773 K for 5 h.

Catalysts characterization

In order to evaluate the mechanical stability and adherence of catalyst coatings, vibration tests have been conducted by ultrasound exposure with monoliths immersed in liquid and monitoring of weight loss. Scanning electron microscopy (SEM) has been used to study in detail the dispersion, uniformity and morphology of the monolithic catalysts, both as prepared and after the stability tests. Confocal microscopy has been used also to analyze the 3D coating dimension and dispersion. Surface composition has been determined by X-ray photoelectron spectroscopy.

Catalytic tests

DME steam reforming has been carried out at atmospheric pressure using a conventional flow reactor

(20 mm ID). Prior to reaction, catalytic monoliths have been activated at 573 K with a 10% H_2/N_2 mixture for 1 h. A DME:H_2O=1:3 (molar) gaseous mixture balanced in N_2 has been passed through the reactor at 473-723 K under different GHSV. Reactants and products have been analyzed continuously with a on-line gas micro-chromatograph.

Acknowledgments

Financial support from *Ministerio de Educación y Ciencia* (ENE2006-06925) is acknowledged.

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KINETICS OF THE BIOFUELS-ASSISTED SCR OF NO_x OVER Ag/ALUMINA-COATED MICROCHANNELS

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Introduction

The growing concern for the environment and the strict legislations regarding the mobile sources emissions have led to an emerging research in the area of environmental catalysis. Biofuels are regarded as an alternative solution for reducing the oil dependence in the transport sector. The European Union (EU) has set the use of biofuels to be of 5.75% of the total vehicle fuel consumption in the EU by 2010. The goal for 2020 is set to 10%. The exhaust treatment of conventional fuels has been studied in detail in a large amount of industrial and academic publications [1]. However, it is essential to understand the NO_X reduction as biodiesel is used. On the other hand, microreactors have emerged as an alternative to conventional reactors: enormous improvements in energy efficiency, faster reactions, improved yield, safety, reliability and better process control are achieved [2]. We present here a systematic kinetic study for the selective catalytic reduction of NO_X with biodiesel. It is based on the rigorous treatment of the chemical transformations occurring in selective catalytic reduction of NO_X in microchannels.

Microreactor System

The gas-phase microreactor was designed at Åbo Akademi and the parts were purchased from the Institut für Mikrotechnik Mainz GmbH (IMM). The device consists of a two-piece cubic chamber with two inlets and one outlet, each with a tube diameter of 710 μm. The lower part of the chamber has two recesses, each filled with a stack of ten micro-structured platelets, which are connected by a diffusion tunnel. The first stack contains a total of ten mixing platelets with nine semicircular channels of different radii but with a common center. They are arranged in the stack so that they meet the two inlets in alternation. The second stack consists of ten rectangular platelets with nine parallel shallow microchannels (Ø = 460 μm and depth = 75 μm) coated with an Ag/Al_2O_3 catalyst (see Fig. 1). A maximum gas flow of 50 mL/min is permitted. Pressures and temperatures up to 50 bar and 600 ºC, respectively, can be achieved, making it possible to carry out a wide range of chemical transformations in gas-phase. The kinetic experiments were carried out in the microreactor and the concentrations of the species were determined by GC and MS [3].

Kinetic Experiments

Hexadecane, that can be produced from renewable sources and is regarded as a high-quality diesel [4], was selected as a model compound for the second generation biodiesels. The reaction orders of NO, O_2 and $C_{16}H_{34}$ were determined by varying the concentration of the components in the gas mixture. Concentrations of 300-1500 ppm NO, 150-1000 ppm hexadecane, and 1-8 vol.% O_2 were used, keeping helium as balance gas. The concentration of H_2O was kept constant at 12 vol.%. The results were mathematically treated to obtain the reaction orders with respect to NO, $C_{16}H_{34}$ and O_2. Typical experimental results obtained in the SCR of NO_X in microchannels are illustrated in Fig. 2. The reduction conversion with octane is used for comparison purposes, as a representative component for fossil fuels.

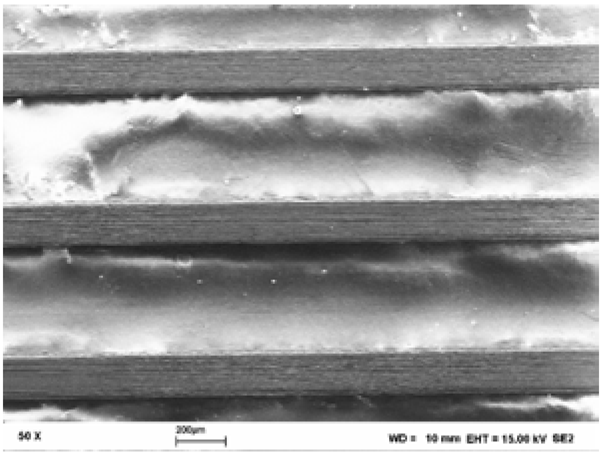

Figure 1: SEM picture of a microplatelet – 50X

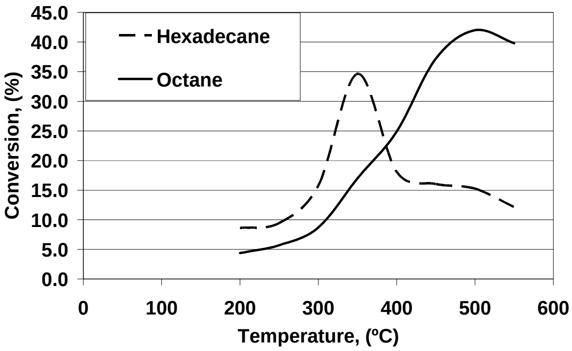

Figure 2: NO to N_2 conversion of hexadecane in a microreactor for octane and hexadecane. Gas flow: 500ppm NO, 187.5ppm $C_{16}H_{34}$ (or 375ppm C_8H_{18}), 6 vol.% O_2, 12 vol.% H_2O and He balance.

Two important reactions in the SCR were found to be as follows: $2\ NO + C_{16}H_{34} + 23.5\ O_2 \rightarrow N_2 + 16\ CO_2 + 17\ H_2O$; and $C_{16}H_{34} + 24.5\ O_2 \rightarrow 16\ CO_2 + 17\ H_2O$. Based on experimental data, the reaction orders were calculated. The reaction orders with respect to NO are close to zero at the low temperature range (200-400 ºC), possible due to the NO_X species coverage of the active sites. The order with respect to NO increased at higher temperatures (400-550 ºC). Oxygen displayed the opposite behaviour: decreasing the order with respect to O_2 while increasing temperature; while hexadecane appeared to have a two-fold behaviour: for temperatures below and above 350 ºC. Apparently, the reaction orders with respect to hexadecane decreased with raising temperature. This was the case at temperatures below 350-400 ºC. At higher temperatures, however, the reaction orders increased again reaching a minimum around 350 ºC. Additionally, the orders with respect to $C_{16}H_{34}$ were found to be higher than the orders in O_2 and NO, which might suggest that the hydrocarbon-oxidation step dominates over the NO_X-reduction one.

Summary

A gas-phase microreactor (Ø = 460 μm) was used for the kinetic investigations of the selective catalytic reduction of NO_X. As a model compound, hexadecane, a high quality diesel fuel and a representative component of the second generation biodiesels, was employed. The kinetic parameters were estimated with non-linear regression by using combined simplex and Levenberg-Marquardt algorithms and with plug flow model for the microchannels. Reaction orders with respect to NO, O_2 and $C_{16}H_{34}$ were obtained.

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OP-V-13

DESIGN OF PILOT REACTOR AND MONOLITHIC CATALYST FOR AUTOTERMAL REFORMING OF OXYGENATES

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Transformation of biofuels into syngas via selective oxidation/autothermal reforming is now considered as one of the most important task of catalysis in the energy-related fields. However, due to a high reactivity of oxygenates a heavy coking is observed leading to the catalyst deactivation. To deal with this phenomenon, active components comprised of complex oxides with a high lattice oxygen mobility (favors efficient gasification of coke precursors) promoted by precious metals (responsible for oxygenates activation) are suggested. For achieving a high performance, monolithic substrates with a good thermal conductivity could be promising for providing an efficient heat transfer from the inlet exothermal zone of the reactor (where oxygen is consumed) into its rear part, where endothermal steam and dry reforming occur. To prevent thermal cracking of oxygenates and provide an efficient evaporation of fuel at a small overheating degree, ensure its good mixing with steam/air, new types of evaporators/mixers are to be designed. This paper presents results of research aimed at addressing these problems at the pilot-scale level.

As heat-conducting substrates, fechraloy foil (thickness up to 0.2 mm) and gauze (wire diameter 0.2-0.3 mm, square mesh ~ 0.5x0.5 mm) protected by corundum layer via blast dusting were used. Stacked flat and corrugated bands of foil were winded into the Arkhimed spiral (external cylinder diameter ~50 mm, length 20 mm) forming triangular channels with sizes up to 3 mm. After spark-welding of tungsten rods as electrical current inlets, this heated monolithic substrate was used for the evaporation of liquid fuels sprayed via a nozzle directly into its inlet part. Similar fechraloy substrates or discs cut from fechraloy gauzes were used for preparation of monolithic catalysts by washcoating with a slurry of Ln-Ce-Zr-O mixed oxides (Ce:Zr = 1:1, Ln = La, Pr, or Sm) prepared via Pechini route and ultrasonically dispersed in water with addition of peptizers and surfactants (loading up to 10 wt.%). Precious metals up to 1% wt.% of Pt, Pd, Ru,) and/or Ni (up to 10 wt. %) with respect to doped ceria-zirconia oxide were supported by incipient wetness impregnation. For preparation of pilot-scale monolithic catalysts, best compositions of active components selected on the base of extensive lab-scale studies in the reactions of methane and oxygenates (acetone, ethanol) steam reforming at short contact times in stoichiometric feeds were selected.

A pilot tubular stainless steel reactor equipped with these catalysts and a front thermal shield was connected to the fuel/water evaporation unit with liquids supplied by the plunger pumps through nozzles, air being fed via a mass-flow controller. As fuels, acetone and anisole (methoxybenzene) of commercial grade and purified edible sunflower oil were used. Oxygen content in the feed was varied in the range of 15-20%, H_2O 0-18%, fuel 1-10%, flow rate up to 2 m^3/h (contact times in the range of 5-50 ms at operating temperature).

For all types of studied fuels, stable autothermal performance with the maximum temperature at foil monolith up to 1000 °C was maintained with the inlet feed temperature as low as 200 °C. In these conditions, the oxygen slip was not observed at all contact times. The maximum syngas yield was up to 45% with H_2/CO ratio increasing from ~ 0.8 to 1 with increasing water content up to 10%. In products, along with CO_2 (in the range of 4-6%) some amount of CH_4 (1-2%) and olefins (up to 1%) were observed. This demonstrates occurrence of cracking reactions as well. For longer contact times, and especially for feeds without water, ignition of fuels at the thermal shield was observed followed by the excessive carbon deposition at walls in the inlet part of the reactor. At a proper optimization of contact times and feed composition, no coking was observed for hours-long pilot tests even for sunflower oil as a fuel. No carbon build-up was observed for the monolithic evaporator as well. Addition of stack of gauzes or thin–foil monolith after thick–foil monolith allowed improving syngas yield and removing residual olefins from products. No spallation or cracking of the active components supported on metallic substrates was revealed.

Hence, pilot-scale tests in the reactor equipped with an original evaporator/mixer of liquid biofuels (acetone and anisole as model fuels and edible sunflower oil as realistic fuel) revealed a high and stable performance in the autothermal reforming of monolithic catalysts comprised of heat-conducting fechraloy foil/gauze substrates with supported doped ceria-zirconia complex oxides promoted by precious metals and/or Ni. This provides new possibilities for transformation of a broad range of complex biofuels (such as products of biomass pyrolysis) into syngas.

This work is supported by INTAS 05-1000005-7663 and INTAS YSF 06-1000014-5773 Projects.

OP-V-14

DEVELOPMENT OF A LAB SCALE CATALYTIC CHANNEL REACTOR FOR CO-PROX

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CO preferential oxidation (CO-PROX) is a promising method to reduce CO concentration in H_2-rich gas streams, produced by fossil fuels reforming in a fuel processor (FP), with minimal loss of H_2. An essential requirement for PEMFC is, in fact, to deliver clean H_2 to the FC anode, which can be poisoned even by traces (~10 ppm) of CO.

$Pt-Al_2O_3$ catalysts were extensively studied and found very active towards CO oxidation [1]; more recently Pt-supported zeolite catalysts were proposed thanks to their enhanced selectivity [2]. Previous studies on different Pt-A zeolite catalysts [3] showed that the best catalytic performance, in terms of catalyst activity and selectivity, was obtained with a 1% Pt-3A catalyst, thanks to the specific structure of 3A zeolite support. In this work 1% Pt-based catalyst, supported on a mixed system zeolite 3A and Al_2O_3, suitably developed to be deposed with good adhesion on the metallic surfaces of a structured channel reactor, was prepared and tested for CO-PROX in H_2-rich streams.

A powder catalyst consisting of 1% Pt over a mixed support 50% 3A zeolite and 50% Al_2O_3 (1% Pt-MIX) was prepared at 500°C via a slightly modified solution combustion synthesis (SCS) technique [4], because of the presence of fine zeolite solid particles. The obtained 1% Pt-MIX catalyst was analyzed by HRTEM to investigate the metal dispersion on the support and examined by SEM-EDS to evaluate the morphology and elemental distribution. The powder catalyst was tested for the CO-PROX with a synthetic reformate gas flow in a temperature range of 100÷300°C. The CO and O_2 conversions and the O_2 selectivity to CO oxidation were determined in each test. The employed fixed bed microreactor and the bench rig scheme were described in detail in a previous work [3]. With $\lambda=2O_2/CO=4$, the 1% Pt-MIX catalyst allowed to reach the complete CO conversion (simultaneously with O_2 conversion equal to 1) in the temperature range $\Delta T_{CO} = 112 \div 136°C$.

The second stage of the investigations was related to the performance analysis of the 1% Pt-MIX deposed on structured channel reactor, composed by four flat metal plates (50x50x 1 mm^3) stacked to form three square channels 0.6 mm depth each. Before the deposition of 1% Pt-MIX by spray pyrolisis, the metal plate surface was covered with a $\gamma-Al_2O_3$ layer; the γ- Al_2O_3 particles were produced in our lab via SCS method and deposed on the plate surfaces via Plasma Spray technique by Bekaert BV with two different thickness: a thin and a thick layer, of 30 μm and 100 μm, respectively. In preliminary catalytic tests on metal plates with thin γ-Al_2O_3 layer, performed with a space velocity WHSV of about 2,000 h^{-1} and λ=4, the 1% Pt-MIX catalyst superficial load deposed on the metal plates was equal to 0.42 mg/cm^2; in these conditions, the maximum CO conversion remained lower than 1 and the minimum value of CO concentration reached at the reactor outlet was about 100 ppm, probably because of the low catalyst load into the structured reactor. Successively, catalytic tests carried out on metal plates with both thin and thick γ-Al_2O_3 layer, the catalyst superficial load was increased to 5 mg/cm^2, reaching in this way the complete CO conversion in all cases. As shown in Fig. 1, the complete CO conversion was reached in a temperature range of 194÷214°C for the plates with thin γ-Al_2O_3 layer, and similarly, in the range 188÷211°C for the plates with thick γ-Al_2O_3 layer.

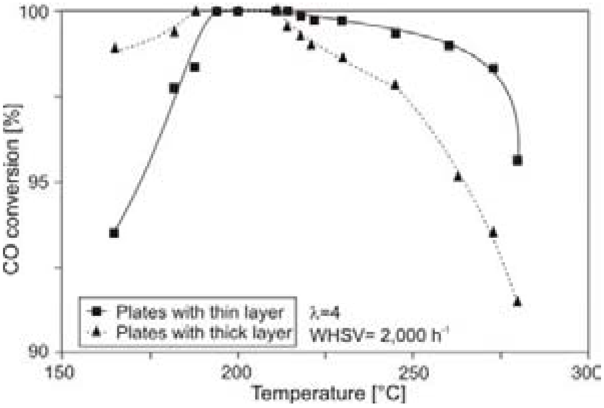

Fig. 1: CO conversion vs. T for thin and thick layered plates loaded with 5 mg/cm^2 of catalyst.

Since in these catalytic activity tests WHSV was too low compared to the real conditions in FP, activity tests at higher space velocity, equal to 4,800 h^{-1}, were carried out employing thin γ-Al_2O_3 layered plates. In these operating conditions, the temperature range of CO complete conversion shifted to higher values and the range width was reduced: 215÷225°C.

In conclusion, selective removal of CO by PROX reaction was performed over 1% Pt-MIX catalyst deposed on thin metal plates previously covered with γ-Al_2O_3 in a structured reactor. Catalytic activity tests shown complete CO conversion in a satisfactory temperature range with acceptable WHSV values.

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OP-V-15

DEVELOPMENT OF TWO-STAGE PROCESS OF PREPARATION OF MICRO- AND MESOPOROUS CARBONS WITH DEVELOPED TEXTURE FROM HIGH-ASH BIOMASS

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There are many ways to synthesis of amorphous carbon materials with high specific surface area from a lot of precursors – from chemicals and polymers to petrochemical wastes and biomass [1]. Vegetable biomass is often used for preparation of carbon materials by physical or chemical activation. There is the type of biomass, possessing anomaly high ash content, the main component of the ash is amorphous SiO_2 (more than 95 w. %). Other ash components are the oxides and some of other compounds of alkaline and alkaline-earth metals, iron, copper etc. Rice husk (RH) is a «leader» on content of the ash among the biomass and contains up to 23 w. % of silica [2-4]. So the main feature of RH as a carbon precursor is that the silica can affect on texture properties of the preparing carbon materials.

The work is devoted to a development of a two-stage method of micro- and mesoporous carbons preparation from high-ash biomass by the example of rice husk (RH). The process of carbonaceous materials preparation, in the whole, consists of two main stages: a preliminary carbonization of the high-ash biomass in fluidized catalyst bed reactor and a treatment of the prepared carbon-silica composite with sodium and/or potassium compounds in a static reactor. At the same time, the both stages have the following principle differences:

- in order to prepare the microporous carbons, one impregnates the product of the RH carbonization by solution of KOH with following drying and activation at 700–900 °C;
- in order to prepare the mesoporous carbons, one mixes equimolar mixture of Na_2CO_3 and K_2CO_3 with the product of RH carbonization mechanically with following high-temperature leaching at 750–1000 °C.

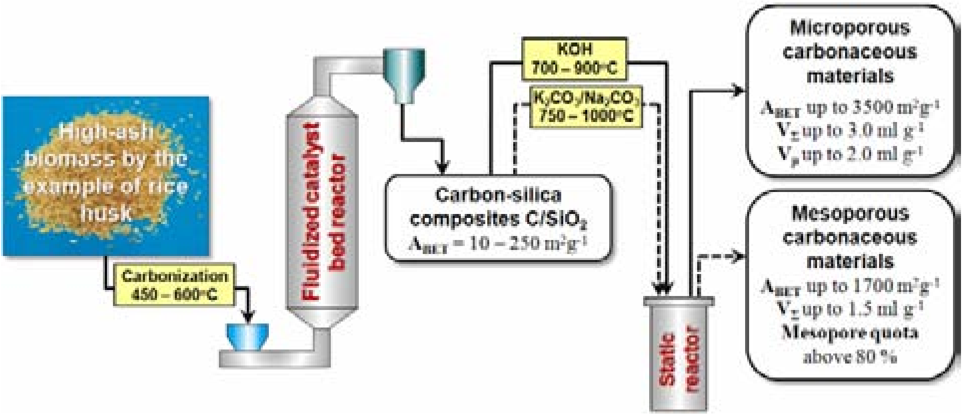

Fig. 1. The principle scheme of the process of micro- and mesoporous carbons producing from rice husk

An effect of preliminary RH carbonization conditions and other conditions of the processes of the alkali activation and the high-temperature leaching of SiO_2 by the mixture of K_2CO_3/Na_2CO_3 on properties of the preparing materials was investigated. It was showed, that the carrying out the carbonization in fluidized catalyst bed (T = 450–600 °C, contact time $\tau \sim 1$ sec, molar ratio of air oxygen to carbon of RH $\alpha \sim 2$, catalyst of deep oxidation CuO + MgO + $Cr_2O_3/\gamma\text{-}Al_2O_3$ with granule's size 2–3 mm) of leads to preparation of carbon-silica composites with better properties for preparation of the final carbons, than in case of pyrolysis.

In Table 1, the results of an investigation of an effect of activation temperature on texture and adsorptive properties in relation to hydrogen and methane of the microporous carbons prepared from RH, carbonized in fluidized catalyst bed at 500 °C are listed.

Table 1. Activation temperature effect on texture and adsorptive properties of microporous carbon samples obtained at different temperatures by KOH activation.

Activation temperature, °C	A_{BET}, m^2g^{-1}	V_Σ/V_μ, ml g^{-1}	Vol. micropore quota, %	H_2 adsorptive capacity, w. % (50 bar, 77 K)	CH_4 adsorptive capacity, w. % (60 bar, 273 K)
700	3170	1.77/1.45	81.9	4.7	28
750	3450	2.01/1.68	83.6	5.7	27
800	3360	2.18/1.87	92.3	6.3	33
850	3170	2.26/1.74	77.0	5.8	34
900	3210	2.97/1.48	49.8	6.2	41

The analogies of the materials – microporous carbons, such as Maxsorb (Kansai Coke and Chemical Co Ltd., Japan) are produced from petroleum coke and pitch also by KOH activation at 700–800 °C but through a preliminary treatment of the precursors by concentrated nitric acid that leads to mordant and toxic wastes. In addition, these materials possess lower texture characteristics (A_{BET} about 2700 m^2g^{-1}, V_μ about 1.2 ml g^{-1}) [4]. A comparison of the technical conditions leads to a resume that the proposing method is cheaper and environmentally more appropriate.

In Table 2 the data on an effect of temperature on mesoporous carbons properties are showed. The carbons were prepared by high-temperature leaching of SiO_2 from RH, carbonized in the fluidized catalyst bed reactor, by pyrolysis in inert atmosphere and from non-carbonized RH.

Table 2. Effect of the leaching temperature on texture properties of mesoporous carbons prepared from RH by high-temperature leaching with equimolar Na_2CO_3/K_2CO_3 mixture

Pretreatment conditions	T, °C	A_{BET}, m^2g^{-1}	V_Σ/V_μ, ml g^{-1}	Vol. mesopore quota, %	Deep of graphitization, % (by XRD)	Ash content, %
FCB[1)], 500 °C	750	1190	1.11/0.20	82.0	0.0	1.7
FCB, 500 °C	800	1485	1.36/0.29	78.7	0.0	2.4
FCB, 500 °C	850	1447	1.24/0.31	75.0	0.0	4.5
FCB, 500 °C	900	1581	1.44/0.31	78.5	0.0	2.0
FCB, 500 °C	950	776	0.88/0.21	76.1	39.5	1.8
FCB, 500 °C	1000	652	0.84/0.13	84.5	46.5	2.3
Pyrolysis, 400 °C	900	1479	1.17/0.40	65.8	[2)]-	4.1
-[3)]	900	1350	1.00/0.49	51.0	-	4.5

[1)] – FCB – fluidized catalyst bed; [2)] – not investigated; [3)] – raw RH was used

The data of Table 2 show, that the prepared carbons, in the whole, possess, from one hand, high mesopore quota and from the other hand – high specific surface area.

The proposed method of preparation of the mesoporous carbons differs from traditional template synthesis method by that the traditional template synthesis includes several studies, such as synthesis of template mesoporous SiO_2, impregnation of SiO_2 by carbonaceous precursor, carbonization at 500–1000 °C and the last – remove the template SiO_2 by HF or NaOH [6]. The obtaining carbon materials possess texture properties comparable with the properties of carbons from RH. Nevertheless, the traditional way of synthesis of the materials is more difficult, expensive and includes the using of a lot of chemicals.

Thus the proposing process allows preparing microporous or mesoporous carbons with developed texture, in dependence on the necessity; it is less expensive, more technologic and environmentally appropriate as against with traditional methods of preparation of micro- and mesoporous carbonaceous materials with developed texture.

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OP-V-16

EFFECT OF MICROREACTOR GEOMETRY IN PERFORMANCE OF CATALYTIC MICROREACTOR OF HYDROGEN PRODUCTION BY CFD MODELING

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Abstract Hydrogen production from steam reforming of methanol for fuel cell application was modeled in a wall coated micro channel reactor by CFD approach. Heat of steam reforming was supplied from catalytic total oxidation (TOX) of methanol in neighboring channel of steam reforming (SR) channel and conduct from TOX to SR channel through metal divider wall of the channels. Heat integration was compared in zigzag and straight geometry of microreactor by CFD modeling. The model is 2 dimensional, steady state and containing five zones: TOX fluid, TOX catalyst layer, steel wall of the channel, SR catalyst layer, SR fluid. Set of partial differential equations (PDEs) including x and y momentum balance, continuity, partial mass balances and energy balance was solved by finite volume method. And stiff reaction rates were considered for methanol total oxidation (TOX), methanol steam reforming (SR), water gas shift (WGS) and methanol decomposition (MD) reactions, in the model. The results show that zigzag geometry is beeter than straight geometry because of increasing of heat and mass transfer, mixing. Keywords: Wall Coated Catalytic Micro Channel Reactor, Microreactor, CFD Modeling, Methanol Steam Reforming, Hydrogen Production, zigzag geometry.

OP-V-17

ENERGY PRODUCTION FROM BIOMASS VIA LOW-TEMPERATURE CATALYTIC PYROLYSIS

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Introduction. Nowadays biomass is an important source of energy in the world. Thus, thermochemical conversion technology, e.g. pyrolysis, gasification and combustion are studied extensively [1 – 3]. Pyrolysis is known to be an efficient way of converting biomass into gases, oil-like liquid products and char.

The aim of the investigations is to study the low-temperature pyrolysis of peat in the presence of catalytic systems on the basis of natural alumosilicate materials and synthetic zeolites. Although peat has a relatively fast released CO_2 retake rate binding CO_2 on a similar levels to a growing forest, the total regrowth rate of a single peat bog could be slower than 1000 years, therefore peat is considered somewhere between truly renewable bio-fuels and fossilized fuels. Compared to the other fossil fuels, peat is characterized by the lowest content of fixed carbon along with the highest content of volatile matter.

The use and selection of a suitable catalyst is of crucial importance for the pyrolysis process because it permits to operate at lower temperatures and can provide selectivity towards the desired products, avoiding any post-process upgrading, thus enhancing the benefit of the process and turning it economically feasible.

Experimental. As the catalysts of peat pyrolysis both natural silica-alumina materials (caoline, bentonite and cambrian clays and clay mergel) and synthetic zeolites (H-Beta-25 and H-Mord purchased from «Zeolyst International» (USA)) were used.

Catalytic action of natural silica-alumina minerals and synthetic zeolites was estimated basing on the volume of the evolving gaseous mixture, on the concentrations of hydrocarbons in gaseous mixtures and also on the heat of combustion of combustible gases.

Physicochemical analysis of silica-alumina catalytic materials was carried out via XFA and nitrogen physicosorption.

To analyze the gaseous mixture (hydrocarbons, CO, CO_2, H_2) and to estimate the heat of combustion the analytic complex – gas chromatograph and specially developed analyzer of specific heat of combustion of gaseous media realized on the base of flame-temperature detector – was used [4].

Results and discussion. The preliminary experiments showed that the addition of 2% (wt.) of synthetic zeolites and of 30% (wt.) of natural silica-alumina materials to peat was optimal. Significant distinction in percentage of optimal amount of alumosilicate component of reaction mixture between natural and synthetic alumosilicates was likely due to the different structures of these substances. Moreover, natural alumosilicates when present in significant amounts in the reaction mixture, besides having a catalytic function also acted also heat-carriers, considerably increasing the heat conductivity of the mixture, thus promoting more uniform heating.

In the presence of catalysts the amount of hydrocarbons in gaseous mixture noticeably increased. For all the catalysts the average value of the specific heat of combustion was higher approximately by twofold in comparison with the data obtained for non catalytic process (8.52 MJ/m^3). Among both natural and synthetic catalytic materials bentonite clay showed the highest heat of combustion – 23.88 MJ/m^3 – at optimal loading.

The influence of the temperature in the range from 410 to 600 °C on peat pyrolysis in the presence of bentonite clay was investigated. It was demonstrated that the highest heat of combustion (23.88 MJ/m^3) was reached at 460 °C. From the data obtained during the temperature variation it was revealed that the value of apparent activation energy for the catalytic process is lower almost twice compared to non-catalytic one, while the value of frequency factor (k_0) is higher in several orders.

Conclusion. The application of synthetic zeolites and natural clays as the catalysts allowed increasing the heat of combustion of resulting gaseous mixture and rate of pyrolysis process as well as decreasing the temperature of peat pyrolysis from 700 °C (average temperature of non catalytic pyrolysis) to 460 °C. The highest heat of combustion (23.88 MJ/m^3) was shown to be reached while using bentonite clay at 460 °C and concentration of 30% (wt.).

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CATALYTIC PARTIAL OXIDATION OF METHANE TO SYNTHESIS GAS OVER CORUNDUM SUPPORTED MIXED OXIDES: TAP STUDIES

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Introduction

The catalytic partial oxidation of methane is a potential energy efficient alternative to the capital intensive syngas generation by steam reforming [1]. Synthesis gas formation from methane may involve two routes depending on the nature and state of the catalyst, a total oxidation – reforming route or a direct generation, i.e. literal partial oxidation [2,3]. Using the TAP technique with short contact time and negligible thermal effect is one of the most promising ways to obtain mechanistic information enabling to conclude on the impact of the oxidation state. The catalyst performance in primary synthesis gas formation is probed, while this presents a major difficulty for the very fast oxidation steps at atmospheric pressure. The present study outlines the development of suitable experimental strategies for exploring the syngas generation over the concerned catalysts with the TAP technique.

Experimental

The preparation of the fluorite type mixed oxide support involves an adapted Pechini route [4]. Monolithic substrates were separate triangular channels of α-Al_2O_3 monoliths. Coating with the complex mixed oxides $Pr_{0.3}Ce_{0.35}Zr_{0.35}O_x$ and $Gd_{0.3}Ce_{0.35}Zr_{0.35}O_x$, respectively, was accomplished by the peptization method. Pt (1.4 wt.%) was deposited from H_2PtCl_6 solution by incipient wetness impregnation followed by drying and calcination at 900°C in air. A high temperature TAP reactor was charged with 10mm of the catalyst channel sandwiched between inert quartz sections. Prior to experiments samples were heated to 800°C and pulses of an O_2 / Ar mixture were introduced to remove residual carbon. The catalytic performance was estimated at 700°C using pulses of O_2 /Ar and CH_4/Ar mixtures, both in a molar ratio of 1:1. Pulse intensities of oxygen and methane were set to inject twice as much of methane than oxygen using pulse sizes of $4.1 \cdot 10^{15}$ – $6.8 \cdot 10^{15}$ molecules per pulse. Pulse response detection at characteristic masses and wider scanning for TPD experiments were accomplished with a UTI quadruple mass-spectrometer. Conditioning the catalyst to a quasi stationary operation proceeded via repeated cyclic oxygen/methane pulsing («working state»), dynamic saturation with additional oxygen pulses and immediately following pump-probe experiments allowed defined investigations with oxidation profiles close to those present at atmospheric pressure in a short contact time reactor.

Results and discussion

Impacts of the oxidation state and co-presence of methane and oxygen clearly differ as a function of dopants promoting the fluorite structured ceria/zirconia solid solution supporting Pt as active metal. Employing Pr as dopant yields a catalyst capable to preserve a minimum selectivity in all studied cases using the «working state» of the catalyst as origin. A significant and fast hydrogen release was observed, which varied only slightly altering the oxidation state of the sample by pre-injected oxygen. Furthermore, the co-presence of O_2 and CH_4 injecting both reactants at short time offset did not lead to an entire loss of selectivity. The weakness of the Pr doped sample relates to the relative slow formation of CO. It is currently not entirely clear if the low CO formation rate, i.e. the freeing of the catalyst surface from CH_x species, leads to a build-up of carbonaceous species impacting under ambient pressure conditions on the activity. However, the presence of CH_x at «working state» is clearly confirmed for the Gd doped sample. The activity of the Pr doped catalyst is clearly lower than that of the Gd doped catalyst, which may be slightly observed in terms of hydrogen release, but it become much more obvious when focusing on the formation of carbon monoxide as primary carbon oxides product. The Gd doped sample shows a complex behavior of performance as a function of the catalyst's oxidation state.

The Gd-doped catalyst seems more selective towards synthesis gas at the «working state» established by reaction of oxygen with methane injected at 0.5 seconds offset at a ratio of 1:2. The Pr-doped catalyst reveals a more stable behavior showing no major loss in selectivity when the «working state» determined quantity of oxygen becomes altered or when oxygen and methane become injected with shorter time offset.

Acknowledgement: Support by the joined European laboratory on catalysis between France and Russia (LFRC,LEA-313) and support by the RFBR-CNRS 05-03-34761 project is acknowledged.

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OP-V-19

A PHOTOCATALYTIC REACTOR FOR SEPARATE HYDROGEN AND OXYGEN EVOLUTION FROM WATER SPLITTING

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The photocatalytic splitting of water into hydrogen and oxygen using solar energy is a challenging research topic which has received much attention in recent years for its potential to provide clean and renewable H_2 as an energy resource. Almost all photocatalytic water splitting systems described so far imply the evolution of a mixture of hydrogen and oxygen; of course, a separation step would be required prior to any use of hydrogen.

A Plexiglas cell [1] has been set up, which allows the separate evolution of the two gases, resulting in streams of hydrogen and oxygen that do not need any further purification. The two cell compartments (see Fig. 1) were filled with NaOH (side A) and H_2SO_4 (side B) water solutions, separated by a 10 cm^2 titanium disk (1); a thin titanium dioxide layer had been deposited by radio frequency magnetron sputtering on the irradiated disk face in contact with the basic solution, while platinum was deposited on the opposite side. TiO_2 deposition at 600°C led to the formation of a layer of pure rutile phase, whereas deposition at 450°C led to the formation of a mixture of almost equal amounts of rutile and anatase phases. A cation exchange membrane (2) was mounted below the photoactive titanium disk, in the frame separating the two cell compartments. Upon illumination of side A of the cell (Fig. 1) through a square window, in which different cut off glass filters could be inserted (3), water splitting into molecular hydrogen and oxygen occurs at almost constant rate. The evolved gases can be collected in the two upside down burettes (4) surmounting the two cell compartments.

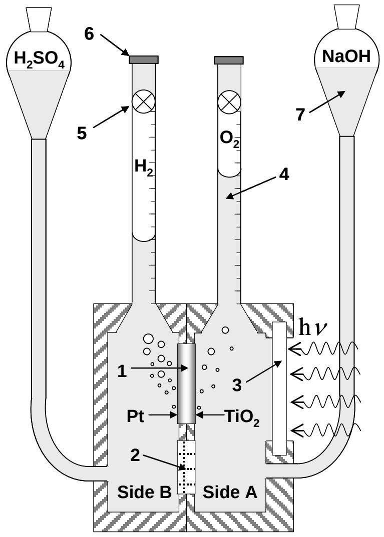

Fig. 1 Sketch of the cell for photocatalytic water splitting, with separate H_2 and O_2 evolution:
1 titanium disk;
2 cation exchange membrane;
3 glass filter;
4 burette;
5 stopcock;
6 rubber septum;
7 reservoir.

The rates of H_2 and O_2 evolution under irradiation with differently filtered light (cut off filters at 300, 350 and 400 nm) were evaluated by taking into account the effective composition of the gas mixtures in the two compartments of the cell, as determined by gas chromatographic analysis. The rutile phase, predominant when TiO_2 was deposited at 600°C, appears to be more active in the photocatalytic production of hydrogen with respect to the anatase phase, present in higher amount when the TiO_2 layer was deposited at 450°C. This is compatible with the better capability of the rutile phase to absorb light of longer wavelength. Indeed, the 600°C photoelectrode showed active also under irradiation at wavelengths above 400 nm. In general, the amount of oxygen evolved in side A of the cell was lower than expected on the basis of H_2 evolution, probably because photocatalytically produced O_2 was in part retained in the NaOH solution.

Our results show that hydrogen production from photocatalytic water splitting should be regarded as a practically viable, extremely promising way for clean, low cost and environmentally friendly conversion of solar energy into chemical energy, which could in future replace fossil fuels as a major energy source.

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OP-V-20

BIOMASS GASIFICATION IN A CATALYTIC FLUIDIZED REACTOR WITH BEDS OF DIFFERENT MATERIALS

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The shortness of oil resources combined with the alarming emission level of pollutants drive the research to find cleaner fuels, from production to consumption. In this framework biomass represents an abundantly available, renewable energy resource and has a CO_2 - neutral impact on the environment [1]. Biomass gasification is one of the best way to optimise the extraction of energy from biomass in terms of conversion-efficiency. In particular, production of hydrogen-rich syngas is very attractive, [2] provided that undesired species co-produced during the gasification process are completely converted. More specifically elimination of the condensable organic compounds, called TARs, which can cause the plugging in the colder parts of the plant, is one of the major issues not resolved yet. Catalytic TAR decomposition is considered as a technology with the highest potential to contribute to the solution of this problem [3]. Two catalytic approaches exist: hot gas cleaning after the gasifier (secondary methods) and treatment inside the gasifier (primary methods) [4]. The secondary method includes tar cracking, and mechanical separation using cyclones, filters or scrubbers. Although these methods have proven to be effective, the primary methods are gaining more attention since they are less complex and expensive. In this framework the fluidized bed technology assisted by catalysis is very promising, since it favors a fast heating rate of the biomass fuel and provides a good contact between the biomass and catalyst, both critical parameters for increasing the gas yield and cleanness. In addition the catalyst has to be suitable not only for its activity but also with reference to its mechanical properties and of course to its availability and price.

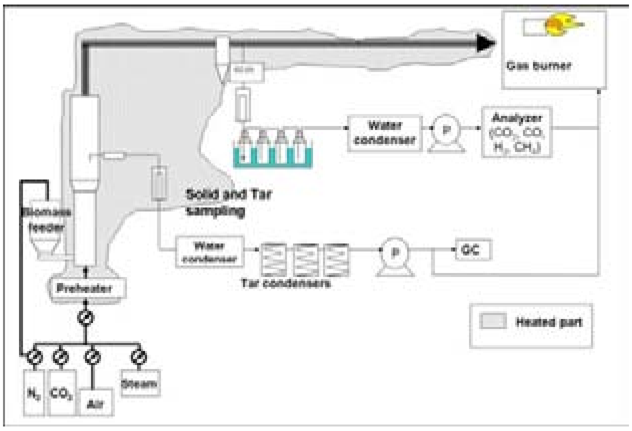

Figure 1. Experimental apparatus used for catalytic gasification tests.

In this work the efficiency of in-bed catalysts of different types in tar conversion has been investigated in a pilot catalytic fluidized bed gasifier. The scheme of the plant is reported in figure 1. The fluidized bed reactor consists of a 140mm I.D. stainless steal column operating under bubbling regime. Gasification products are sampled isokinetically inside the reactor and passed through a hot quartz fiber thimble to collect solid particles and in sequence through a condenser system to trap tars and water. The concentration of permanent gases are measured on-line by means of a continuous analyzer for H_2, CO, CO_2, CH_4 and a gas chromatograph. Collected condensed tars are analyzed off-line using the GC.

Different gasifying agents (steam, carbon dioxide and air, diluted or not in N_2) and fuel (maple wood chips with a low ash content (0.7wt%) and commercial pellets) have been used.

Coarse ash by products of thermoelectric coal-combustion plant (ENEL), never used before in biomass catalytic gasification process, have been used as catalyst. The ashes main component and physical characteristics are reported in table 1 in comparison with those of other materials used.

***Table 1**. Physico -chemical characteristics of the used different bed materials.*

	Constitutive compounds (wt%)										
	SiO_2	Al_2O_3	Fe_2O_3	Mn_2O_3	$Na_2O + K_2O$	MgO + CaO	Ni	Density kg/m^3	Mohs hardness	Surface area (m^2/g)	Melting point (°C)
Sand [5]	**85**	**8.4**	**1.4**	**-**	**4.20**	**1.90**	**-**	**2650**	**7**	**1 - 10**	**1450**
Olivine [5]	**40**	**0.8**	**9**	**0.8**	**-**	**50**	**-**	**3300**	**6.5 -7**	**10**	**1760**
Ash [6]	**75.6**	**21.4**	**1.3**	**-**	**0.1**	**1.6**	**-**	**2200**	**7**	**-**	**1400**
Ni-Al_2O_3[7]	**-**	**77**	**-**	**-**	**-**	**-**	**23**	**3700**	**-**	**2**	**2050**

The idea of using coal ashes as catalytic material has been made on the basis of their good mechanical resistance to attrition and the content of some active elements (Ca, Mg, Fe) also present in the well-studied olivine [8]. Furthermore elements to be taken into account are that ashes have a lower density than olivine (3300 kg/m^3) and are cheaper not only than synthetic (Ni based) catalysts but also than natural ones. The performances obtained the bed made of coarse ash have been compared to those obtained with inert sand, natural olivine and commercial Ni-Al_2O_3 catalysts in terms of H_2/CO ratio, quantity and distribution of produced tars and elutriated fines.

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OP-V-21

ESTIMATION OF OPTIMAL REACTOR VOLUMES FOR BIOCATALYST PRODUCTION USING NLP FORMULATION

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Abstract

Many novel applications of kefir grains as biocatalyst or raw biomaterial in recent years (Plessas *et al.*, 2005; Rimada and Abraham, 2001; Athanasiadis *et al.*, 2001; Athanasiadis *et al.*, 2004) require incorporating of economically efficient reactor systems into kefir grains production processes. Traditionally, production operates in batch mode. However, there are several well-known advantages for using continuous operation instead of batch one (Williams, 2002). Despite the promising idea of incorporating the continuous mode operation in classic kefir grains production, no research papers concerning this kind of design have been published so far.

Therefore, the main goal of the present study was to design a continuous multi-stage reactor system for kefir grains production. In order to minimize total volume of CSTRs, V_T, in multi-stage reactor system, for desired kefir grains capacity, $q_{m,\mathrm{KG,pr}}$, and final conversion in Nth CSTR, $X_{\mathrm{o},N}$, with regard to decreasing of fermentation medium pH, a NLP optimization problem has been formulated:

$$\begin{aligned}
\min V_\mathrm{T} &= \sum_{j=1}^{N} V_j \\
V_1 &= f\left(X_{\mathrm{o},1}\right);\; X_{\mathrm{o},1} = \text{constant};\; N = 1 \\
V_1 &= f\left(X_{\mathrm{o},1}\right);\; N > 1 \\
V_j &= f\left(X_{\mathrm{o},j}, X_{\mathrm{o},(j-1)}\right);\; N > 2;\; 1 < j < N \\
V_N &= f\left(X_{\mathrm{o},(N-1)}\right);\; N \geq 2
\end{aligned} \tag{1}$$

where: V_1, V_j, V_N – volumes of first, jth and Nth CSTR in multi-stage reactor system, N – number of CSTRs in multi-stage reactor system, $X_{\mathrm{o},1}$, $X_{\mathrm{o},j}$, $X_{\mathrm{o},(j-1)}$, $X_{\mathrm{o},(N-1)}$ – conversions with regard to decreasing of fermentation medium pH value in outlet from the first, jth, (j–1)th and (N–1)th CSTR. The NLP problem was based on kefir grains mass balances in CSTRs and on experimentally evaluated predictive Gompertz growth and exponential pH models. For this purpose, in the first part of the research, some experiments with optimally activated inoculum were performed in the computer-controlled laboratory RC1 batch reactor.

All experiments were conducted at previously defined optimal process conditions (Goršek and Tramšek, 2007). On the basis of experimental data of time-depended kefir grain mass increase growth parameters in Gompertz predictive growth model were determined. Simultaneously, during individual experiments at different batch propagation times the pH values of fermentation medium were dynamically measured. Experimental dynamic pH profiles were mathematically analyzed and the values of shape parameters of the supposed exponential pH model were determined. In the second part of the study, we estimated the optimal volumes of a five in series connected CSTRs for desired capacity of kefir grains production, $q_{m,\mathrm{KG,pr}}$ = 3 kg/h and final conversion, $X_{\mathrm{o},N}$ = 0,98 by implementing NLP optimization problem using high-level modeling system GAMS (Rosenthal, 2006). At the same time the total reactor volume of five-stage system was compared with the potential reactor volume if only one CSTR is considered.

With our analysis it has been verified that multi-stage continuous reactor system compared to the one-stage one is technologically and economically much more reasonable, because its total volume is more than twelve times lower. We also proved the importance of proper multi-stage bioreactor system design using NLP methodology.

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POSTER PRESENTATIONS

Section 1. *Kinetics of catalytic reactions*

The Section is dedicated to the 100th anniversary of Professor M.I. Temkin, the outstanding specialist in the field of physical chemistry and chemical kinetics

Section 2. *Physico-chemical and mathematical fundamentals of the processes in chemical reactors*

Section 3. *Catalytic processes' development and reactors design: modeling, optimization, new catalyst application*

Section 4. *Catalytic technologies in fuel and energy production*

- ***production of hydrogen***
- ***production of environmental friendly fuels***
- ***environmentally friendly engineering***

Section 5. *Catalytic processing of renewable sources: fuel, energy, chemicals*

Section 1.

Kinetics of catalytic reactions

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of Professor M.I. Temkin, the outstanding specialist in the field
of physical chemistry and chemical kinetics

PP-I-1

CONVERSION OF ETHANOL OVER COPPER-BEARING CATALYSTS

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One of the most perspective directions of chemical industry development is application of bioethanol for manufacture of valuable chemical compounds. The biotechnology developing by fast rates already now enables to produce ethanol by non-polluting technologies of organic waste products and biomass conversion by enzymes. The vegetative biomass is a renewable source of organic raw material and due to a huge annual gain is capable to solve completely human needs for fuel and chemical products. Worldwide conducted researches witness substantial growth of competitiveness of manufacture on the basis of bioethanol. The last one due to tendencies of decreasing the dependence from raw oil can take a important place in industrial organic synthesis.

On the other part, last years in the world chemical industry the necessity of the decision of environmental problems is got a special urgency. These problems can be solved due to creation of the new, alternative manufactures described by a minimum quantity of harmful waste products and basing renewed sources of raw material.

Recent studies carried out in MITHT named by M.V. Lomonosov have shown a number of valuable products to be formed in ethanol conversion in presence of copper-bearing catalyst systems. The direction of ethanol transformation depends on both conditions for process operating and nature of the used carrier for the copper-bearing catalyst preparation.

One of the promising ways of bioethanol processing is catalytic dehydrogenation with formation of acetaldehyde the valuable intermediate product for organic synthesis. To increase effectiveness of ethanol dehydrogenation process with acetaldehyde formation and in connection with mention above adventures the development of new highly active, selective and stable catalyst systems is necessary.

In presence of catalyst based on carbon to carbon composite material sibunit, developed in Institute of catalysis named by G.K. Boreskov of the Siberian Department of the Russian Academy of Science, acetaldehyde, not reacted ethanol and hydrogen and water received together with acetaldehyde were observed. Diethyl ether was stated to be formed with low yield in the high temperature range. It is necessary to note, that in presence of carbon-based catalyst no ethyl acetate has been observed. The acetaldehyde yield reached under optimum conditions of process was high as 65%. This allowed considering such way of acetaldehyde production as competitive to commercial one.

The main industrial method of acetaldehyde production is ethylene oxidation in the presence of $PdCl_2$ and $CuCl_2$ water solutions. It has a number of drawbacks such as formation of great amounts of toxic chlororganic by-products and waste water. At the same time acetaldehyde production by ethanol dehydrogenation in the presence of heterogeneous catalysts has a number of advantages: absence of toxic wastes, soft conditions of the process and formation of hydrogen, which can be used in other processes. Ethyl alcohol the only raw material can be produced from biomass and allows not using petroleum.

When ethanol conversion was carried out in the presence of copper-bearing catalyst on the basis of Ciment Fondu – galumin, developed in Institute of organic chemistry named by N.D. Zelinsky of the Russian Academy of Science and Novomoskovsk institute of nitric industry, essential increase of ethanol conversion was observed. Therefore this catalytic systems were stated to reveal higher activity. In this case the basic component of liquid products is ethyl acetate formed by reaction of ethanol and acetaldehyde.

For ethanol conversion carried out in the presence of copper-bearing catalyst on the basis of silica gel, the main product of ethanol transformation was ethylene formed by ethanol dehydration due to acid properties of a carrier surface.

Thus, as a result of the carried out investigations effective copper-bearing catalysts on the basis of sibunit, galumin and silica gel for bioethanol dehydration process with acetaldehyde, ethyl acetate and ethylene production have been developed.

LATERAL INTERACTIONS, FINITE MOBILITY AND MULTIPLICITY OF STEADY STATES FOR LANGMUIR – HINSHELWOOD MECHANISM. MONTE CARLO AND TRANSFER-MATRIX TECHNIQUES

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The simplest model for CO oxidation on platinum surface is the well known three steps Langmuir-Hinshelwood mechanism

$$A_2 + 2Z \leftrightarrow 2AZ; \qquad B + Z \leftrightarrow BZ; \qquad AZ + BZ \rightarrow AB + 2Z, \tag{1}$$

where AZ and BZ are the adsorbed species on the catalyst Z, and A_2, B and AB the gas phase substances. The conventional mean-field (MF) kinetic equations can be written as [1]

$$\begin{cases} dx/dt = 2k_1 P_{A_2}(1-x-y)^2 - 2k_{-1}x^2 - k_3 xy \\ dy/dt = k_2 P_B (1-x-y) - k_{-2}y - k_3 xy \end{cases}, \tag{2}$$

where x and y are the adsorbate coverages, P_{A_2} and P_B the reactant pressures, and k_1, k_2, k_{-1}, k_{-2}, k_3 the rate constants for adsorption, desorption and reaction, respectively; t is time. For simplicity we are going to consider the case of irreversible adsorption ($k_{-1}, k_{-2} = 0$). For some parameter sets there exists the domain of the multiplicity of the steady states in the plane $(\lg P_{A_2}, \lg P_B)$. This domain contains only two internal steady states. The simplest MF equations (2) ignore the non-ideality of surface rate processes. We considered earlier the MF equations incorporating the adsorbate-adsorbate lateral interactions via the coverage dependence of the rate constants. It is known that in the frameworks of the lattice gas model and the transition state theory there are the exact expressions for the rate constants. We considered a lattice gas model as a model of adsorbed overlayer. Two kind of adsorbed species can occupy lattice sites of a square lattice. We take into account only nearest-neighbor lateral interactions. Within the framework of our model the exact analytical expressions of the right hand parts of equations (1) are absent and hence we should use an approximate technique. It is well known, that the one of the most effective approach is the transfer matrix method. Using the latter approach one can solve the problem of deriving expressions for the rate constants as functions of concentration. Experience shows that the transfer matrix technique yields very good results. It was shown that the number of the internal steady states can be equal to arbitrary integer number. We have studied numerically twenty seven models with lateral interaction energies ε_{AA}, ε_{AB}, ε_{BB} which possess the values 10; -10; 0 kJ/mol. All calculations were carried out at T = 500 K. For these interaction energies sets the total number of the steady states was found to be equal up to twelve [1]. All of the MF models possess the same limitation: the adsorbed particle mobility is assumed to be infinite.

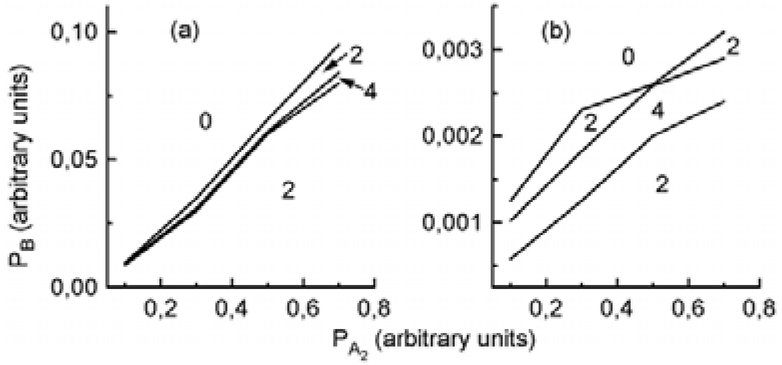

Fig.1.
Multiplicity diagrams for: (a) low mobility, (b) high mobility of adsorbed species.

The goal of the present work is the study of lateral interactions and finite mobility effect on the multiplicity of the steady states for Langmuir-Hinshelwood mechanism.

The finite mobility of adsorbed species means that we have to use the Monte Carlo method. We used a standard Metropolis algorithm. The diffusion describes in the same way as the other processes. The lateral interaction energies were chosen as 10, 0, 10 kJ/mol respectively. The multiplicity diagrams obtained with Monte Carlo method are shown in Fig. 1. The diagram (b) obtained for model with high mobility is in quality agreement with that obtained with transfer matrix method. It is easily seen that mobility of the adsorbed particles is an essential model parameter.

In the framework of the microscopic model of non-ideal adsorbed overlayer the kinetical behavior of the Langmuir-Hinshelwood mechanism was shown to become essentially more complex than for ideal overlayer [i]. The results obtained with Monte Carlo method is in agreement with the results obtained in the framework of MF model.

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UTILIZATION OF TAFT EQUATION: KINETIC MODELLING OF CARBOXYLIC ACIDS PERHYDROLYSIS OVER HETEROGENEOUS AND HOMOGENEOUS CATALYSTS

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Linear free energy relationships (LFER) assume the existence of a correlation between kinetics and thermodynamics. These relations are strong tools to understand the mechanism and to predict the rate and equilibrium constants of a chemical reaction. On this assumption, two families of equation were developed: Hammett equation which describes the behaviour of meta- and para-substituted aromatic compounds; and Taft equation, which addresses the reactivity of aliphatic derivatives. Although the application of these equations for homogeneously catalyzed reactions is widespread in the literature, few examples are found [1-2] for heterogeneous catalysis reactions, mainly due to the difficulty of utilizing the intrinsic rate constant. The Taft equation is given by:

$$\log\left(\frac{k}{k_O}\right) = \delta E_S + \rho^* \sigma^*$$

where

- k: rate constant of a particular perhydrolysis reaction
- k_o : rate constant of acetic acid perhydrolysis
- δ : constant giving the susceptibility of a given reaction series to steric effect
- E_S : steric substituent constant
- ρ^* : constant giving the susceptibility of a given reaction series to polar substituents
- σ^* : polar substituent constant for the group R relative to the standard CH_3 group

The synthesis of peroxycarboxylic acids from carboxylic acid and hydrogen peroxide ($RCOOH + H_2O_2 = RCOOOH + H_2O$) was selected to illustrate the use of Taft equation. This reaction is still industrially catalyzed by sulphuric acid [3], leading to several drawbacks (corrosion, catalyst separation and threat to environment). One way to avoid these problems is to implement heterogeneous catalysts.

We have demonstrated that the use of cation exchange resins such as Amberlite® is beneficial because it is resistant toward deactivation, the mass transfer resistance can be suppressed and the activity is similar to sulphuric acid.

Based on our experimental data (Figure 1) and information from literature, the polar part $\rho^*\sigma^*$ of the Taft equation is negligible for the acid-catalyzed systems. The rate constants used to plot the Figure 1 are the apparent ones. From this Figure, one can see that the steric effects govern the perhydrolysis and not the polar effect. However, the values of δ are different for both series of experiments carried out in similar conditions. In order to explain this observation and to have a better comparison between a homogeneous and a heterogeneous catalyst, kinetic modelling of perhydrolysis over heterogeneous catalysts will be described in the final presentation.

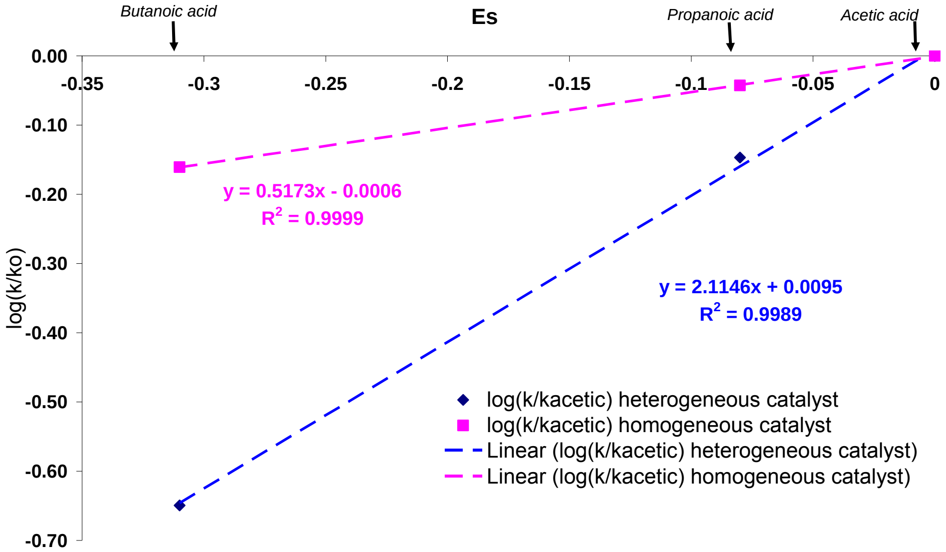

Figure 1. Taft equation for perhydrolysis of different carboxylic acids with H_2SO_4 and Amberlite IR-120 at 45 °C

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SELECTIVE HYDROGENATION OF CINNAMALDEHYDE OVER SUPPORTED IONIC LIQUID CATALYSTS (SILCA)

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Ionic liquids, or room temperature salt melts, have been a hot topic in many research areas in recent times. The significance of ionic liquids comes from the fact that they are completely ionic compounds and are liquid at ambient conditions. Ionic liquids are a highly solvating, non-coordinating medium in which many organic and inorganic compounds dissolve. Many of them have common characteristic features like the often negligible vapor pressure ($\sim10^{-8}$ bar), wide liquidus range, high thermal stability, wide electrochemical window as well as good ion conductivity[1,2]. Ionic liquids have shown a good performance in various kinds of catalytic reactions as well as in the preparation of nanostructured materials and nanoparticles suitable for catalysis[3,4]. Indeed, catalysis is one of the areas, where ionic liquids represent a considerable potential, also considering the fact that the immobilized ionic liquid catalysts result in a very efficient use of the ionic liquid and relatively short diffusion distances compared to conventional two-phase systems.

Catalysts were prepared according to the method described previously[5]. Palladium acetyl acetonate, and ionic liquid were dissolved in acetone. Solution was poured over an active carbon cloth (ACC), Kynol®. Acetone was evaporated in a rotary evaporator leaving $Pd(acac)_2$ dissolved in ionic liquid supported on ACC. The catalysts were pre-treated in a batch reactor at 120 °C under 10 bar hydrogen flow. This procedure resulted into formation of Pd nano-particles in ionic liquid immobilized on ACC (Fig. 1). The catalysts were applied in the hydrogenation of cinnamaldehyde. Cinnamaldehyde, a multi saturated aldehyde, is an industrially important precursor for many fine chemical products, flavoring agents, perfumes, fungicides and steel corrosion inhibitors. Experiments were conducted in the batch reactor, at constant temperature (from 60 to 150 °C) and constant hydrogen pressure (from 5 to 30 bar). The progress of the reaction was monitored by withdrawing small samples from reactor and analyzing them by gas chromatography.

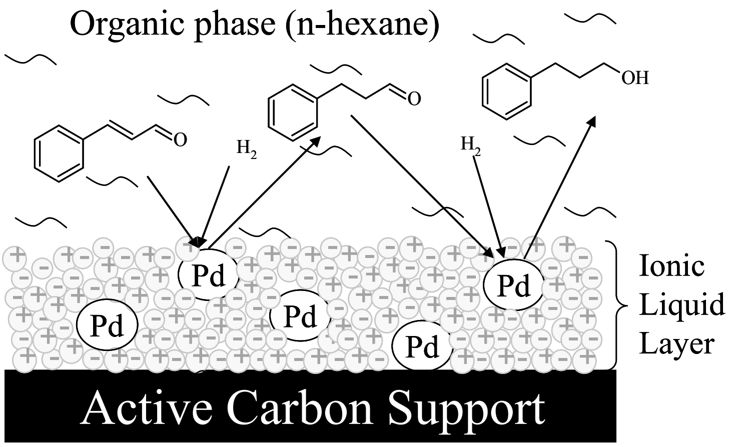

Figure 1. Picture of SILCA used in hydrogenation of cinnamaldehyde.

Kinetic evaluation of catalysts with two different ionic liquids was performed with the results obtained from the hydrogenation experiments. Experiments showed that ionic liquid layer on ACC can improve the hydrogenation reaction rate and tune the selectivity for various products, depending on the ionic liquid applied. Kinetic modeling was based on the reaction scheme in Fig. 2. A classical Langmuir-Hinshelwood-Hougen-Watson type of kinetic model was applied in the estimation of rate and adsorption parameters.

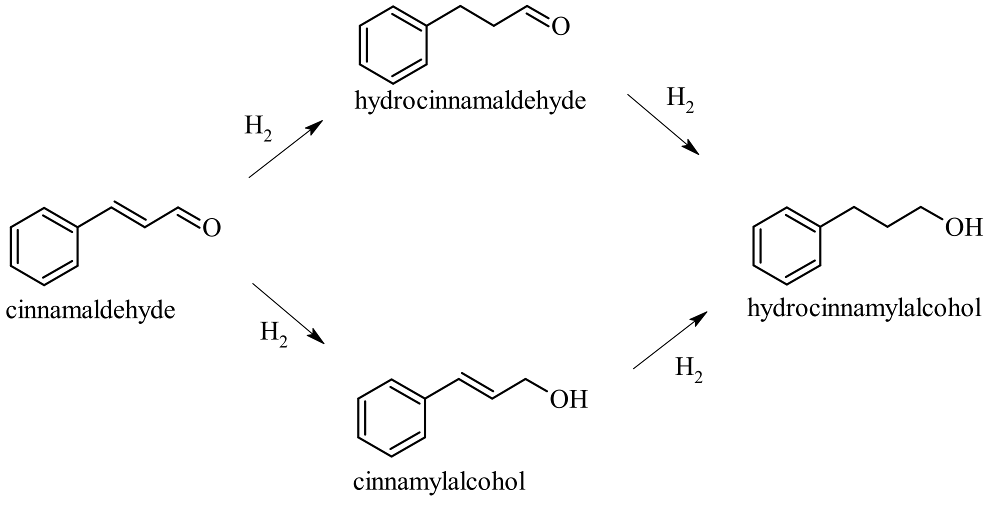

Figure 2. A reaction scheme for cinnamaldehyde hydrogenation over SILCA

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PP-I-5

NON OXIDATIVE REGENERATION METHODS OF DEACTIVATED FCC CATALYST IN FLUIDIZED BED REACTOR

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Deposition of coke on FCC catalyst has received considerable attention in catalysis field; little work has been reported on non-oxidative regeneration especially hydrogen at elevated temperature and high pressure over coked catalysts followed by extraction method. The deficient hydrogen type cracked catalyst was treated for 8 hrs at different temperatures. The sample was left under hydrogen pressure overnight to increase the adsorption time of hydrogen on zeolite surface and pores. Cycles of regenerations were applied to enhance the volatility of coke precursors at longer time. Deconvoluted peaks of TG-DTG were showing several volatile materials at certain combustion temperatures indicating the type of coke molecules. There was correlation between peaks of adsorbed materials of coke precursors in TGA and TPD. Hydrogen adsorbed at higher temperature over 400°C in TPD curve implies that high temperature hydrogen diffuses through catalyst matrix causes significant reduction and morphological changes of coke species. FTIR peaks shows the intensity of the coke profiles appeared in coked and diminished in regenerated ones. Continuous regeneration of coked samples was showing gradual loss of coke percentage weight. Toluene and more polar solvent like pyridine leached the hydrocarbon compounds adsorbed on the surface of the zeolite. The resulted extract was sent for GC-Ms to identify the kind of hydrocarbons products restored, while coked catalyst was examined for coke yield and surface area using thermal analysis and BET. The activity of FCC catalyst was restored by more than 50% due to formation of polycyclic type of coke depending on the feed type.

KINETICS OF ESTERIFICATION OF LACTIC ACID BY PRIMARY ALCOHOLS

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Introduction

The alkyl esters of lactic acid become more and more attractive as solvents for various technical purposes. Such situation derives from the following trends in the world market of chemical products: (1) permanent growth of crude oil price; (2) more and more strict demands for environmental protection which results in searching for sustainable source of manufacture of chemical products which undergo biodegradation easily after their use; (3) latest achievements in the technology of fermentative production of L-lactic acid (LA) that make it competitive in price as a feedstock for industrial organic chemistry.

The aim of the present work is investigation of kinetics of esterification of lactic acid by primary alcohols in concentrated solutions in the presence of cation-exchange resin as a catalyst.

Experimental section

The kinetics of esterification was investigated in a batch stirred reactor and in a tubular flow reactor with fixed catalyst bed. As a second reagent methanol, ethanol and 1-butanol were used. Lewatit-S in H^+-form was used as a catalyst.

Results

The experiments in the batch reactor showed that in the kinetic regime reaction rate obeys the equation of quasi-homogeneous model:

$$r = k_1^0 \exp\left(-\frac{E_1}{RT}\right)\left(C_{LA}C_{Alc} - \frac{C_E C_W}{K}\right) + k_2^0 \exp\left(-\frac{E_2}{RT}\right) Cct \left(C_{LA}C_{Alc} - \frac{C_E C_W}{K}\right) \quad (1)$$

Where: k_1^0, k_2^0 – preexponential factor of rate constant of noncatalitic and catalytic reaction correspondingly; E_1, E_2 – activation energy of noncatalitic and catalytic reaction correspondingly; K – equilibrium constant; C_{Ct}, C_{LA}, C_{Alc}, C_E, C_W – concentration of catalyst, lactic acid, alcohol, ester and water correspondingly.

Calculated parameters in equation (1) for methanol and ethanol are listed in the Table 1.

Table 1. Parameters in kinetic equation (1) for methanol and ethanol.

Alcohol	k_1, $l^2mol^{-2}min^{-1}$	k_2, $l^2g_{ct}^{-1}mol^{-1}min^{-1}$	K
Methanol	$2.82\times10^5\exp^{-60630/RT}$	$4.84\times10^5\exp^{-50180/RT}$	2,5
Ethanol	–	$3.623\times10^5\exp^{-64956/RT}$	3,5

It was found that the rate of esterification of LA by butanol in the kinetic regime in the batch reactor and tubular flow reactor obeys the equation of Langmuir-Hinshelwood model:

$$r = \beta C_{Ct}\frac{k_2 C_{LA} C_{Alc} - k_{-2} C_E C_W}{1 + b_W C_W} \qquad (2)$$

Where: k_2, k_{-2} – rate constant of esterification and hydrolysis of ester correspondingly; b_W – adsorption constant of water; β – diffusion factor.

Calculated parameters of equation (2) are listed below:

$k_2 = (1.45\pm0.035)\times10^3\cdot\exp^{-(45880\pm510)/RT}$, $l^2g_{ct}^{-1}mol^{-1}s^{-1}$;

$k_{-2} = (4.60\pm0.22)\times10^2\cdot\exp^{-(46090\pm480)/RT}$, $l^2g_{ct}^{-1}mol^{-1}s^{-1}$;

$b_w = (0.93\pm0.019)\times\exp^{-(11500\pm230)/RT}$, l/mol;

β is equal to 1 in case of batch reactor (kinetic regime) and 0.22 in case of tubular flow reactor (diffusion regime).

Conclusions

The kinetics of esterification of lactic acid by methanol, ethanol and 1-butanol was investigated in the batch and tubular flow reactors. The kinetic equations which allow to describe processes adequately were obtained.

THE NEW METHOD FOR KINETIC SCREENING OF CATALYSTS FOR SELECTIVE HYDRATION OF ETHYLENE OXIDE

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Introduction

Ethylene glycol (EG) is one of the major large-scale products of industrial organic synthesis, with the world annual production of about 14 million t/y. EG is currently produced by noncatalytic (thermal) hydration of ethylene oxide (EO) which proceeds on a serial-to-parallel route with the formation of homologues of glycol:

$$H_2O \xrightarrow[k_0]{C_2H_4O} HOCH_2CH_2OH \xrightarrow[k_1]{C_2H_4O} HO(CH_2CH_2O)_2H \xrightarrow[k_2]{C_2H_4O} \text{etc.} \qquad (I)$$

where k_0, k_1, k_2 - rate constants.

All of the largest ethylene glycol producers, such as Shell, Dow, BASF and Mitsubishi, conduct their studies on elaboration of high selective catalysts of ethylene oxide hydration[1]. It is known that typical examples of such catalysts are some anions of salts of weak acids and metallate-anions[1]. Unfortunately till now there is no formulated criteria for choice of such catalysts.

In present report we propose the new method for kinetic screening of catalysts for selective hydration of ethylene oxide.

Theoretical background

Generally hydration of EO (I) proceeds by four routs: noncatalytic, base-catalytic (by OH^-), acid-catalytic (by H^+) and nucleophyl-catalytic (by anions A^-). The selectivity of each rout is characterized by distribution factor b_i which is equal to ratio of k_1/k_0 (reaction I). Evidently the lower b_i is,the higher selectivity of EG formation is. The distribution factors of noncatalytic, base-catalytic and acid-catalytic reactions are known to be equal to 2.6, 14.8 and 1.6 correspondingly[2]. Hence the overall selectivity is determined by the value of distribution factor of nucleophyl-catalyzed reaction and ratio of reaction rate of that route to the rates of all others. Effective rate constant of reaction (I) concerning EO consumption is described by following equation:

$$k_{eff} = k_{nc} + k_1 C_A + k_a [H_3O^+] + k_b [HO^-] \text{ , } s^{-1} \qquad (1)$$

where: k_{nc} , k_l , k_a , k_b – rate constant of noncatalyzed, nucleophyl-catalyzed, acid-catalyzed and base-catalyzed reaction correspondingly.

The value of k_{nc} , k_a , k_b are known, the concentration of H_3O^+ and HO^- can be calculated by pH value so the value of k_l can be calculated by measuring k_{eff} in kinetic experiment.

Results and discussion

We've shown that the value of ratio k_l/k_{nc} calculated from kinetic experiment by equation (1) is quite close to that obtained by treating the data of composition of products of hydration of EO (table 1).

Table 1.

Catalytic system	T, °C	pH	Balance experiment		Kinetic experiment
			b	k_l/k_{nc}, l/mol	k_l/k_{nc}, l/mol
$HOCH_2COONa$	85	4.4	0.45	9.6	11.1
Sodium hydrocitrate	85	5.7	0.75	8.1	7.3
EDTA/$Cr(OAc)_3$	85	4.6	1.2	16.7	21.2
EDTA/$Cr(OAc)_3$/NaOH	85	4.6	1.0	14.8	16.9
EDTA	85	4.6	0.85	10.4	10.6
$NaHCO_3$	85	8.2	1.2	4.7	4.7

We determined the range of conditions which provide the correct application of this method and tested the number of catalytic systems that allowed to choose the most promising ones.

Conclusions

The elaborated kinetic method of catalyst screening is much easier in use and shorter in time then procedure based on balance experiments followed by GC analysis of products' composition.

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STOCHASTIC SIMULATION OF ADSORPTION PROCESSES PERFORMANCE OVER SUPPORTED METAL NANOPARTICLES

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In heterogeneous catalysis, adsorption processes usually occur on supported metal nanoparticles. To study such processes experimentally, a vast variety of surface science techniques came into the use in the last decades of the 20th century. Besides, considerable progress in manufacturing of model catalysts with well-defined properties has been achieved. Despite this progress, the cognitive potential of the experimental studies in this field is still limited because the measurements are usually indirect and the information derived demands quantitative processing and interpretation. This can be done only with the use of mathematical models. The use of stochastic simulations based, e.g., on the Monte-Carlo technique, is almost inevitable [1, 2].

Model

As a model of the catalytic metal particle we shall consider the Kossel crystal or, more exactly, the SOS (solid-on-solid) model [3, 4] located on a neutral support. The surface morphology of the particle is defined by distribution of heights of the metal atom columns. The metal atoms attract the nearest neighbour ones and the atoms of the support. The attraction is characterised by energies: J_{mm} - the interaction energy between the nearest neighbour atoms situated at the same level and one on the lower, J_{ms} - the interaction energy between the metal atom and the rigid support underneath. The particle surface morphology is changed due to the thermal diffusion of the surface atoms. To model the diffusion of the metal atoms over the metal and support surfaces the Metropolis algorithm [5] has been used.

Results and discussion

To study the influence of adsorption on the «equilibrium» shape and surface morphology of the catalytically active particle we assume that the adsorption and/or desorption of the diatomic molecule $\boldsymbol{B_2}$ can occur only on the two neighbouring metal atoms situated at the same level, adsorption and/or desorption of the monoatomic molecule $\boldsymbol{A}$ can occur on any metal atoms. Adsorption on the support surface is prohibited. The molecules $\boldsymbol{B_2}$ dissociate immediately after adsorption on atoms $\boldsymbol{B_{ads}}$ which are able to diffuse over the particle's surface.

After each adsorption or desorption attempt several trials of metal and/or adsorbate atom diffusion has been executed. By simulation of the adsorption isotherms the supported particle was preliminary established in equilibrium at given temperature. Then, step by step rising the pressure of adsorbate, we perform the simulations at each pressure value trying to achieve the equilibrium state both for the adsorbed layer and for the particle surface morphology itself.

The adsorption isotherms has been simulated at different ratios of interaction (attraction) between adsorbed species and metal atoms at T = 500 K ($J_{ma} = 0.5 \times J_{mm}$, J_{mm} and $2 \times J_{mm}$, where J_{mm} - the interaction energy between metal atoms, J_{ma} – the interaction between adsorbed species and metal atoms).

The increasing of J_{ma} value leads to the transformation of the particle to the pyramidal shape, at that with increasing of the «metal-adsorbate» bond strength the height of the pyramid rises. But at strong interaction «metal-adsorbate» ($J_{ma} = 2J_{mm}$) for bimolecular dissociative adsorption we have instead of the pyramidal shape of the particle the hemispherical one with very ulcerated surface in comparison with initial equilibrium particle and in the high-pressure interval the simulated coverages are lower in comparison with equilibrium values. In our opinion, it is due to the fact that the adsorbed on the surface $\boldsymbol{B_2}$-molecules attract immediately the neighboring metal atoms at that decreasing the probabilities of their own desorption and diffusion. As a consequence, at each next increasing of the pressure the coverage of the surface by $\boldsymbol{B_{ads}}$ increased only slightly: the particle surface morphology is positioned on a metastable long-lived state (for more details see [6]).

After the removing of the adsorbed layer the shape and the surface morphology of the particle returned to the equilibrium characteristics peculiar to the given temperature. The simulations show that if the «adsorbate-metal» interaction energies become comparable with the metal-metal ones the nanoparticle undergoes reversible adsorbate-induced reshaping and that the particles size determines the degree of reshaping as in experiments [7].

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STUDY ON CATALYTIC ESTERIFICATION OF METHANE IN OLEUM CATALYZED BY IODINE

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Conventional conversions of methane into other useful chemical, such as methanol and higher hydrocarbons, require the energy-intensive step of synthesis gas formation. Recently, substantial research activity has been conducted in the area of methane conversion without the use of synthesis gases. One of the most promising processes in this field is the oxidation of methane to methanol via methyl bisulfate using either sulfuric acid or oleum. The reaction is catalyzed by mercury [1, 2], platinum [3], palladium [4], iodine [5, 6] ions. This process has some obvious advantages: (i) bypassing synthesis gas formation; (ii) low reaction temperature; (iii) high methane conversion.

In present paper, we focus on the study of the methane esterification rate under different experimental conditions for iodine catalysts. Systematic experiments were applied to define the equation describing the reaction rate. The reaction rate depends on the concentration of the catalyst, temperature, the sulfur trioxide concentration, and the methane pressure. The process was run in an autoclave under 2 – 7 MPa pressure, at 90 – 180 °C. We examine oleum concentrations 0 – 25 wt% SO_3. Bjerrum at al. [5] investigated iodine as catalysts for conversion of methane to methyl bisufate in 65 wt% oleum to optimize the reaction. It is very useful to use weaker oleum than Bjerrum. The focus of the publication by Periana et al. with iodine as catalyst [6] in weak oleum (2 – 3 wt% SO_3) was the reaction mechanism and not reaction rate.

We have found that the following reactions took place:

$$CH_4 + SO_3 + H_2SO_4 \rightarrow CH_3OSO_3H + SO_2 + H_2O \qquad [1]$$

$$CH_4 + 4SO_3 \rightarrow CO_2 + 4SO_2 + 2H_2O \qquad [2]$$

$$H_2O + SO_3 \rightarrow H_2SO_4 \qquad [3]$$

The selectivity of methane oxidation to methyl bisulphate was close to 100%. The carbon dioxide yield was below 1%. Practically, the only product of methane oxidation is CH_3OSO_3H.

In the reactor a phenomenon of mass transfer with chemical reaction takes place. The system of differential equations which represents the process can not be solved analytically so we decided to find empirical equation of the ester formation.

The increase in pressure, in the concentration of sulphur trioxide in oleum and in the temperature cause a raise of the methane esterification rate. Therefore the reaction rate (r) consists of the function of the sulfur trioxide concentration, function of the methane partial pressure, function of the temperature (equation [a]).

$$\frac{dC_E}{dt} = r = f_0(T) \cdot f_1(C_{SO_3}) \cdot f_2(p_{CH_4}) \qquad [a]$$

C_E, C_{SO_3} – methyl bisulfate, sulfur trioxide concentration [mol·dm^{-3}]
p_{CH_4} – methane partial pressure [MPa]
$f_0(T)$ – function of the temperature
$f_1(C_{SO_3})$ – function of the sulfur trioxide concentration
$f_2(p_{CH_4})$ – function of the methane partial pressure

We have found that the theoretical equation of the reaction rate for methane to ester conversion can be defined by equation [b]:

$$r = k_T\left(C_{0SO_3} - 2C_E + a\right)^{n_1}\left[\left(p_{0CH_4} - \frac{0.00082\,T \cdot C_E}{0.15 - 0.0043\,C_E} + 0.10\,C_E\right)^{n_2} + b\right] \qquad [b]$$

T – the temperature of the process [K]
k_T – the reaction rate constant at the temperature T
p_{0CH_4} – initial methane partial pressure [MPa]
C_{0SO_3} – initial sulfur trioxide concentration [mol·dm^{-3}]
a, b, n_1, n_2 – empirical factors

On the base of the experimental work the empirical factors and reaction rate constant at different temperatures were determined. The relationship of the logarithm of the reaction rate and the inverse temperature was the straight line. The activation energy was calculated.

Acknowledgment

A financial support from the Polish Scientific Research Committee (Research Project 205 3705 33) is gratefully acknowledged.

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KINETICS OF METHANE OXIDATION OVER NIOBIUM(V) OXIDE CATALYSTS

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The selective methane oxidation to oxygenates is very attractive as it would eliminate an energy-consuming process of methane to synthesis gas steam reforming, the former of which is nowadays the basic raw material used to produce methanol and later formaldehyde. This would lead to a considerable reduction of cost production of both these compounds and other ones, which are produced from them. This is one of the most fundamental problems of contemporary technology, which until now has not yet been solved. Despite the fact that methane to formaldehyde and methanol oxidation using both O_2 and N_2O is thermodynamically possible, carbon oxides are much more privileged products. The activation of only one of the four equivalent C-H bonds is interesting also from the scientific point of view. The process of direct methane to formaldehyde synthesis should be carried out in conditions which exclude deep methane oxidation and which prevent secondary oxidation reactions of the desirable product. This is possible by means of heterogeneous catalysts.

The selective methane to formaldehyde oxidation was examined over various catalysts, which mainly contained oxides of transition elements, such as molybdenum [1], iron [2] and vanadium [3] antimony [4], as well as ZSM-5 [5] and MCM-41 [6].

The work is continuation of former investigations [7] of methane one-step oxidation to formaldehyde and/or methanol using as catalysts various compounds. As catalyst niobium(V) oxide and Nb_2O_5 on silica support. were used.

The experiments were carried out at the range of temperatures between 420 and 750°C. The contact time differed from 0.7 to 1.8 s (5150-2000h^{-1} space velocity at NTP) while keeping a constant ratio of methane to oxygen. The substrates and products were analyzed by means of the chromatograph SRI 8610C equipped with a TCD.

The kinetic studies were run in the differential reactor. Two series of measurements were conducted. In the first one the temperature was kept constant while the contact time was changed. In the other one, the process was carried out at different temperatures, with the same contact time.

PP-I-10

The analysis of the composition of the outlet gases at various temperatures and at different contact times, has led to the assumption that the following reactions take place in the reactor:

$$CH_4 + O_2 \xrightarrow{k_1} HCHO + H_2O \quad (1)$$

$$HCHO + O_2 \xrightarrow{k_2} CO_2 + H_2O \quad (2)$$

$$CH_4 + 2\,O_2 \xrightarrow{k_3} CO_2 + 2\,H_2O \quad (3)$$

The following reaction rate expressions have been suggested:

$$r_{HCHO} = k_1\left(p_{CH_4}\right)^{N1_{CH4}}\left(p_{O_2}\right)^{N1_{O_2}} - k_2\left(p_{HCHO}\right)^{N2_{HCHO}}\left(p_{O_2}\right)^{N2_{O_2}} \quad (4)$$

$$r_{CO_2} = k_2\left(p_{HCHO}\right)^{N2_{HCHO}}\left(p_{O_2}\right)^{N2_{O_2}} + k_3\left(p_{CH_3OH}\right)^{N_{CH3OH}}\left(p_{O_2}\right)^{N3_{O_2}} \quad (5)$$

$$r_{O_2} = -k_3\left(p_{CH_4}\right)^{N3_{CH4}}\left(p_{O_2}\right)^{N3_{O_2}} - k_1\left(p_{CH_4}\right)^{N1_{CH4}}\left(p_{O_2}\right)^{N1_{O_2}} \quad (6)$$

r_x – the rate of generating the product x

k_i – the rate constant for the reaction i (k_p – the pressure constant)

p_x – the partial pressure of the compound x at the reactor outlet

Ni_x – the order of reaction i with respect to reactant x.

The reaction rate constants (k_i) and the order of the reaction (Ni_x) were determined by the Hooke-Jeeves method.

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KINETICS STUDIES AND MECHANISM OF β-PICOLINE OXIDATION TO NICOTINIC ACID OVER V_2O_5–TiO_2 CATALYST

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Introduction

The gas-phase catalytic oxidation of β-picoline over oxide vanadia-titania catalysts allows the nicotinic acid (NA) production with the yield above 80% [1-3]. A previous study of this reaction with β-picoline conversion 20-85% revealed a parallel-consecutive scheme of NA formation, via the intermediate pyridine-3-carbaldehyde (PA) and directly from β-picoline (βP) [4]. The prospect of industrial implementation of this method makes it necessary to study kinetics and to develop a kinetic model applicable to real-shaped pellets of the catalyst.

Experimental procedure

The catalyst 20%V_2O_5–80%TiO_2 (wt.%) was prepared by spray drying of an aqueous suspension of vanadyl oxalate and TiO_2 (anatase) followed by its shaping into rings 2 mm ID, 4 mm OD and 5 mm length and calcining in air at 450 °C [1]. The BET specific area of the catalyst was 25 m^2/g.

The kinetic studies were performed in a differential reactor in a flow-circulating setup with chromatographic analysis of the reaction mixture components.

Kinetic experiments were performed at ambient pressure and range temperature 250-300 °C over a wide range of reagent initial concentrations, %vol.: 0.5-2.5% of βP, 10-22% of O_2, 5-40% steam, and nitrogen – balance.

In situ FTIR spectroscopy was used to study the mechanism of oxidation of βP and PA into NA on a V_2O_5–TiO_2 catalyst.

Results and discussion

In fig., the rate of βP consumption and the rates of product accumulation (a) and selectivities (b) are shown as a function of βP conversion in the temperature range 270-300 °C. The main product of the reaction in the whole investigated range of conversion is NA. Selectivity to it is 85-90 %, other products is 3-pyridine nitrile (PN) and carbon oxides (COx).

The complementary support of a parallel-consecutive network for the NA formation is a FTIR in situ study of βP and PA oxidation. NA is formed through the same surface species from βP as well as from PA [5, 6].

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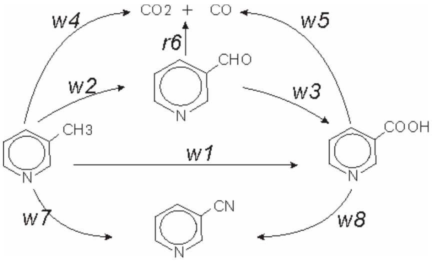
The network of βP oxidation can be described as follow:



where r_j – the product formation rates($j=1\div8$): 1 and 3 – NA from βP and PA, according; 2 – PA from βP; 4, 5, 6 – CO_X from βP, NA and PA, according; 7, 8 – PN from βP and NA, according.

Water was found to accelerate the formation of PA and NA, but do not affect their further oxidation and deep oxidation of βP [4].

The concentration of βP and O_2 has different effects on the rates of partial reactions and selectivities to products. The activity and selectivity of the V_2O_5–TiO_2 catalyst in the oxidation of βP to NA strongly depend on the ratio of oxygen and βP concentrations, and the high oxygen content in the reaction mixture is necessary for the optimal catalyst performance.

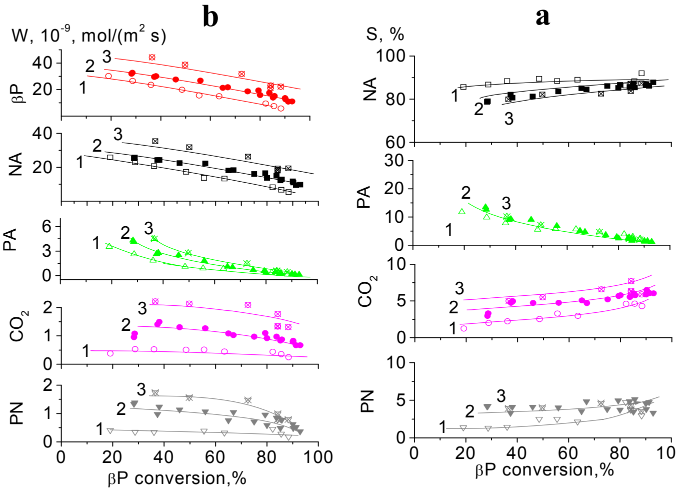


Fig. Dependencies on conversion βP at 270 C (1), 285 C (2), 300 C (3) of: a-selectivity, b-reaction rates.

Reaction mechanism determined by IR spectroscopy and experimental kinetics data were resulted in the kinetics equations for the reaction rates according to reaction network scheme. Equations were derivated applying the graph theory [7]. The kinetic parameters were evaluated by minimizing the function which represents the difference between the experimental and the calculated concentration.

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MECHANISTIC ASPECTS OF STEAM REFORMING OF METHANOL OVER COPPER-BASED CATALYSTS

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1. Introduction

Steam reforming of methanol (SRM) is a simple and efficient way of producing H_2. When one designs methanol reformers, the kinetics and mechanism of the reforming reaction is important in sizing the reactor. A number of different mechanisms for the SRM over Cu-based catalysts have been proposed in the literature and disagreements exist about the mechanism of CO by-product formation and the methyl formate reaction route [1]. Steady-state isotopic transient kinetic analysis (SSITKA) has long been documented and widely accepted as one of the most powerful techniques to elucidate in a precise way mechanisms of heterogeneous reactions [2]. Many studies have been reported on application of SSITKA techniques over a wide range of surface-catalyzed reactions including ammonia and methanol synthesis, ammonia oxidation, CO oxidation, NO-CO reduction, methane activation e.t.c.

In the present study, SSITKA-Mass Spectrometry experiments were performed in order to study mechanistic aspects of the steam reforming of methanol over three Cu-based catalysts, namely: CuMnO and CuCeO catalysts and a commercial $CuZnAl_2O_3$ catalyst.

2. Experimental

The isotopes used in the experiments were $^{13}CH_3OH$ (99atom% ^{13}C, Isotec) and $H_2{}^{18}O$ (97atom% ^{18}O, Isotec). SSITKA experiments performed in order to follow the «C-path» of reaction, involved the switch: $^{12}CH_3OH/H_2O/He/Ar \rightarrow {}^{13}CH_3OH/H_2O/He$, while those to follow the «O-path» of the reaction, involved the switch: $CH_3{}^{16}OH/H_2{}^{16}O/He/Ar \rightarrow CH_3{}^{16}OH/H_2{}^{16}O/\ H_2{}^{18}O/He$. All experiments were performed at 190°C, ensuring methanol conversions below 20%. $Cu_{0.30}Mn_{0.70}$ and $Cu_{0.15}Ce_{0.85}$ samples were prepared with the combustion method, as reported elsewhere [3].

3. Results and discussion

The quantitative results obtained from the SSITKA experiments are summarized in Table 1. It is observed, that in the case of CuCeO catalyst, the total steady-state amount of intermediate species present on the catalyst surface that leads to CO_2, is more than three times lower than that of CuMnO or $CuZnAl_2O_3$ catalysts, while the rate of CO_2 formation is one order of magnitude lower. This is in accordance with the lower catalytic activity of the CuCeO catalyst for the SRM [4]. Moreover, the shape of the transient response of the C-labeled CO_2 in the case of CuCeO catalyst is much different than those of the other two samples, indicating a different mechanism.

Table 1. *Overall mean surface time (τ) and total amount (N) of all adsorbed intermediate species which lead to* CO_2*, overall reaction rate (r) at steady-state and pseudo-first-order rate constant (k) accumulated under steady-state SRM reaction conditions at 190 °C over Cu-Mn-O, Cu-Ce-O and* $Cu\text{-}Zn\text{-}Al_2O_3$ *commercial catalysts measured by SSITKA-mass spectrometry.*

catalyst	$\overline{\tau}^{CO_2}$ (sec)	$\overline{N}^{CO_2}$ (μmol g_{cat}^{-1})	$\overline{r}^{CO_2}$ (μmol g_{cat}^{-1} s^{-1})	k (sec^{-1})
$Cu_{0.30}Mn_{0.70}$[a]	198.76	632.61	3.18	0.0050
$Cu_{0.15}Ce_{0.85}$[b]	841.62	273.32	0.33	0.0012
$Cu/Zn/Al_2O_3$[c]	256.74	734.90	2.86	0.0039

[a] W_{cat} = 9mg, S_{BET} = 7 m^2 g_{cat}^{-1}, MeOH conversion = 20%
[b] W_{cat} = 60mg, S_{BET} = 43 m^2 g_{cat}^{-1}, MeOH conversion = 11.2%
[c] W_{cat} = 10mg, S_{BET} = 63 m^2 g_{cat}^{-1}, MeOH conversion = 20%

Additionally, O-labeling experiments were conducted in order to find indications about the reaction pathway of the SRM reaction. The most interesting finding in these experiments was the observation of $CH_3{}^{18}OH$, suggesting that SRM proceeds through the methyl formate reaction route, in which methanol dehydrogenates to methyl formate, which subsequently react with water (labelled) for the production of methanol (labelled) and formic acid [5].

4. Conclusions

The application of the SSITKA technique revealed that the total steady-state amount of intermediate species that leads to CO_2, of the three catalysts studied follows the order $CuZnAl_2O_3$>CuMnO>CuCeO, with the CuCeO catalyst being the less active of all. Furthermore, there were found indications about the mechanism of the SRM, which follows the methyl formate path.

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SSITKA IN CONTINUOUS-STIRRED TANK AND PLUG-FLOW REACTORS: EFFECT OF REACTOR SYSTEM ON ISOTOPIC RESPONSES

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Steady-state isotopic transient kinetic analysis (SSITKA) is a very powerful technique to obtain *in situ* kinetic information about the reaction mechanism and the catalyst-surface reaction intermediates [1]. It involves monitoring the time-resolved appearance of isotopically labeled atoms from reactants as they become incorporated into reaction products. However, the effect of reactor system on the isotopic transient responses should be taken into account.

Both continuous-stirred tank reactors (CSTR) and plug-flow reactors (PFR) have been used in SSITKA. It is shown that gas-phase mixing levels the peculiarities of isotopic responses that are intrinsical of different reaction mechanisms [2], so that at large gas-phase residence time they completely disappear. Although SSITKA in PFR is more informative, data interpretation can be substantially complicated due to gradient of isotope concentration along the catalyst bed. On the Fig.1a the calculated profiles of label concentration for simplest reaction scheme with reversible adsorption (A↔[zA]→B, [zA] – adspecies) have been presented. The fraction of labeled atoms in reagent A decreases with reactor length because of isotope exchange with the intermediate [zA]. Therefore, the labeled molecules of the product B will appear as soon as the isotopic label of the reactant penetrates the reversible pool of adsorbed reactant in the inlet part of the catalytic bed. As the result, the labeled product B can appear at the reactor outlet earlier than the labeled reagent A (Fig.1b). The most interesting effect of the reactors system can be in the case when several (>2) isotopomers of reaction products have been formed due to isotope transfer. So, in the reaction $A_2 \leftrightarrow 2[zA]$ (or $[zA_2]$) $\rightarrow B_2$ the ratio between fractions of isotopomers, i.e. BB, BB*, B*B* (B* is the labeled atom) is usually considered as the criterion of dissociative or molecular adsorption mechanism. In the case of dissociative mechanism this ratio should correspond to binomial distribution. In CSTR this distribution is realized, while in PFR the fraction of BB* will be lower than predicted (Fig.1b). The sharper the gradient of label concentration in adspecies, the lower is concentration of BB* at the reactor outlet, and can be zero in the extreme case.

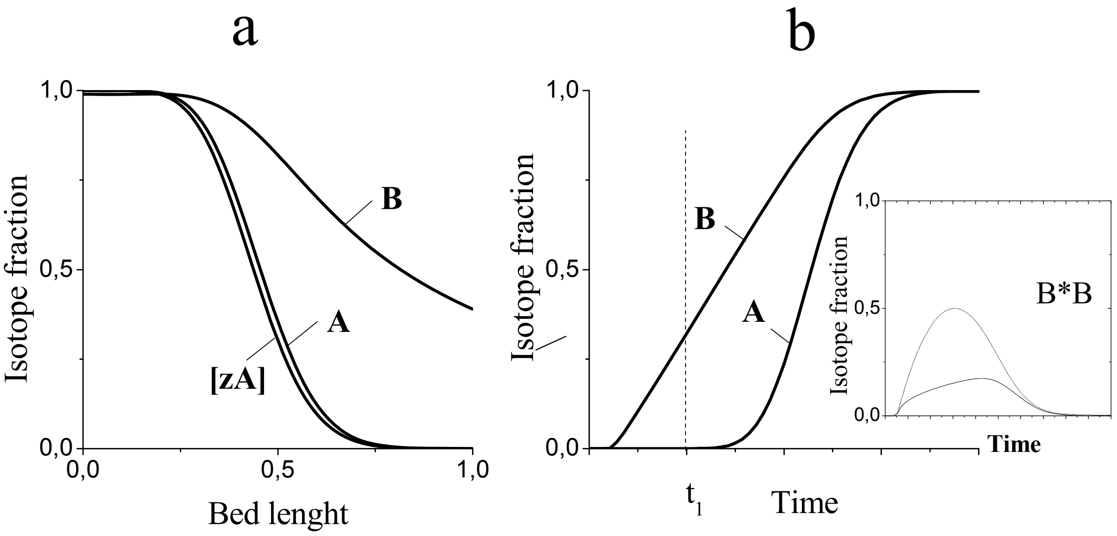

Fig. 1. Variation of isotope fractions in reactants, adspecies and reaction product along the catalyst bed at time point t_l (a) and their temporal dependencies at the reactor outlet (b) as calculated in accordance with schemes A↔[zA]→B and A_2↔2[zA]→B_2 (insert). Dotted line shows isotope fraction of BB* corresponding to binomial distribution.

Such effects were observed by us in the reaction of NO selective reduction by methane ($NO+CH_4+O_2 \rightarrow N_2+CO_2+H_2O$). At the initial period of time after ^{14}NO replacement by ^{15}NO label fraction in N_2 was higher than in NO, while $^{14}N^{15}N$ concentration was substantially lower than it should be in the case of binomial distribution. Using of proper models of isotope transfer accounting for change of isotope concentration with reactor length both in gas phase reagents and adspecies allowed description of isotope responses, elucidation of the scheme of reaction mechanism and estimation of both reactions coefficients, and their activation energies [3].

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KINETICS OF AN AQUEOUS ALKALI OXIDATION OF BOUNDEDLY WATER-SOLUBLE PRIMARY ALCOHOLS

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Oxidation of boundedly water-soluble primary alcohols, such as isoamyl alcohol, phenoxyethanol, phenylethanol and so on, with oxygen in aqueous alkali solutions on noble metals is attractive method for preparation of some valuable acids:

$$RCH_2OH + O_2 + NaOH \longrightarrow RCOONa + 2\ H_2O.$$

Kinetics of above reaction on the Pd/C catalyst has been studied by the examples of isoamyl alcohol, and also such homologues as *n*-butyl and *i*-butyl alcohols. Though among oxidation products in significant quantities there is an aldehyde and an ester of initial alcohol and a target acid, a main product is salt of a target acid (Fig. 1; *t* = 80°C, the catalyst of 2 % Pd/C; *1* — isoamyl alcohol, *2* — sodium isovalerate, *3* — isovaleraldehyde, *4* — isoamyl isovalerate).

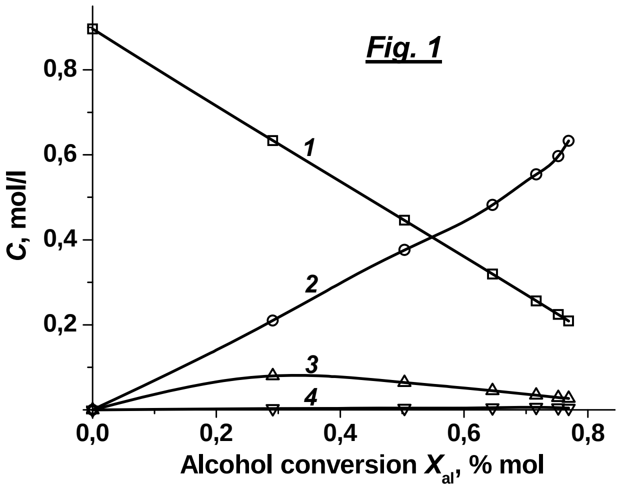

Fig. 1

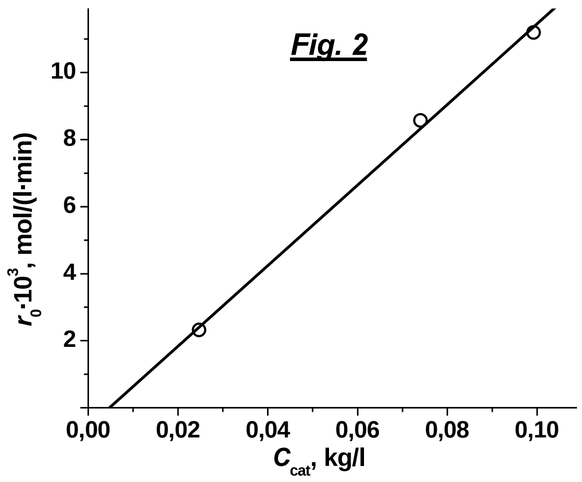

Fig. 2

Salt formation kinetics was investigated in batch reactor. Isoamyl alcohol oxidation rate linearly grows with increase in the catalyst content, however curve quits not zero (Fig. 2; $t = 80°C$, $C_{al,0}$=0.87 mol/l, $C_{NaOH,0}$=0.9 mol/l). At the same time rate relation to the alcohol content in reaction mixture is complex (Fig. 3): the range *1* corresponds to complete water-solubility of alcohol, and ranges *2* and *3* corresponds to presence of an organic phase. The kind of relationship 'rate *vs* catalyst content' in a Fig. 2 is characteristic for range 3.

Relations 'rate *vs* alcohol content' for *n*-butyl (*1*) and *i*-butyl (*2*) alcohols are analogous to one for isoamyl alcohol (Fig. 4, $t = 60°C$). It is caused by higher water solubility of butanols in comparison with isoamyl alcohol.

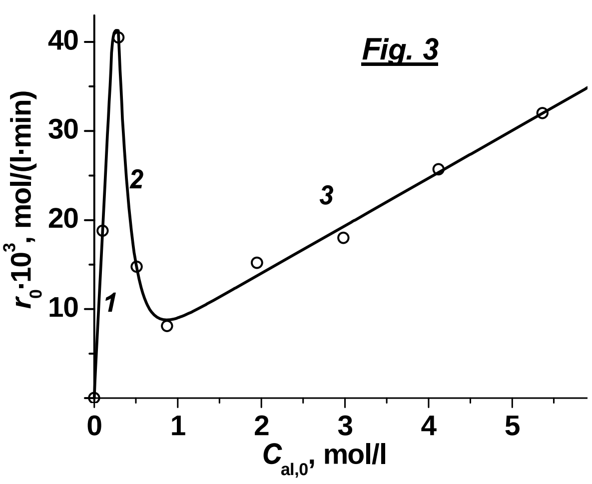

Fig. 3

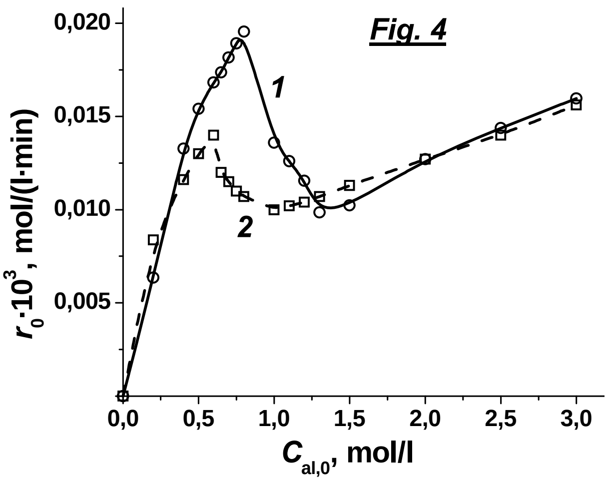

Fig. 4

The analysis of finding has resulted in kinetic equation including rate of alcohol oxidation $R_{cat,aq}$ on the aqueous phase wetted catalyst surface and rate of non-catalytic oxidation in the volume of the organic phase $R_{ncat,org}$:

$$R = R_{cat,aq} + R_{ncat,org}$$

It has been established that the catalyst during reaction loses activity owing to reversible over-oxidation. Reaction rate decreasing in the range *2* in a Fig. 3 is caused by formation of an organic phase and snowballing of a fraction of the organic wetted surface of the catalyst.

The contribution of catalytic reaction to oxidation rate is determined by catalyst content C_{cat}, organic wetting degree of catalyst surface β, alcohol (θ_{al}) and oxygen (θ_{Ox}) surface concentrations, and also by catalyst over-oxidation degree X_{Ov}:

$$R_{cat,aq} = k_{cat,aq}(1-X_{Ov})C_{cat}(1-\beta)\theta_{al}\theta_{Ox}$$

The non-catalytic reaction contribution is determined by a volume fraction of an alcohol organic phase α and an oxygen partial pressure p_{Ox}:

$$R_{ncat,org} = k_{ncat,org}\alpha p_{Ox}$$

It has been displayed that over-oxidation and reactivation of the catalyst occur on the aqueous phase wetted surface. The catalyst over-oxidation key factor is the oxygen surface concentration, and rate of a reactivation is determined by the reduction properties of an aqueous phase, including alkali concentration.

PP-I-15

THE KINETICS OF ACETOACETYC ACID'S ETHYL ESTER REACTION WITH ACRYL- AND α-METHYL ACRYL AMIDS IN CONDITIONS OF INVERSE PHASE TRANSFER CATALYSIS

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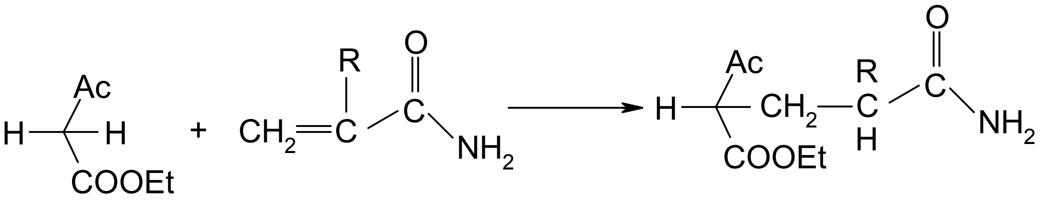
By condensation of ethyl ester of acetoacetic acid (EEAA) (oil soluble) with acryl- (AA) and α-methyl acryl amides (MAA) (water soluble) in the aqueous phase making use the «inverse phase transfer catalysis» (IPTC) ethyl-2-acetyl-4-carbomoylbutanoate (III) and ethyl-2-acetyl-4-carbamoylethanoate (IV) have been synthesized [1].

The reaction kinetics is studied making use UV spectroscopy. The products are identified by means of TLC, IRS and NMR methods.

On the ground of obtained experimental data it is established that in both cases derivatives of EEAA (in case of I → III and in case of II → IV) are being obtained. The overall chemical reaction is:



EEAA

$R\equiv H$ (I)

$R\equiv CH_3$ (II)

$R\equiv H$ (III)

$R\equiv CH_3$ (IV)

A both compounds (III and IV) synthesis the kinetics of corresponding reactions has been studied.

Taking into consideration that in all cases the kinetic curves are identical only one example will be demonstrated.

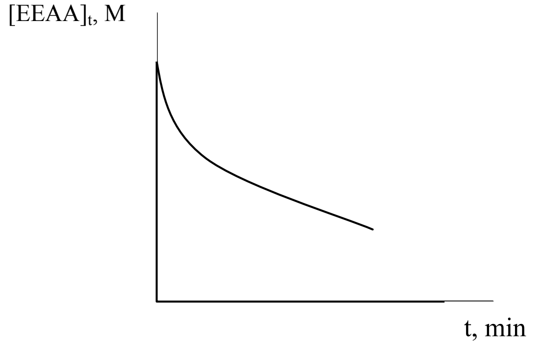


Figure 1. The kinetic curve of the reaction EEAA+AA+KOH+TMCAC at 293 K. $[EEAA]_0=[AA]_0$

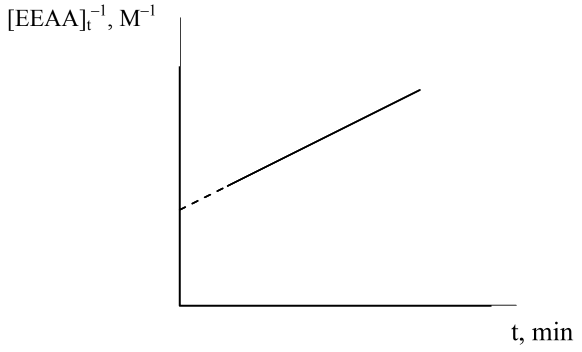


Figure 2. The anamorphosis of the kinetic law in coordinates $[EEAA]_t^{-1} \div t$ (min)

The analysis of kinetic data showed that the all considered reactions are bimolecular and first order with respect to each reagent: EEAA and either AA or MAA.

$$-\frac{d[EEAA]}{dt} = k[EEAA][AA](or[MAA]) \qquad (1)$$

In the case when $[EEAA]_0=[AA]_0$ (or $[MAA]_0$), as was our (1) may be expressed by the following rate law:

$$-\frac{d[EEAA]}{dt} = k[EEAA]^2 = k[AA]^2 = k[MAA]^2 \qquad (2)$$

which solution is:

$$[EEAA]_t^{-1} - [EEAA]_0^{-1} = kt \qquad (3)$$

It must be noticed that the R was determined by means of remained (unreacted) EEAA analysis.

So from the obtained experimental data it follows that the use of IPTC method opens new perspectives to enlarge the possibilities to synthesize lots of polyfunctional compounds by means of condensation of α,β-unsaturated amids with C-H acids.

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KINETIC DECOMPOSITION OF FORMIC ACID OVER VANADIA-TITANIA CATALYST

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Vanadia-titania catalysts are highly selective towards the oxidation of formaldehyde into formic acid in the temperature range 100-140 °C. At higher temperatures the selectivity decreases sharply because of the decomposition of formic acid [1]. The present work is aimed at the study of the decomposition of formic acid.

The experiments were performed at 50÷190 °C in air flow containing 1 vol.% of the formaldehyde. A sample of the catalyst containing 20 wt.% of V_2O_5 and 80 wt.% of TiO_2 was prepared by the procedure described elsewhere [1] and then calcined at 450 °C.

The kinetic scheme with the minimal amount of steps that appropriately describes the experimental data was chosen. It includes 3 steps

$$HCOOH + [Z] \leftrightarrow [Z\text{-}HCOOH] \rightarrow [Z] + H_2O + CO.$$

The first step involves an interaction of formaldehyde with active site [Z] with generate of the surface intermediate [Z-HCOOH]. Than, this intermediate is decomposed with water and carbon monoxide formation.

The kinetic equations was developed. The proposed kinetic model was used to estimate the rate constants, reaction orders, activation energies and surface intermediates. It satisfactorily describes the experimental data.

Acknowledgment

The authors acknowledge to RFBR (Grant № 06-03-32473-a) for the financial support.

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PP-I-17

NEW OSCILLATING REACTION: CARBONYLATION OF PROPARGYL ALCOHOL TO DIMETHYL ESTER OF ITACONIC ACID

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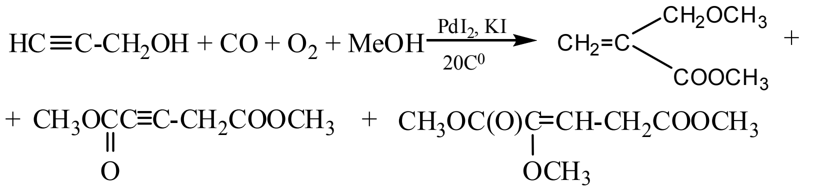
Some years ago we had found out a number of alkynes oxidative carbonylation processes which proceeded in an oscillatory mode [1, 2]. This report deals with one more new process expanding a range of organometallic catalytic reactions with nonlinear dynamic behavior. It was shown that the carbonylation of propargyl alcohol can proceed in system KI - PdI_2 - CO - O_2 - CH_3OH in an oscillatory regime (reaction 1).



(1)

The reaction was carried out in the closed system at T=20^{0}C with intensive mixing of liquid and gas phases. The values of electric potential of a platinum electrode (E_{Pt}) and glass electrode (pH) were continuously measured during the reaction. Products of reaction were identified using gas chromatography and chrom-mass spectrometry. Dimethyl ester of pentyne-2-dioic acid, dimethyl ester of 2-methoxypentene-2-dioic acid, dimethyl ester of itaconic acid have been found out in a reaction solution as main products. The triethyl amine (TEA) in concentration 0,7-4,0 M was added into the system before the propargyl alcohol addition. TEA addition created necessary acidity in reaction system (pH = 5-6) for the beginning of oscillations of intermediates concentrations. These oscillations occur in accordance with E_{Pt} and pH values oscillations (Fig. 1).

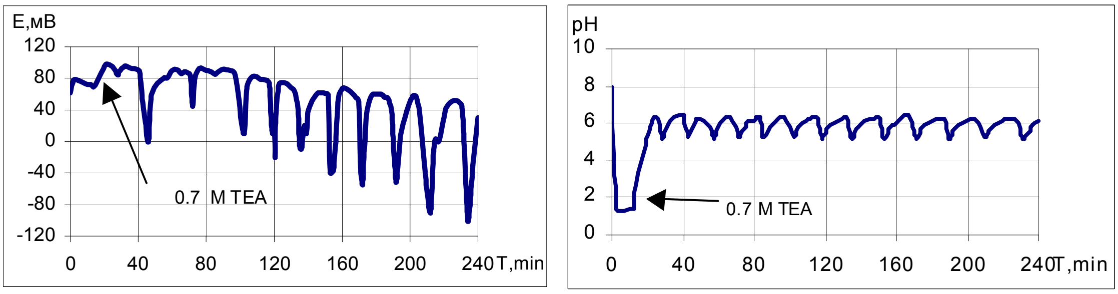


Fig. 1. Change of E_{Pt} and pH during reaction
[KI (0,4M), PdI_2 (0,01M), propargyl alcohol (0,068M), TEA (0,7M)]

The preliminary mechanism of propargyl alcohol carbonylation reaction including formation of all identified products has been offered. The ranges of an oscillatory area for substances concentrations and a gas mixture composition are determined. The dependence between amounts of TEA that are necessary to add for the beginning of oscillations and $[PdI_2]_0$ was established.

Acknowledges

This work was supported by the Russian Foundation for Basic Research (projects №№ 05-03-33151-a, 08-03-00412-a).

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PP-I-18

NEW OSCILLATING REACTIONS OF ALKYNES CARBONYLATION CATALYZED WITH Pd COMPLEXES

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The oscillating reactions were discovered in many chemical and biological systems. The most part of oscillatory homogeneous reactions investigated in chemistry are processes of organic substrate oxidation by strong oxidants. Our team has discovered the critical phenomena in typical reactions of the organometallic catalysis in which synthesis of complex molecules occurs. So, the reactions (1, 2) proceed in the system $PdBr_2$ – KBr – HBr – BuOH–dimethylsulphoxide:

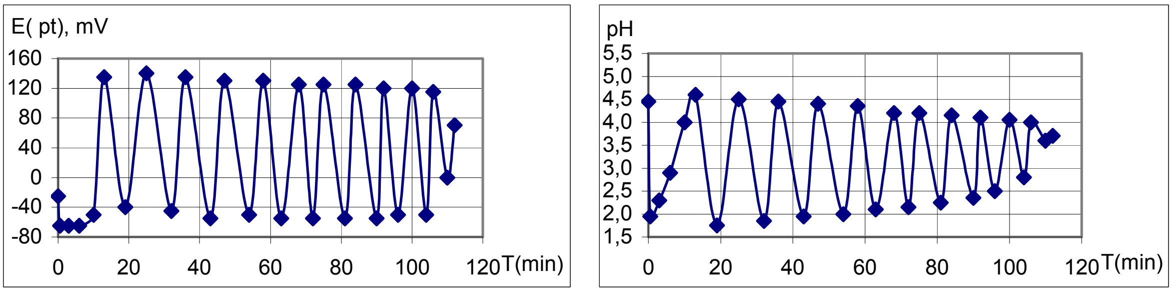
$$2CO + C_2H_2 + 2BuOH + (CH_3)_2SO \longrightarrow BuOCOCH{=}CHCOOBu\ (E, Z) + (CH_3)_2S + H_2O \quad (1)$$

$$CO + (CH_3)_2SO \longrightarrow CO_2 + (CH_3)_2S \quad (2)$$

with periodic change of carbon monoxide and acetylene consumption rate, values of platinum electrode potential (E_{Pt}), pH and color of the reaction solution [1]. Oscillations of E_{Pt} and pH were found out [2] during the study of various alkynes oxidative carbonylation reactions in the system PdI_2 - KI - MeOH (reaction 3)

$$RC{\equiv}CH + 2CO + 2MeOH + ½\,O_2 \longrightarrow MeOCOC(R){=}CHCOOMe\ (E, Z) + H_2O \quad (3)$$

where R: Ph, Me, $C(CH_3)_2OH$. Oxidation CO to CO_2 in this system occurs also. It was the first example of oscillating process including the complex molecules synthesis occurs on the base of relatively simple reagents using (Fig. 1)



(a) (b)

Fig. 1. The change of E_{Pt} (a) and pH (b) in the contact solution during of phenylacetylene oxidative carbonylation reaction; KI(0,4 M) – PdI_2(0,01 M) – PhC≡CH(0,1 M) – CO(60% v.) – O_2(40% v.)

We have showed that the phenomenon of oscillations can be observed for reactions with participation of different alkynes, and also in different catalytic systems, for example, in system $PdBr_2$ - LiBr, in which the occurrence of chaotic oscillations was demonstrated. One more reaction - oxidative carbonylation of phenylacetylene in system $PdBr_2$-LiBr-H_2O-acetone can proceed in an oscillatory mode also. The preliminary mechanism of this process is proposed.

Conclusion

The study of mechanisms of some other processes in organometallic catalysis allows us to expect occurrence of self-oscillations and other critical phenomena. The searching for such phenomena is important for development of the theory of catalytic reaction mechanisms. The presence of oscillations is the powerful tool of the mechanistic hypotheses discrimination.

Acknowledges

This work was supported by the Russian Foundation for Basic Research (projects № 05-03-33151, 08-03-00412).

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PP-I-19

KINETICS OF GAS–LIQUID PROCESSES OF OZONATION OF VERATROLE AND ITS DERIVATIVES

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Investigation in the areas of conversion of plant raw materials has intensely been developed in recent years. Lignin is the major component of the plant raw materials. One of promising routes is the oxidative destruction of lignin by ozone, which is highly reactive toward aromatic and unsaturated compounds.

The reaction of ozone with lignin is of interest from the viewpoint of designing new technologies for delignification and cellulose bleaching, sewage purification in the cellulose and paper industry, and production of valuable products from lignin.

Lignin is a natural polyfunctional phenolic polymer with an irregular structure. To study the kinetics and mechanism of its ozonation, researchers often use compounds modeling different structural fragments of lignin, for example, compounds of the guaiacyl, syringyl, and veratryl series with various substituents.[1,2]

The purpose of this work is to study the reactivity of lignin and various model lignin compounds. For this purpose, we studied the kinetic regularities of the oxidation with ozone of soluble sodium ligninsulphanate and the simplest model lignin compounds: phenol, guajacol, veratrole, veratric alcohol, and veratric aldehyde.

Ozonation was carried out in the new gaslift unit with a natural circulation of liquid phase at 298 K, an initial ozone concentration of $0.9–1.1 \cdot 10^{-3}$ mol L^{-1}, and the flow rate $w = 25$ L h^{-1}. The volume of the reaction mixture was 0.55 L.

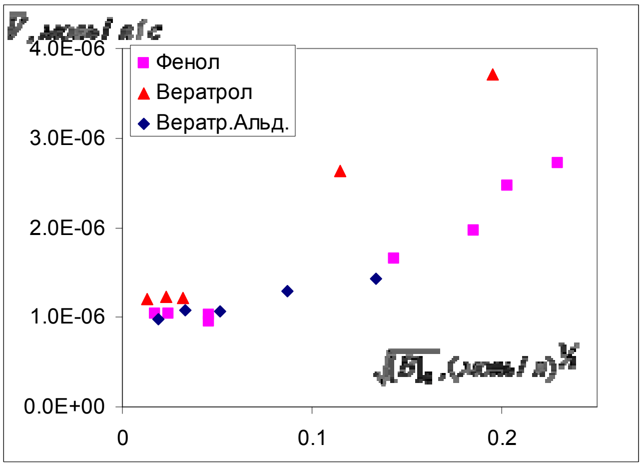

Fig. 2. Plots of the ozone absorption rate *vs* $\sqrt{[B]_0}$ for phenol (*1*), veratrole (*2*), and veratric aldehyde (*3*).

The model based on the film theory[3] is most convenient to study processes impeded by mass transfer. Using this model, it is assumed that a film is formed near the interface and ozone can penetrate through the film only due to molecular diffusion. The plot of the rate of ozone absorption V^- *vs* $\sqrt{[B]_0}$ ($[B]_0$ is the initial substrate concentration) is shown in Fig. 1.

A process course region, the interface surface and the Hatta number was stated from the experimental data to determine the rate constants of the chemical reaction. The reaction rate constant was determined by both ozone absorption and a change in the substrate concentration(see Tables 1).

Based on the results obtained, we can conclude that the nature of substituents in the aromatic ring of veratrole affects the reactivity of the compounds under study. The presence of electron-releasing substituents in the aromatic ring increases the reactivity, whereas for electron-withdrawing substituents the reactivity decreases appreciably, which is indicated by the rate constant values for the ozonation of model lignin compounds.

Table 1. Kinetic parameters in the reactions of ozone with model compounds calculated from the experimental data on ozone absorption as well as from the chromatographic data

Substrate	$[B]_0$/mol L^{-1}	k_{O3}, k/L mol^{-1} s^{-1}	k_B, k/L mol^{-1} s^{-1}
Phenol	$2{,}9\cdot10^{-4}$ - $5{,}3\cdot10^{-2}$	$6{,}8\cdot10^{3}$	$5{,}7\cdot10^{3}$
Veratrol	$1{,}1\cdot10^{-5}$ - $3{,}8\cdot10^{-2}$	$1{,}6\cdot10^{4}$	$1{,}5\cdot10^{4}$
Veratric alcohol	$3{,}1\cdot10^{-4}$ - $1{,}2\cdot10^{-2}$	$3{,}9\cdot10^{4}$	$4{,}4\cdot10^{4}$
Veratric aldehyde	$3{,}6\cdot10^{-5}$ - $1{,}8\cdot10^{-2}$	$4{,}1\cdot10^{3}$	
Veratric acid	$3{,}0\cdot10^{-3}$ - $9{,}0\cdot10^{-3}$	$7{,}7\cdot10^{3}$	
Guajacol	$3\cdot10^{-4}$ - $1\cdot10^{-3}$	$>5\cdot10^{5}$	

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COMPLETE OXIDATION OF HARMFUL ORGANIC COMPOUNDS OVER ALUMINA SUPPORTED Cu-Mn MIXED OXIDE CATALYSTS

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The purification of harmful organic substances from waste gazes is important task in respect to environmental protection [1-4]. The main problem of this is the creation of catalysts, active even at low temperatures and low concentration of the harmful component.

Irrespective to the large number of publications on this topic the investigations continue in respect to optimization of the processes of complete oxidation of harmful organic substances [5-10].

It is known, that the reactions of complete oxidation on oxide catalysts proceed by oxidation-reduction mechanism. An important condition for this mechanism is the presence of metal couples in a different oxidation state that could be oxidized or reduced so that to be realized the reaction.

These metal ions in various oxidation states form catalytic active sites mentioned earlier as catalytc active complex. In this case the oxidation-reduction mechanism in the complete oxidation of organic substances is facilitated by this complex and the catalysts show high activity at low temperatures.

In several papers of ours [11,12] it has been shown that cooper-manganese oxides with a spinel-like structure are highly active in the neutalization of various toxic gases such as CO and NO.

Mixed cooper and manganese oxides differing in their crystal structure are also known. In recet studies the acetate precursors are often applied for preparation of catalysts by pore volume impregnation of γ-Al_2O_3 instead of traditional metal nitrate solutions [13]. In Ref. 14 it has been shown that when copper and manganese formates are used as initial compounds, $Cu_{0.4}Mn_{4.5}O_8$ or $Cu_{1.5}Mn_{1.5}O_4$ can be formed at low temperatures (below 710 K) of formates as precursors permits formation of mixed formates an their decomposition without preliminary melting thus resulting in the formation of oxide phase of high dispersity [15]. This is especially important for the synthesis of supported oxide catalysts. The formation of the catalytically acive oxide phase in this case is a complex process because it is affected both the presence of a chromatographic effect [16] and the crystallization in the pores of the support [17]. The chemical nature of the support on wich the spinel phase is formed alsoinfluences the catalytic activity [18].

For that reason the present paper is aimed at studing the effect of the coper manganese ratio and the structure of mixed alumina-supported cooper-manganese oxides prepared by using metal formate solution for pore volume impregnation of γ-Al_2O_3 on the catalysts activity during complete oxidation of CO, ethylacetate, toluene and benzene.

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PP-I-21

THEORETICAL RESEARCH OF SURFACE REACTIONS KINETICS

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One of the aspects about solid surfaces that have the largest fundamental and technical importance is the way in which chemical reactions are affected by the presence of a surface. At the most general level the role of the surface can often be regarded as a mean of stabilizing intermediates in the reaction. The synthesis of NH_3 directly from N_2 and H_2, for instance, is extremely slow in the gas phase because it requires an extremely large energy to break the N-N bond. At a metal surface the N atoms are stabilized by the chemisorptive bond to the surface and this means that reaction can proceed with reasonable activation energy [1].

A kinetic description of chemical reactions is much simpler than a full dynamical description. Because of the thermal averaging, only certain features of the adiabatic potential energy surfaces, namely the minimum energy barriers separating the minima, enter into the rate [2]. We also get a chance to use our understanding of the adiabatic potential energy surface with the ability of relating the properties of chemisorbed molecules and atoms directly to the kinetics of high pressure catalytic reactions for chemisorptions to explain some of the general questions in the field of catalysis. This is what we shall attempt to illustrate in the this paper. The kinetics developed for the ammonia synthesis will be used to explain why the transition metals of iron type are the most active catalysts for this reaction and in which form oxygen (atomic or molecular) presents in such reactions.

The collision complexes: Fe…NH_3, Fe…O_2, Fe…O have been calculated by quantum-chemical MNDO methods for evidence of the first stage of catalytic transformation, namely – particles adsorption on the metal surface (table 1). The Fe … NH_3 collision complex has been calculated at the distance between particles from 1 till 3.2Å. The calculation of ammonium molecule on the clear Fe shows the insignificant interaction. The comparison of activation energy shows that the less barrier is for ammonia and molecular oxygen adsorption (E_{act} = 4,03 eV and E_{act} = 4,45 eV, accordingly). For atomic oxygen adsorption the activation energy has slightly bigger value E_{act} = 6,74 eV. It is necessary to note, that there is attraction between atomic oxygen and iron. The activation energy analysis of investigated adsorption complexes (table 1) shows that almost at the same distance between particles (R = 1,9Å) the activation barrier of Fe…O complex is a little bit bigger than analogical values for other interacting components. Therefore at the adsorption stage in the competition between particles the molecular oxygen is predominating. It is coincide with experiments [5]. It is also agreed with suggested explanation of molecular oxygen participation in the formation complexes at the surface due to particularities of its electronic structure (the triplet ground state with two unpaired electrons).

Table 1. Results of MNDO calculations of the processes on the Fe catalyst during ammonia oxidation.

Collision complexes	NH_3…Fe	O_2…Fe	O…Fe	Fe…O_2…NH_3	Fe...O...NH_3
Total energy, E_{tot} eV	–350,689	–745,635	–427,04	–989,23	–668,7
Heat of formation ΔH^0_{298}, kcal/mol	164,77	72,00	29,216	211,19	219,94
Distance between particles and Fe, R, Å	1,9	1,95	1,9	2,05	1,75
The activation energy, E_{act}	4,03	4,45	6,74	1,16	4,2

The next research stage is calculation of ammonia with Fe interaction in the presence molecular or atomic oxygen. As for as NH_3…O…Fe, collision complex shows considerable interaction and energy minimum at R = 1.8Å. According to the electronic density distribution analysis we can see that oxygen atom almost «seats» on the d-orbitals of iron. There is the weak overlapping between ammonia molecular orbitals and oxygen atomic orbitals. Besides, there is the significant interaction of the oxygen p-orbitals and iron d-orbitals. It can be explained by stronger influence of the atomic oxygen on the iron, than on the NH_3. The calculation of all collision complexes confirmed significantly deep interaction between ammonia and atomic oxygen over Fe catalyst. Therefore it is necessary to admit that atomic oxygen can be more active in the ammonia oxidation on the Fe surface. It is agreed with traditional point of view concerning the ammonia oxidation mechanism.

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PP-I-22

INFLUENCE OF ORGANIC HELATES ON THE OXIDIZATION PROCESS OF CYCLOHEXANE

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By the reactions of oxidization in industry get a lot of organic substances. For providing of high-rate reactions use the catalysts. The main problem in industrial process is very low conversion of cyclohexane.

Process of oxidization of cyclohexane in presence helates and naftenate of cobalt is investigated at 418K and pressure of 1 MPa. The duration of reaction is about 60 min. The concentration of basic catalyst (cobalt naftenate (CN)) is about 10-5 ÷ 10-4 mol/l.

It is known that these catalysts strongly influence on speed of the process, but practically does not influence on composition of reactionary mixture.

Use as catalyst cobalt soluble helate (CSH) allowed to attain in times of identical reaction of conversion more high on 40%, than at the use of cobalt naftenate, and selectivity a purpose products remained without changes.

Process in present of catalysts cobalt insoluble helate (CIH) and cobalt pirazol polichelat (CPP) results in a growth speed of oxidization a cyclohexane. Thus, if the use of CPP results in the insignificant growth of conversion which is arrived at in times of identical – approximately on 10%, application of CIH results in a growth conversion practically in 5 times. Alike results are observed on influence of these catalysts CIH and CPP on total selectivity after having a special purpose products: use of CPP provides the same selectivity practically, as well as in presence the CN, and here the use of CIH does not allow even at conversion of cyclohexane to 1% to attain selectivity more high after 80%.

Use cobalt helates catalyst does not change substantially the ratio of purpose products – cyclohexanol (CHL) and cyclohexanone (CHN). At conversion of cyclohexane approximately 4% it is within the limits of 1,5-1,9. Use the catalyst CIH results in some decline of this correlation (0,7 comparatively with 1,6 at the use cobalt naftenate), but such result it is attained only at conversion of cyclohexane to 1%, so as on this catalyst, attaining higher conversion of cyclohexane was not succeeded.

Taking into account the structure of investigational catalysts, it is possible to draw a conclusion, that increase of oxidization speed at application of catalyst CSH, which is especially notedly observed on the initial stage of reaction, can be caused being in the structure of him ligand of peroxide groups which are initiator of oxidization process. Therefore, is perspective to continue research in this direction.

INVESTIGATION OF METHANOL DECOMPOSITION KINETIC USING ADVANCED FLOW-CIRCULATION METHOD

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Introduction

Investigation of kinetics of methanol convertion processes and methane oxidation process is a very actual problem due to economic and ecological reasons. The study of kinetics and mechanism of methanol catalytic convertions is needed because these processes are perspective for hydrogen production for fuel cells.

To compare catalyst activities the flow integral method is used in most of research works. However more correct determination of catalytic reaction rates could be obtained by precise differential methods. The flow- circulation catalytic method allows to achieve the ideal mixing mode in laboratory reactor [1,2].

This work is devoted to study of kinetic of catalytic decomposition of methanol over a Cu-Zn-O catalyst by means of advanced flow-circulation catalytic reactors.

Experimental

The flow- circulation setup named BI-CATrecycle-uni were designed and constructed for study of kinetic of catalytic convertions of methanol. The catalyst for methanol convertions contained 52-54 wt. % CuO, 24 – 28 wt. % ZnO, 5 – 6 wt. % Al_2O_3 and its BET surface area after reduction was about 87 m^2/g.

Results and discussion

The dependence of the process pathway on contact time was obtained for the reaction of methanol decomposition (Fig.1).

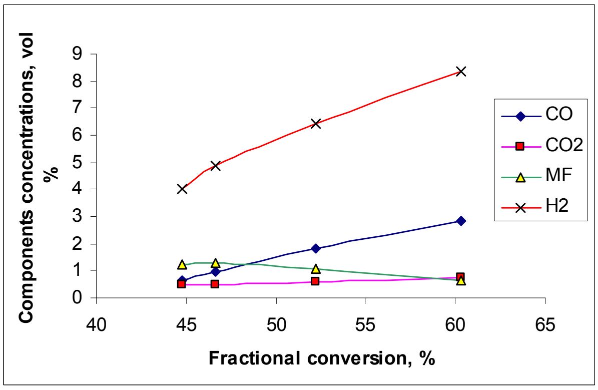

Figure 1. An example of the dependence of the stationary components concentrations on the fractional conversion of methanol in reaction decomposition of methanol.

The equation of the reaction rate (W) dependence on the concentrations of the reaction mixture components (C_i) and some of elementary constants (k_i) was proposed on the base of thermodynamic estimations (advanced model on Fig. 2). The optimal kinetic model of the process was defined by solving the inverse kinetic problem. The difference between the model and experimental reaction rates was minimized. The activation energies and formal reaction orders on reaction components were also determined.

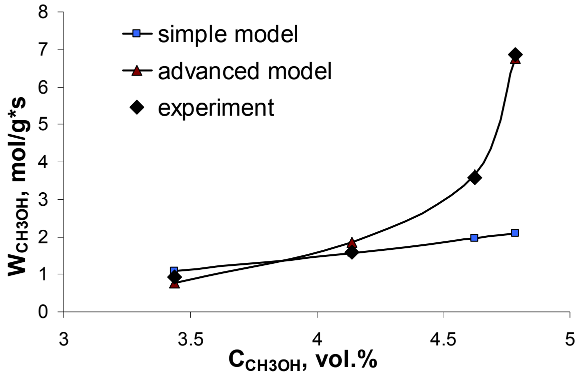

Figure 2. Comparison description experimental dates use of simple and advanced model.

Conclusions

The knowledge of features of methanol convertions and methane oxidation is needed for determination of reaction mechanism, selection of new more active and inexpensive catalysts, optimization of reaction conditions.

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NONLINEAR MODELS OF KINETICS AND THERMOKINETICS

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We considered a series of the nonlinear kinetic models of the catalytic reactions.

Catalytic trigger. Scheme: 1) $2Z \leftrightarrow 2X_1$, 2) $Z \leftrightarrow X_2$, 3) $X_1 + X_2 \to 2Z$.

Model:
$$\frac{dx_1}{d\tau} = 2k_1z^2 - 2k_{-1}x_1^2 - k_3(T)x_1x_2,$$
$$\frac{dx_2}{d\tau} = k_2z - k_{-2}x_2 - k_3(T)x_1x_2, \qquad z = 1 - x_1 - x_2.$$

Catalytic oscillator. Steps 1) – 3) + 4) $Z \to X_3$.

Model:
$$\frac{dx_1}{d\tau} = 2k_1z^2 - 2k_{-1}x_1^2 - k_3(T)x_1x_2,$$
$$\frac{dx_2}{d\tau} = k_2z - k_{-2}x_2 - k_3(T)x_1x_2,$$
$$\frac{dx_3}{d\tau} = k_3z - k_{-3}x_3, \qquad z = 1 - x_1 - x_2 - x_3.$$

Autocatalytic trigger. Scheme: 1) $Z \leftrightarrow X$, 2) $X+2Z \to 3Z$,

Model:
$$\frac{dx}{d\tau} = k_1(1-x) - k_{-1}x - k_2x(1-x)^2.$$

Autocatalytic oscillator. Scheme: 1) $Z \leftrightarrow X_1$, 2) $X_1 + 2Z \to 3Z$, 3) $Z \leftrightarrow X_2$,

Model:
$$\frac{dx_1}{d\tau} = k_1z - k_{-1}x_1 - k_2(T)x_1z^2,$$
$$\frac{dx_2}{d\tau} = k_3z - k_{-3}x_2, \qquad z = 1 - x_1 - x_2.$$

The parametrical analysis method gives a possibility for kinetics and thermokinetic models to build the bifurcation curves, parametric and phase portraits, oscillation regimes. We study the nonlinear dynamic system like the famous classic models CSTR – Aris-Amundson model [1-4].

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PP-I-25

SELECTIVE OXIDATION OF METHANE TO SYNGAS FOR DIMETHYL ETHER PRODUCTION

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Partial oxidation of methane is a challenge in catalytic research due to the fact that it is possible to utilize carbon dioxide as a mild oxidant. Reforming of methane is one of the processes to produce synthesis gas with desired H_2/CO ratios for clean fuels and chemicals. It provides a CO/H_2 ratio (1:1) adapted to the gas-to-liquid processes. It is very suitable for production of dimethyl ether (DME) which can be used as a sulfur free fuel for diesel engines without particulates formation and lower NO_x emission in comparison with gas oil. Most VIII group metals, especially noble metals and Ni-based catalysts are known for steam reforming, dry reforming, partial oxidation and mixed reforming of methane. In the present work we studied the process of partial oxidation of methane to syngas by carbon dioxide at high temperature on the atypical intermetallide catalysts on the base of Ni_3Al and Fe_3Al.

The intermetallide catalysts were prepared by the method of self-propagating high temperature synthesis (SHS) using Ni (PNE-1), Al (ASD-1), Fe (OSCh) powders. The most important characteristics of these catalysts are high thermal stability and conductivity.

It was used a fixed-bed reactor under atmospheric pressure (in a temperature-programmable quartz tube reactor in conditions: temperature range 600 – 950 ºC, space velocity of gas stream 100 ml/min and molar ratio CO_2/CH_4=1:1. Exhaust gases were analyzed using a TCD. The contents of carbon deposites on catalysts were measured by the carbon combustion method.

As an alternative to Ni/oxides catalysts which always present the drawback of possible methanation in the downstream gas tail with the extracted catalyst fines. Ni_3Al-based catalysts were also shown to be active for dry reforming reaction. Some of the experiments showed enough good results. For example, high level of catalytic activity was observed for Ni_3Al modified with Mo. The content of carbon deposits was about 6-10 %(wt).

The intermetallides on the base of nickel modified with Mo are rather active catalysts for dry reforming of methane and are promising for DME production.

Acknowledgement

Authors acknowledge Yu. Naiborodenko, N. Kasatskiy, N. Golobokov for help in synthesis of catalysts.

PP-I-26

FIVE-PHASIC OSCILLATORS IN HETEROGENEOUS CATALYSIS

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In works [1,2] for the description of self-oscillations in kinetics of catalytic reactions three-and four-stage schemes have been used. It is known [3] that the increase in number of stages in mechanisms of catalytic reactions results in complication of their kinetic behaviour and allows to describe self-oscillations by schemes with smaller molecularity making stages. It proves to be true results of research of four-stage schemes and their comparison to results of the analysis of three- stage schemes. In the given message the possibility of the description of self-oscillatory regimes in heterogeneous catalytic reactions with the help five-stage bimolecular on intermediate substances of the schemes is investigated.

Let's consider any one-routing heterogeneous catalytic reaction consisting of a stage

$$\sum_e \nu_{ie}^+ A_e + \sum_j a_{ij}^+ X_j = \sum_j a_{ij}^- X_j + \sum_e \nu_{ie}^- A_e,\ d_i,\quad i,j=1,\dots,n;\ e=1,\dots,s, \tag{1}$$

where A_e and X_j – the basic and intermediate substances, ν_{ie}^+,ν_{ie}^- and a_{ij}^+,a_{ij}^- – stoichiometric coefficient ($\sum_j a_{ij}^+ = \sum_j a_{ij}^-$), $d_i > 0$ – stoichiometric numbers of stages. In conditions of an isothermal differential reactor the non-stationary behaviour of reaction is described by system

$$\dot{x}_j = \sum_i \left(a_{ij}^- - a_{ij}^+\right)\left(r_i - r_{-i}\right) \equiv \varphi_j \tag{2}$$

where x_j – concentration of substances X_j ($\sum_j x_j = 1, x_j \ge 0$); r_i, $r_{-i} \ge 0$ – rates of a stage in the direct and return directions

$$r_i = \omega_i \prod_j x_j^{a_{ij}^+},\ r_{-i} = \omega_{-i} \prod_j x_j^{a_{ij}^-},$$

$\omega_{\pm i} = k_{\pm i} \prod_e C_e^{\nu_{ie}^{\pm}}$ – frequencies of stages, $k_{\pm i}$ – constants of stage rates; C_e – concentration of basic substances A_e.

For kinetic model (2) we shall enter a characteristic multinominal

$$\lambda\left(\lambda^{n-1} + \sigma_1 \lambda^{n-2} + \dots + \sigma_{n-1}\right) = 0 \tag{3}$$

one of which λ roots is equal to zero in view of validity for heterogeneous catalytic reactions of the law of preservation $\sum_j x_j = 1$. Coefficients of characteristic multinominal (3) can be calculated as:

$$\sigma_1 = -\sum_j \frac{\partial \varphi_j}{\partial x_j},\ \sigma_2 = -\sum_{j<k}\left(\frac{\partial \varphi_j}{\partial x_j}\frac{\partial \varphi_k}{\partial x_k} - \frac{\partial \varphi_j}{\partial x_k}\frac{\partial \varphi_k}{\partial x_j}\right), \dots \tag{4}$$

Sufficient condition of occurrence of self-oscillations is presence of a unique unstable stationary state. A condition of instability of a stationary state is negativity of one of younger coefficients of the equation (3). Uniqueness of this stationary state is provided with positivity of last coefficient σ_4. In work [4] it is established that for the reactions of a kind (1) consisting of any number of intermediate substances and bimolecular and linear stages on intermediate substances coefficient σ_1 of the characteristic equation cannot be negative. Thus instability of the reactions proceeding under five-stage schemes will mean negativity of one of coefficients σ_2 or σ_3 a characteristic multinominal (3).

With application of these conditions in language Maple the program of the analysis of self-oscillations has been developed. With its help the mechanisms describing self-oscillatory regimes have been selected from set of the generated five-stage schemes. Generation of all possible five-stage schemes was carried out by program specially developed by us in language Delphi. The received schemes have been grouped on number of stages included in them various molecularity: schemes containing 3 linear and 2 bimolecular stages and schemes consisting from 2 linear and 3 bimolecular stages.

The examples of the elementary schemes describing self-oscillations in reactions of catalytic oxidation CO and H_2 are below resulted

1. $CO + O_2 + 2K \leftrightarrow KO + KCO_2$,
2. $O_2 + KCO_2 \leftrightarrow KO_2 + CO_2$,
3. $CO + KO_2 \leftrightarrow KO + CO_2$,
4. $CO + KCO_2 \rightarrow KCO + CO_2$,
5. $KO + KCO \leftrightarrow KCO_2 + K$;

1. $H_2 + 2K \leftrightarrow 2KH$,
2. $O_2 + K \leftrightarrow KO_2$,
3. $H_2 + KO_2 \leftrightarrow KO + H_2O$,
4. $O_2 + H_2 + KH \leftrightarrow KOH + H_2O$,
5. $KO + KOH \leftrightarrow 2K + H_2O$;

1. $H_2 + 2K \leftrightarrow 2KH$,
2. $O_2 + K \leftrightarrow KO_2$,
3. $H_2 + KO_2 \leftrightarrow KO + H_2O$,
4. $KO + KH \leftrightarrow KOH + K$,
5. $KO + KOH \leftrightarrow 2K + H_2O$.

Thus we computerize process of construction of the five-stage schemes describing self-oscillations in kinetics of catalytic reactions. The examples confirming applicability of simplest received schemes for reproduction of self-oscillations in reactions of catalytic oxidation of carbon monoxide and hydrogen are considered.

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KINETIC REGULARITIES OF N-PROPYL ALCOHOL OXIDATION REACTION OVER METALZEOLITE CATALYST

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The results of investigations of catalytic oxidation reaction of n-propyl alcohol have shown that from the number of catalysts prepared on the basis of natural and synthesized zeolites, the process of oxidation of n-propyl alcohol into propionic acid proceeds with high activity and selectivity over zeolite CaA modified by 3.0 wt.% Cu^{2+}. The kinetic regularities of the reaction over metalzeolite catalyst CuCaA have been studied.

Introduction

The catalytic oxidation of aliphatic alcohols is a highly perspective method of obtaining of carboxylic acids. The known catalysts such as transition metals over the different carriers, oxides of the transition metals are not effective for the given process because of the proceeding of some side reactions and high temperature of the process[1]. The mechanism of this process over metalzeolite catalysts is studied insufficiently[2]. The given paper is dedicated to the investigation of kinetic regularities of the reaction of n-propyl alcohol oxidation into propionic acid over polyfunctional zeolite catalyst CuCaA modified by 3.0 wt.% Cu^{2+} ions.

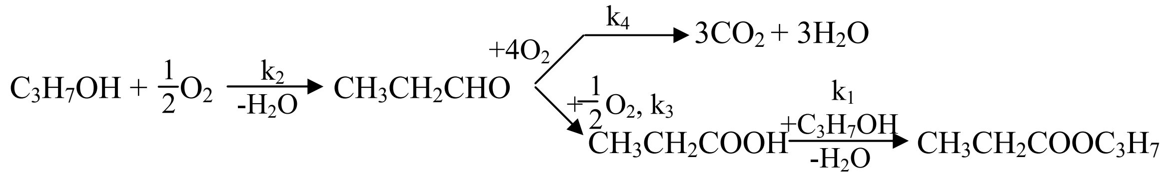
Experimental

Catalytic tests of activity of the synthesized samples of metalzeolite catalysts (natural – clinoptilolite, mordenite and synthetic zeolites – NaA, CaA, NaX, NaY modified by ion-exchange method with Cu^{2+}, Pd^{2+}, Sn^{2+}, Zn^{2+} cations) in the oxidation reaction of n-propyl alcohol were carried out on a flow installation with the fixed bed of catalyst. The experimental kinetic investigations of vapor-phase oxidation reaction of n-propyl alcohol into propionic acid were carried out over zeolite catalyst CuCaA (Cu^{2+}-3.0 wt.%) at pressure 101.325 kPa, in the range of the reaction temperatures 453-523 K, space velocity 900-4500 h^{-1} and partial pressures of reagents P_{O_2}= 5-40 kPa, $P_{C_3H_7OH}$= 5-40 kPa. Before studying catalyst CuCaA (2 cm^3) was activated by air current at 723 K, space velocity, 2400 h^{-1} for 2 hours and then cooled up to the reaction temperature. The reaction products were analyzed by GC and IR-spectroscopy.

Results and discussion

Comparison of received data has shown that zeolite CuCaA containing 3.0 wt.% Cu^{2+} cations is the most effective catalyst for the reaction of direct oxidation of n-propyl alcohol into propionic acid. The given results showed that with increasing of partial pressure of n-propyl alcohol selectivity of process on propionic acid is increased at temperatures 453-498 K. The yield of propionic acid reaches maximal value (66.4%) at partial pressure of n-propyl alcohol 10 kPa (T=498 K) and then yield of propionic acid begins to decrease. The decrease of yield of propionic acid can be explained in such way that at the given partial pressure of oxygen (P_{O_2} =30 kPa) relatively high partial pressures of n-propyl alcohol prevent to the coordination of oxygen to the active centers of metalzeolite catalyst. The increase of partial pressure of oxygen at temperatures T= 453-498 K results in the negligible increase of selectivity of the process on propionic acid and increase the yield of propionic acid. The results of the carried out investigations have also shown that the greatest yield of propionic acid and the greatest selectivity of the process on propionic acid are observed at relatively low space velocity (900 h^{-1}) and reach to maximal value in the range of temperatures 488-498 K.

On the basis of the experimental data the total kinetic scheme of oxidation reaction of n-propyl alcohol over catalyst CuCaA can be depicted as:



$$C_3H_7OH + \frac{1}{2}O_2 \xrightarrow[-H_2O]{k_2} CH_3CH_2CHO \begin{cases} \xrightarrow[+4O_2]{k_4} 3CO_2 + 3H_2O \\ \xrightarrow{+\frac{1}{2}O_2,\ k_3} CH_3CH_2COOH \xrightarrow[-H_2O]{+C_3H_7OH,\ k_1} CH_3CH_2COOC_3H_7 \end{cases}$$

where k_1, k_2, k_3 и k_4 – constants of the reaction rate of propylpropionate, propionic aldehyde, propionic acid and carbon dioxide.

On the basis of kinetic equations kinetic model of n-propyl alcohol oxidation process over zeolite catalyst CuCaA was presented and subjected to statistical analysis on the basis of experimental kinetic data. Kinetic parameters of the given model have been determined on the basis of kinetic equations of n-propyl alcohol oxidation reaction into propionic acid by means of comparison of experimental and calculated kinetic data.

Conclusions

It has been established that polyfunctional zeolite catalyst CuCaA containing 3.0 wt.% Cu^{2+} shows the high activity and selectivity in the direct oxidation of n-propyl alcohol into propionic acid. The kinetic regularities of the given reaction have been studied over catalyst CuCaA. On the basis of experimental data kinetic scheme of n-propyl alcohol oxidation reaction has been proposed and kinetic model of the present process has been developed.

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KINETICS OF *n*-BUTANE CONVERSION OVER SULFATED MORDENITE-ZIRCONIA CATALYST

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Introduction

It has been shown in publications [1, 2] that promotion of dealuminated mordenite by zirconia and sulfate-ions results in a considerable increasing of zeolite isomerizing activity and allows to perform isomerization of *n*-butane at lower temperatures. The results of investigation of kinetic regularities of the process essential for understanding of action mechanism of sulfated mordenite-zirconia catalysts in *n*-butane isomerization are presented in the given paper.

Experimental

The kinetics study of reaction was carried out in a flow microreactor at 0.1MPa pressure and temperature range 473-513 K. Before testing a catalyst was heated in a dry air stream at 773 K for 3 hours. Partial pressures of *n*-butane and hydrogen were varied in the range 0.01-0.08 and 0.01-0.04 MPa, respectively. For ensuring of velocity constancy of gas stream nitrogen was used as an inert diluent. The products of reaction were analyzed by gas chromatography method.

Results and discussion

The dependences of main products formation velocities of *n*-butane conversion (isobutane, isopentane, propane) on partial pressures of reactants were determined at moderate conversion of *n*-butane, i.e. in the range of pseudo zeroth order of reaction. The obtained results are presented in Table 1 at temperature of 473 K.

Table 1. Influence of reactants partial pressures on *n*-butane conversion and reaction rate (temperature – 473 K, stream rate – 500 ml·h^{-1})

Partial pressures, MPa		Conversion of *n*-butane, %	Reaction rate, $W_i \cdot 10^4$ mole·g^{-1}·h^{-1}		
$P_{n\text{-}C_4H_{10}}$	P_{H_2}		isobutane	isopentane	propane
0.01	0.01	2.6	0.28	0.04	0.03
0.02	0.01	2.9	0.67	0.09	0.06
0.04	0.01	3.2	1.41	0.23	0.17
0.06	0.01	3.7	2.46	0.35	0.27
0.08	0.01	5.1	4.58	0.70	0.47
0.01	0.02	1.9	0.21	0.03	0.02
0.01	0.04	1.4	0.15	0.02	0.01

In the studied range of temperatures formation rates of all products are increased with growth of $P_{n\text{-}C_4H_{10}}$. Influence of P_{H_2} on reactions rates depends on temperature: at 473 K negative order on hydrogen is observed which with increasing of temperature is approached to zeroth one. Therefore, dependences of formation rates of *n*-butane conversion products on partial pressures of reactants are described by one total equation:

$$W_i=k_i P^{n}_{n\text{-}C_4H_{10}} P^{m}_{H_2} \qquad (1)$$

Reaction orders n and m were determined from the slops of lines fitting rate vs. reactant partial pressures on logarithmic coordinates. It has been found, that for all reaction products and at different temperatures n has 1.3±0.2 value, at 473 K m is equal to -0.5±0.1 and with increasing of temperature is approached to zero. Apparent activation energies calculated from Arrhenius plots of reaction rates for isobutane, isopentane and propane formation are equal to 72 ± 4; 102 ± 6 and 116 ± 6 kJ mole^{-1}, respectively.

Different kinetic models of the process were considered. It has been shown that the reaction has complex nature and it specific mechanism depends on both catalyst nature and process operation conditions. Both monomolecular and bimolecular mechanism of reaction may be predominant with changing of temperature. As the reaction network is complex and the primary and secondary reactions not resolved, the kinetic results cannot be regarded as more than just empirical; they represent overall reactions and not a resolution of the individual reactions. Nevertheless, on the basis of obtained results a search of the promoters, permitting to decrease an isomerization reaction temperature and to provide a higher selectivity, may be considered as the perspective approach to a development of the effective mordenite catalysts for *n*-butane isomerization.

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THE CONVERSION OF LIGHT OIL FRACTION TO HIGH-OCTANE FUEL OVER SUPERHIGH-SILICA ZEOLITES

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ZSM-type zeolites (pentasil family) find extensive use as catalysts of various petrochemical processes. Their catalytic activity in transformations of hydrocarbons of various classes is determined by their molecular sieve and acid properties. The obtained zeolites can be used as the main component of catalysts for refining low-octane gasoline fractions into hydrocarbons.

Superhigh-silica (SHS) ZSM-type zeolites with silica moduli (M) of 100–220 were synthesized using hexamethylenediamine as a structure-forming additive. Physicochemical methods were used to identify them as ZSM-5-type zeolites, determine their degree of crystallinity, specific surface areas, and morphology of crystals, and study the phase and elemental composition. We showed the possibility of synthesizing SHS zeolites with silica moduli of 100–220 with the use of hexamethylenediamine as a structure-forming component.

The SHS catalysts prepared were also tested in the transformation of directly distilled gasoline fraction (initial boiling point 180 °C) of composite West-Siberian oil (19.7 % n-alkanes, 65.1 % iso- and cycloalkanes, 15.2 % aromatic hydrocarbons, octane number 52). Studies were performed on a flow unit with a stationary catalyst bed ($V = 5$ cm^3) over the temperature range 300–420 °C under atmospheric pressure. The volume raw material flow rate was 2 h^{-1}. Reaction products were analyzed by gas chromatography, and gasoline octane numbers were calculated from the chromatographing data. The activities of SHS zeolites in transformations of directly distilled gasoline oil fractions were studied and compared for three samples with silica moduli of 60, 150 and 220.

The results listed in Table show that the concentration of aromatic hydrocarbons in gasolines obtained on zeolites with various silica moduli increases as the temperature grows. Simultaneously, the fraction of isoalkanes decreases, whereas the content of normal and cycloalkanes changes insignifi-cantly. The SHS zeolites obtained can be used in the preparation of effective catalysts for refining low-octane gasoline petroleum fractions.

Table. Reaction temperature influence on the composition (wt %) and yields (wt %) of liquid products of directly distilled oil fraction transformations on zeolites with different silica moduli

Product	Temperature, °C			
	300	340	380	420
	M = 60			
n-Alkanes	10.8	7.7	4.8	4.3
Alkenes	4.2	3.3	2.0	1.6
Isoalkanes C_{5+}	29.7	22.0	18.5	15.9
Cycloalkanes C_{5+}	5.9	5.6	4.6	4.3
Arenes	49.4	61.4	70.1	73.9
Octane number	91	96	100	102
Yield	80	65	54	47
	M = 150			
n-Alkanes	11.6	9.6	8.1	6.5
Alkenes	4.2	3.1	2.5	2.3
Isoalkanes C_{5+}	30.5	28.6	23.6	22.3
Cycloalkanes C_{5+}	4.4	4.2	3.7	2.0
Arenes	49.3	54.5	62.1	66.9
Octane number	91	93	96	98
Yield	80	68	57	50
	M = 220			
n-Alkanes	12.0	10.5	9.2	8.2
Alkenes	4.9	3.5	3.1	2.2
Isoalkanes C_{5+}	36.2	36.1	35.1	34.3
Cycloalkanes C_{5+}	6.6	5.6	5.2	5.7
Arenes	40.3	44.3	47.4	49.6
Octane number	84	86	88	91
Yield	85	73	62	57

These catalysts allow the yield of the desired products to be increased with a simultaneous decrease in the concentration of aromatic hydrocarbons and especially benzene, whose content in gasoline for cars is subject to severe limitations, without additionally modifying them. Zeolites with silica moduli of 60 and 150 were characterized by stronger acid centers and higher concentrations of such centers. Liquid products obtained on these catalysts therefore contained large amounts of aromatic hydrocarbons with high octane numbers. Catalyst acidity decreases substantially as the zeolite silica modulus increases to 220. Transformations of the directly distilled gasoline fraction in the presence of zeolite catalysts resulted in the formation of gasolines with octane numbers exceeding 80 over the whole temperature range studied.

KINETICS OF CO OXIDATION OVER Co-ZSM-5 AND Co-Pd-ZSM-5 CATALYSTS

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Metal-containing zeolites, in particular on the base of ZSM-5, are studied as catalysts of a number of redox proceccеs [1, 2], therefore a research of their mechanism is very interesting. The kinetic regularities of carbon monoxide oxidation on Co-(Pd-)containing zeolite ZSM-5 are investigated in this paper. The kinetics of CO oxidation over active low-loaded metal catalysts – 1.2%Co-ZSM-5 and 0.8%Co-0.5%Pd-ZSM-5 – is observed.

The catalyst 1.2%Co-ZSM-5 is obtained via impregnation of the zeolite with $Co(NO_3)_2$ solution, and 0.8%Co-0.5%Pd-ZSM-5 – with $[Pd(NH_3)]Cl_2$ solution and then with $Co(NO_3)_2$; dried samples are treated in hydrogen at 350 °C during 1 hr. Before kinetic experiments the samples are treated at 100 – 110 °C in reaction gaseous mixture ($1\%CO+10\%O_2+89\%He$) during 1 hr for a stationary state to be established. The kinetics of carbon monoxide oxidation is studied in a non-gradient reactor of flowing type equipped by reciprocating-engine in the temperature interval 110 – 165 °C. Concentration of carbon monoxide is changed from 0.25 to 2vol.% at constant initial concentration of oxygen 20vol.% ($C_{O2}=8{,}93\cdot10^{-3}$ mole/l); oxygen concentration is changed from 5 to 25vol.% at constant initial concentration of CO 1vol.% ($C_{CO}=4{,}46\cdot10^{-4}$ mole/l).

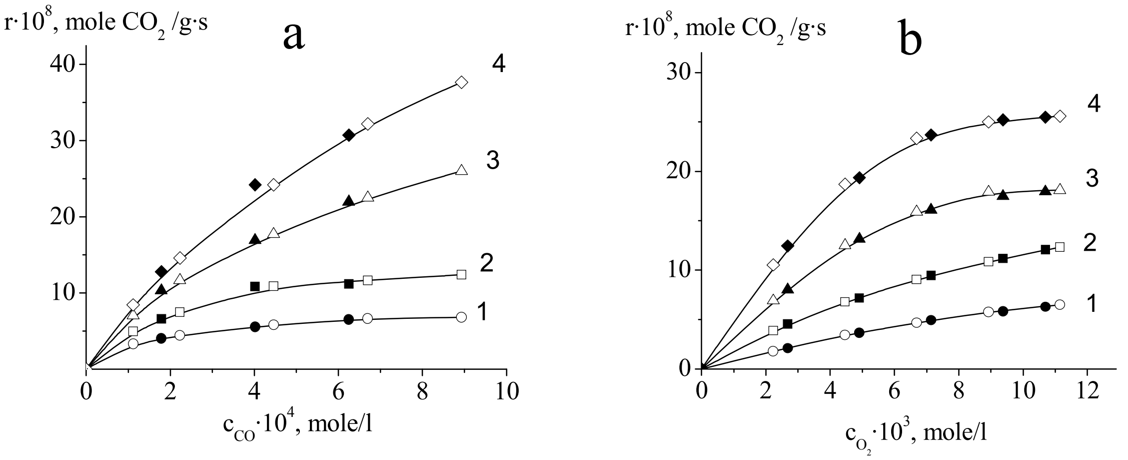

Fig. Dependences of the reaction rate a) on concentration CO and b) on concentration O_2 for the catalyst 1.2%Co-ZSM-5: 1 – 110°C; 2 – 130°C; 3 – 150°C; 4 – 165°C.

The investigation of the CO oxidation kinetics showes that the dependencies of the reaction rate on concentration of reagents for both the catalysts at 110, 130 and 150 °C and at 165 °C for the Co-ZSM-5 have a view of curves with «saturation» which coincide with each other in both direction of the concentration changing (Fig. a, b). Non-linear character of the curves shows reaction order lesser 1. Over the most active system, Co-Pd-ZSM-5, carbon monoxide converses completely at 165 °C. The absence of hysteresis on the dependencies of the reaction rate upon the reagent concentration at all the investigated temperatures implies absence of multiple stationary states, in contrast to Pd-loaded catalysts containing Pd^0 [3].

In the result of the comparative analysis of CO oxidation mechanisms it was established that kinetic dependences of the reaction rate on the Co-ZSM-5 and the Co-Pd-ZSM-5 from concentration of the reagents can be described by Eley-Rideal's mechanism, that intends the opportunity of oxygen adsorption on the catalyst surface both in atomic and in molecular form and the following CO interaction from gaseous phase with adsorbed oxygen (Scheme). At that on the catalyst surface the chemisorption of oxygen happens forming intermediate compounds ZO_2; a formation of ZO arises from interaction of CO with ZO_2 (and very likely in the result of dissociation of chemisorbed oxygen on free active sites of the catalyst surface). The activation of carbon monoxide can be realized at forming of intermediate carboxylated complex [ZOCO*]. At the same time CO is chemisorbed on the catalyst surface in a weak form that agrees with IR-spectroscopy of adsorbed CO (practically complete desorption of adsorbed CO occurs after vacuuming to 0.8 Pa at 20 °C).

$$1.\ Z + O_2 \xrightarrow{k1} ZO_2$$

$$2.\ ZO_2 + CO \xrightarrow{k2} CO_2 + ZO$$

$$3.\ ZO + CO \xrightarrow{k3} CO_2 + Z$$

The expression of the reaction rate is:

$$r = \frac{2k_1k_2 \cdot C_{O_2} \cdot C_{CO}}{k_2C_{CO} + \frac{k_1}{k_3} \cdot (k_2 + k_3) \cdot C_{O_2}}$$

The calculated reaction orders are for the Co-ZSM-5: n_{O2}=0.5-0.6, n_{CO}=0.3-0.6, n=0.8-1.2; and for the Co-Pd-ZSM-5: n_{O2}=0.6-1; n_{CO}=0.5-0, n=1.1-1.

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PP-I-31

KINETICS OF SURFACE IRREVERSIBLE REACTIONS IN TURBULENT FLOW IN THE LONG TIME LIMIT

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Surface reaction play an important role in many physical and chemical processes. Some of numerous applications of the surface reactions include catalytical reactions, several types of electrode reactions, dissolution processes. The overall decay rate of reactants is determined not only by the transport of reactants to the surface but also by the rate of chemical reaction constants. For well-developed turbulence when mixing in turbulent flow considerably enhance transport of reactants to the surface, finiteness of rate of chemical reaction can limit the overall decay rate of reactants.

The evolution of chemical reactants concentration in turbulent flow is described by means of passive scalar theory, when a feedback of reactants to the flow is negligible. In non-stationary problems, as it was shown in [1,2], after short intermediate stage the inhomogeneities of the passive scalar are localized near the wall where the advective mixing is not so efficient as in bulk. These results were generalized on the case of bulk chemical reactions in [3]. In [4] the effect of advective diffusion on the decay rate of the chemicals by the first-order surface fast reaction for well-developed turbulence was analyzed.

Here we analyze decay of chemicals due to an irreversible m-order reaction taking place on a flat surface with finite rate constant in turbulent flow in closed vessel and in the case when a chemicals are contained near the wall by an external field, for example, electric, high-gradient magnetic and centrifugal force fields. Since the reactants are rapidly mixed by turbulent flow, their inhomogeneous distribution must be localized in narrow boundary layer near the reaction surface. So in the limit of well-developed turbulence the surface can be considered approximately as a plane and problem can be treated as one-dimensional. The decay of the concentration n of reactant in closed vessel averaged over velocity fluctuations of the turbulent flow is described by the equation [1]:

$$\Delta_t n = \Delta_x [(k + D_{adv}(x)) \Delta_x n], \qquad (1)$$

where k is molecular diffusion coefficient, $D_{adv} = \mu x^4$ is eddy diffusion coefficient, x is the distance from the wall. The parameter μ is estimated as $\mu = V_L^4/Re\,\nu^3$, where V_L is the characteristic scale of velocity fluctuations, ν is kinematic viscosity, $Re = V_L L/\nu$ is the

Reynolds number. The boundary condition is $k\, \Delta_x\, n|_{x=0} = R_m\, n^m|_{x=0}$, where R_m is the m-order reaction constant.

For the first-order reaction (m=1) the evolution of the reactants particle density is given by $n(t) \sim exp(- \lambda\, t)$ at asymptotically long times. In the limit of low rate constants $R < k^{3/4}\mu^{1/4}$ the decrement λ is estimated as $\lambda = R/L$. For the high rate constants $R > k^{3/4}\mu^{1/4}$ the decrement λ is saturated at the levels $\lambda = \mathrm{L}^{-1}\, k^{3/4}\mu^{1/4}$. These estimations were obtained using two asymptotical solutions of the equation (1), one for the region $x < r_b$ where we can omit the advection term and second one for the region $r_b < x < L$ where we can omit the molecular diffusion term, and then to match these solutions at the boundary point $x = r_b$, where $r_b = (k/\mu)^{1/4}$ is the diffusive boundary layer thickness. The increase of the overall decay rate λ_{adv} due to advection is estimated as $\lambda_{adv} / \lambda_{dif} = R/R_0^{dif}$ for $R_0^{dif} < R < R_0^{adv}$ and as $\lambda_{adv} / \lambda_{dif} = L/r_b$ for $R > R_0^{adv}$, where $\lambda_{dif} = k/L^2$ is the decrement of the concentration due to the molecular diffusion, $R_0^{dif} = k/L$ is chemical rate reaction constant above which the diffusion-limited regime is dominated, $R_0^{adv} = k^{3/4}\mu^{1/4}$.

More precise estimations of decrement λ were obtained by means of variational principle. Representing the concentration as $n(x,t) = g(x)\, exp(-\lambda\, t\,)$, we have

$$\lambda = [\, Integrate\{D(x)\, (dg/dx)^2\, dx\} + R\, g^2(0)\,] / Integrate\{\, g^2\, dx\},$$

where $D(x) = k + D_{adv}(x)$ and we used the boundary condition $k\, \Delta_x\, g|_{x=0} = R\, g|_{x=0}$. So decrement λ can be estimaited in the long time limit by minimizing above expression for some trial function.

In case of the reaction order $m >= 2$ the reactants particle density is given by the power law

$$n(t) = (L/\, R_m\, t)^{1/(m-1)}$$

in the long times limit for $t > L\, r_b/k$.

In the case when a chemicals are contained near the wall by an external field $U/T = f\, x$ the evolution of the reactant concentration is described by equation

$$\Delta_t\, n \quad = \quad \Delta_x\, [(k + D_{adv}\,(x))(\, \Delta_x n + f\, n)\,] \qquad (2)$$

with the boundary condition on the wall $\Delta_x\, n|_{x=0} = (\, R_m/k - f)\; n^m|_{x=0}$. In the limit of well-developed turbulence, $1/f > r_b$, the distribution of reactant concentration in the bulk is determined by $n(x) \sim exp(- f\, x)$ due to the effective mixing while the deviation from that steady distribution is obtained in the boundary layer.

For the first-order reaction (m=1) the evolution of the reactants particle density is given by $n(t) \sim exp(- \lambda\, t)$ at asymptotically long times. Matching the two asymptotical solutions of the equation (2) at the boundary point $x = r_b$, we have

$$\lambda = R\, f/(1 + 1.3\, R\, r_b/k).$$

In case of the reaction order $m >= 2$ the reactants particle density is given by the power law

$$n(t) = (1/f\, R_m\, t)^{1/(m-1)}$$

in the long times limit for $t > r_b/f\, k$.

For an arbitrary potential $U(x)$ gradually increasing away from the wall, a similar estimate is obtained by substituting $f = (Integrate\{ exp(U(0)/T - U(x)/T) dx\})^{-1}$.

Advection-diffusion equations (1), (2) was solved also numerically and these results support the analytical estimates obtained above.

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PP-I-32

NANOPARTICLES AND CATALYSIS

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Interest of chemical and petrochemical industry is presently promoted to nanotechnology. Many institutes work in the fields of preparation of nanocatalysts. Researches of the German scientists [1] showed that nanoparticles in the free state possessed extraordinarily high catalytic activity. But in time the activity falls to the level of traditional heterogeneous catalysts. It is related to the active elements of surface of nanoparticles. There are no methods of synthesis of nanoparticles described in literature allow to save them for a long time in a reactionary volume in the free state. Possibly, therefore practically all of scientific researches in this field are directed on the study of chemical reactions with application of nanoparticles of catalyst on carrier.

The aerosol nanocatalysis technology is used nanoparticles of catalyst without carrier. They are generated in situ. The catalytic system is included the moving catalyst particles and dispersing an inert material. It is come by mechanical and chemical activation. The size of formed nanoparticles is measured the method of transmission electronic microscopy (TEM) and EXAFS spectroscopy methods. The results showed there are nanoparticles of catalyst of 8-100 nm as size in the reaction zone. Perhaps, there are the smaller particles. But they are difficult to detect because of the shielding of larger particles [2].

It was considerated the effect of impact of glass ball with the catalyst particle. It was noted that with decreasing particle diameter of the catalyst its surface is growing, increasing the number of active impacts and the length of free runs of molecules. So it would lead to a coagulation of nanoparticles of catalyst with a dispersing material. But the experiment was proved that such events proceed only at the initial moment of the reactor. Then happening «saturation» surface of dispersive material by the catalyst and the system is in dynamic equilibrium as sorption-desorption.

Coagulation of nanoparticles is studied as part of reducing their activity. It's found that in aerosol nanocatalysis technology the particles of catalyst may disappear from the reaction zone by their impacts with dispersing materials or by coagulation with one another. It's calculated the coagulation of nanoparticles of catalyst with one another (Table). The life-time of nanoparticle was calculated near 10^{-5}-10^{-7} sec. [3].

Table

The calculation of time of coagulation of nanoparticles with different sizes

Reducing the number of particles, times	The time decrease of concentration (c) for particle with such sizes		
	20 nm	50 nm	100 nm
2	$2{,}4{*}10^{-7}$	$3{,}8{*}10^{-6}$	$4{,}5{*}10^{-5}$
5	$9{,}7{*}10^{-7}$	$1{,}5{*}10^{-5}$	$1{,}4{*}10^{-4}$
10	$2{,}2{*}10^{-6}$	$3{,}4{*}10^{-5}$	$2{,}9{*}10^{-4}$
100	$2{,}4{*}10^{-5}$	$3{,}8{*}10^{-4}$	$3{,}0{*}10^{-3}$

To prevent such coagulation and to save nanoparticle of catalyst in the free state in the reactor may by mechanical effects in 10^7 impacts in 1 m^3 of reactor per 1 sec. This fact is realized in aerosol nanocatalysis technology at frequency of catalytic system the 2-6 Hz. These fluctuations of reactor multiply to the number of dispersive material by the particles impacts with one another.

Thus, aerosol nanocatalysis technology is a unique technology that could be used the nanoparticles of catalyst in a free state. So, their catalytic activity is increased.

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Section 2.

Physico-chemical and mathematical fundamentals of the processes in chemical reactors

BRØNSTED ACIDITY MEASUREMENT OF FIBERGLASS MATERIALS BY H/D-EXCHANGE METHOD IN A PLUG-FLOW REACTOR

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The catalysts based on silica fiberglass materials can be efficiently used in many gas-phase and liquid-phase catalytical processes [1-3]. However, the physicochemical properties of fiberglass materials, specifically the Brønsted acidity, were not studied in detail. Most frequently used techniques for acidity study could not be applied to fiberglass materials because their structure is disrupted on a sample pretreatment.

For *in situ* characterization of catalyst acidity, i.e. under conditions close to real operating conditions of the catalyst, the isotope-dynamic method (so called SSITKA – Steady-State Isotopic Transient Kinetic Analysis) could be used. This method is unique that being non-steady-state (relaxational) it allows carrying out the kinetic analysis under process steady-state conditions, when the rates of all reaction stages and the catalyst condition remain constant.

In our work, we developed the H/D-exchange technique based on SSITKA for determination of Brønsted acidity of fiberglass materials. The experiments were carried out in a plug-flow reactor at 500°C. Under the dynamic adsorption-desorption equilibrium the H_2 flow was replaced stepwise by the D_2 flow with the following mass-spectrometric analysis of changes in labeled atoms concentrations (so called isotopic response curves) at the reactor outlet. Based on the observed concentrations of the isotope molecules (H_2, HD, and D_2), we calculated the time dependencies of the atomic fraction of labeled hydrogen atoms (α_D) and the molecular fraction of HD (f_{HD}) in the gas phase. The numerical analysis of $\alpha_D(t)$ and $f_{HD}(t)$ response curves was carried out in terms of strict mathematical model taking into account three kinetically resolvable types of isotope exchange on the catalyst surface, namely, 1) homoexchange without participation of OH groups of the catalyst (type I); 2) simple heteroexchange between one deuterium atom of D_2 in gas phase and one hydrogen atom of the catalyst (type II); 3) multiple heteroexchange between D_2 molecule and two hydrogen atoms of the catalyst (type III), and also the diffusion of deuterium atoms in the bulk of glass fiber.

For investigation, we used non-modified fiberglass material and that modified by alumina sulfate. The numerical analysis of the response curves showed that the H/D-exchange obeys the type II mechanism, i.e. it proceeds on the single sites. The modification of the catalyst results in multifold increase in the integral exchange rate which is due to the appearance of additional acid sites. Part of them is located in the subsurface layers of fibers. Besides, the new type of sites is appeared; these sites are located at the external surface of fibers and do not exist in non-modified sample. On the basis of the numerical simulation of H/D-exchange dynamics, we revealed the difference in the H/D-exchange rates with the different acid sites in the subsurface layers of fibers, to estimate the concentration of these sites, and also to determine the overall amount of the exchangeable hydrogen atoms in the catalyst bulk. When compared the H/D-exchange rates over the fiberglass materials with the results obtained over the model samples (zeolite HZSM-5 and aerosil), we estimated the BAS strength of fiberglass materials in proton affinity scale. It was shown that the strength of Brønsted acid sites of fiberglass materials is comparable to that of zeolite.

The developed technique could be used for kinetic investigation of any catalytic processes taking place on fiberglass materials.

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OPTIMIZING OF CHEMICAL REACTORS OPERATION USING A PROGRAM SYSTEM FOR BEST MIXING OF RAW MATERIALS

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In the chemical technology and metallurgy some productions (glass, ceramics, Zn, Cu, Pb, etc.) use a considerable number of initial solid raw materials that differ in their chemical, phase and granulometric content.

The stable operation of the chemical reactors and furnaces requires for a prolonged period of time a mixture with a fixed composition, obtained by mixing of sometimes 10-12 types of initial raw materials and semi-finished products. In this connection a program system was developed, which is a part of the automated system for control of the technological processes. Its main objective is, based on the various raw materials, to offer the most suitable mixture for the specific chemical or metallurgical production.

In this specific case the example taken is the mixing of zinc concentrates for roasting in fluid bed furnaces as a part of the hydrometallurgical production of zinc.

Today eighteen components are under control in the zinc concentrates, which by nature are a polymetallic raw material. In order to avoid difficulties in the process of roasting and leaching, a significant part of these components should be in concentrations lower than certain maximum values.

A program for calculating mixing proportions for zinc production aimed at creating optimal mixes of the zinc concentrates is developed. The program consists of three major modules:

1. Establishment of the necessary data, corrections, processing and drawing of the whole initial information. The program allows easy introduction and storage of data for all offered, received and processed zinc concentrates. Access to the data is easy and an inquiry or a comparison can be quickly made and used in buying zinc raw materials.

2. Calculation of receipts for mixing proportions in two possible regimes:

Automatic Regime. It serves to obtain the proportion of all concentrates at determined limiting conditions. The calculations are made by complete combinations of the entered concentrates and calculating all possible outcomes. The mixes are arranged by an optimizing criterion «Zn dissolved in H_2SO_4». The components that fail to fall within the given limitations are registered.

A basic moment in the automatic regime is the selection of an optimizing concentrate and the concentrates that will be altered at different levels. This happens at the formation of every work base.

Another important point is selecting the step of change in the quantity of every separate concentrate that takes part in the mixing proportion.

Consumer Regime. In it concrete quantities in percents are assigned and there is no checking of limiting conditions.

Both regimes give data for the possible chemical and phase content of the calcine as well as for the expected amount of outgoing dust.

3. Drawing of the final results can be made on the screen, on a printer or saved as a file.

With the help of specialists from Works for Non-Ferrous Metals – SA, Plovdiv data is gathered for the various processed concentrates and mixes are calculated in both automatic and consumer regimes.

The following has been done to achieve this goal: The data for the composition of the processed zinc concentrates are entered and actualized; receipts in automatic and consumer regime are calculated for the processed concentrates; a diverse number of optimizing concentrates and ones that vary from first to fourth level have been worked with. A different step is selected for changing of all concentrates at the calculation of mixes in automatic regime.

The calculations made show that when the concentrates are appropriately proportioned a mix with a very good chemical composition is obtained. This leads to a stable regime of oxidized roasting in fluid bed reactor, a constant in its chemical and phase content calcine and good chemical-technological indexes of both roasting and leaching.

THERMAL MODES FOR THE CSTR WITH COMPLEX CHEMICAL REACTIONS

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The investigation of thermal modes for continuous stirred-tank reactor (CSTR) is useful in two aspects. First, it gives a contribution in the scientific basis of the safety of industrial processes, and, second, it widens our knowledge on the mechanisms of the birth/death of the *e. g.* self-oscillation regime. The dynamic behavior of CSTR with a simple reaction is well investigated [1]. However the problem of the dynamic behavior of CSTR remains still non-solved. In this work, some results of investigations of CSTR with complex reactions have been obtained.

Autocatalysis. It was shown that, depending on the determinant parameters, either one or three steady states can be realized in CSTR with an autocatalytic reaction. Unlike well-investigated first-order kinetics, for an autocatalytic reaction at certain values of parameters (in particular, at not very high values of Semenov criterion), there is a restricted temperature range that is fundamentally inaccessible under stationary conditions. This result is a sequence of the non-linearity of the autocatalytic kinetics, and in the coordinates *temperature – conversion* it appears as **isola**. The mechanism of **isola** formation has been formulated. It is shown that for a strongly exothermal reaction there is possible the existence of self-oscillation regimes only for steady states that are located on the unstable part of the right branch of a thermal isoclinal line (the limit cycle on the phase plane).

The mechanism of stability change has been investigated. Depending on the values of parameters (in particular, at the variation of the Damköhler criterion), both soft and stiff death of the limit cycle can be realized.

Concurrent reactions. For CSTR with two concurrent exothermal first-order reactions, the investigation of the mechanisms of birth and death of self-oscillations has been carried out using third focus coefficient, whose sign is an indication for the mechanism of the birth of self-oscillations. The calculations have been carried out for the steady states that are located on the unstable part of the thermal isoclinal line. It was shown that, in case that a steady state is located near the borders of the unstable part of the thermal isoclinal line, so the birth of self-oscillations proceeds by a stiff mechanism, resulting from the closeness of trajectories. The arising self-oscillations have right away final amplitudes. In this case two limit cycles exist around the steady state – a *stable* and an *unstable* ones. If a steady state is located far from the borders of the unstable part of the thermal isoclinal line, so soft birth of self-oscillations (limit cycle) takes place. In this case the amplitude of self-oscillations is growing smoothly. The solution of the non-steady problem has confirmed the detected mechanisms of the birth/death of self-oscillations.

Consecutive reactions. For CSTR with a two-step consecutive reaction (both stages being exothermal first-order processes), analysis of the multiplicity of the steady states and the mechanism of birth/death of self-oscillations have been carried out. A region of five steady states was discovered for the first time. Its evolution with the change of the ratio of the activation energy of the first stage to that of the second stage has been investigated. It was shown that this region arises within the region of three steady states. With the growth of the above ratio, it is elongated and partly oversteps the limits of the region of three steady states. This part of the domain contains just only three stationary states.

For a definite set of kinetic parameters in the parametric space *Semenov criterion – Damköhler criterion,* a region of the existence of self-oscillations was found. For the region of one steady state, it was shown that at the lower border of the self-oscillation region (small values of *Semenov parameter*) their birth occurs by a soft way. The steady state becomes unstable and gives rise to a stable limit cycle. At the upper border of the self-oscillation region (large values of *Semenov parameter*), stiff death of self-oscillations takes place: a stable limit cycle is joined with an unstable limit cycle. The unstable limit cycle arises at the change of the steady state stability.

For the region of three steady states it was demonstrated that at lower border of the self-oscillation region, the oscillation arise by a stiff way, by the mechanism of a loop formation.

This work was supported by the Russian Foundation of Fundamental Researches, the grant No. 06–03–32053–a.

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DEACTIVATION OF Rh(410) SURFACE IN THE COURSE OF CO OXIDATION UNDER HIGH OXYGEN PRESSURES

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CO oxidation is one of the most studied reactions, due to its ecological importance in cleaning of the tailing gases. But till now there is no common agreement in the understanding of the active state of catalysts in the course of reaction: is it oxide or clean metal surface? This work was devoted to studying the influence of oxide formation under reaction conditions on activity of Rh(410) single-crystal in CO oxidation.

A complex of physical methods was used in the study: temperature-desorption spectroscopy (TDS), temperature-programmed reaction (TPR), low-energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS). The experiments were performed in UHV chamber with residual gas pressure in the chamber ~ 1×10^{-10} mbar. High-pressure experiments were performed in pretreatment chamber[2]. The Rh(410) (4(100)×(110)) surface was choose as a model of a real defective catalyst surface.

It was shown by XPS and ex-situ TDS&LEED studies that at high ratios $R=p(O_2)/p(CO)>10$ and temperature range 300-800 K, the oxide layer forms on the surface of the Rh(410). According to TPR data, the activity of surface covered by oxide is lower, than the clean surface (i.e. at R<10), Fig. 1. The reaction order $n_{O2} \approx -0.6$ at T>550 K. At lower temperatures the dependence lg(W) on lg(p_{O2}) has volcanic shape and finally, at T ≈ 350 K $n_{O2} \approx 1.2$. According to literature [1] at high θ_{CO} (i.e. low temperature) n≈ 1÷2, but at low θ_{CO} and existence of atomic oxygen on the surface (i.e. at T>500 K) the reaction order must be

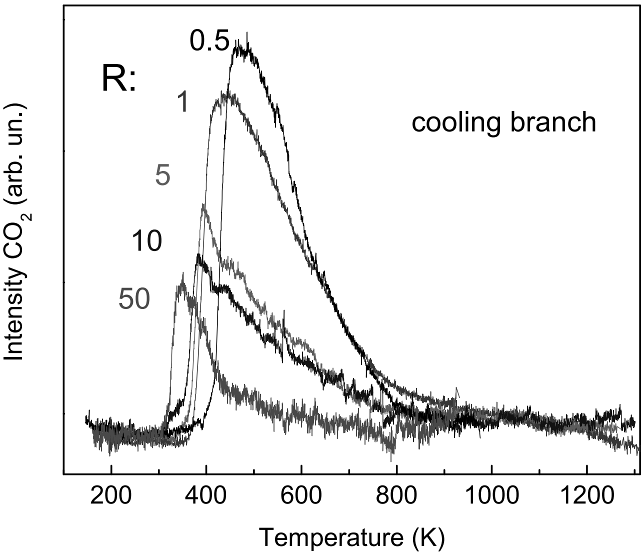

Fig. 1. The decreasing of the catalytic activity of the Rh(410) surface in CO oxidation with increasing of ratio $R=p(O_2)/p(CO)$.

in range 0-1. In our case $n_{O2} \approx -0.6$ – this can be explained only by blocking of the rhodium surface by low-reactive oxide.

The activation energy was found to decrease in range 300-400 K from 33 to 23 kcal/mol. In this temperature range, according to [1], the apparent activation energy is close to activation energy of CO desorption. Indeed, our TDS experiments give the E_{CO} = 23-29 kcal/mol. The decreasing of the apparent activation energy can be explained by changing of the atomic oxygen reactivity at higher coverages, observed as in [1] as well as in our experiments [2].

The activation energy E_r of $CO_{ads}+O_{ads}$ step can be found by analyzing the rate of reaction in 550-800 K range [1]. In this range the surface is covered be oxygen (not by CO_{ads}), therefore $r \sim \exp(E_{CO} - E_r)$. The determined by this way $E_r = 21 \div 25$ increases when R increases – this definitely points to formation of low-reactive oxide on the rhodium surface.

Thus, we found, that at high ratios $R = p(O_2)/p(CO) > 10$ and temperature range 300-800 K, the oxide layer forms on the surface of the Rh(410). This leads to decreasing of the catalytic activity of the rhodium surface.

Acknowledgements: This work was supported by the RFBR Grant # 08-03-00454, 08-03-00825, INTAS # 05-109-5039.

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EPR ENLIGHTED PHYSICO-CHEMICAL FUNDAMENTALS OF PROPANE ODH OVER V_2O_5–SiO_2 AND V_2O_5–Al_2O_3

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The EPR spectral intensity of VO_x/SiO_2 catalysts prepared by flame-pyrolysis (FP) was increasing during ODH reaction, though keeping constant the spectral profile. This pattern is due [1,2] to isolated, tetragonally distorted, paramagnetic complexes of V^{4+} forming a monolayer on the sample surface and with a V^{4+} - O bond perpendicular to it, as indicated by the high value (≅3.60) of the EPR spectral parameter:

$$B = (g_{//} - g_e) / (g_{\perp} - g_e)$$

Higher values of B correspond to shorter out-of-plane bonds with oxygen or to longer distances of the oxygen ligands in the basal plane, both these situations leading to a stronger out-of-plane V^{4+} - O bond. A 10%V-Si-O catalyst (V10Si) prepared by FP has been compared with a sample of the same composition, but prepared by impregnation (V10Si-i).

EPR spectra of the same kind were observed with both of them, but characterized by a bit weaker V^{4+} - O bond ($B \cong 3.50$) with the latter sample. Furthermore, some Ferro Magnetic Resonance (FMR) patterns [3-7] added to the EPR pattern of V10Si-i, due to magnetic particles forming clusters with different shape and/or size, never observed with the FP-prepared catalysts. Therefore, a higher V^{4+} dispersion characterises the FP-prepared V10Si samples with respect to the V10Si-i, prepared by impregnation. It is well known that V^{5+} and not V^{4+} ions are the catalytically active centres, the latter simply being a reaction intermediate. However, V^{4+} ions showed useful labels to characterise the catalysts. For example, FT-IR spectra evidenced a polarisation of SiO_4 groups with the FP-prepared sample only, attributable to incorporation of V into the silica framework. V-O-Si bonds can be partly hydrolysed in this case, as indicated by the high concentration of SiOH and VOH groups shown by the same technique. The EPR spectra indicate that these groups pertain to isolated V species, which are very active and selective for propane ODH.

The comparison between V10Si and V10Si-i samples, evidenced by EPR analysis, indicates that a higher strength of the out-of-plane bond between V^{4+} and O corresponds to samples characterised by a lower oxygen availability and hence with lower catalytic activity, but higher selectivity. Indeed, the activity data [8] show that, under anaerobic conditions and at comparable activity, the V10Si sample gave a substantially higher selectivity to propylene with respect to V10Si-i.

The investigation has been extended to a VO_x/Al_2O_3 sample with 10%V (V10Al). A by far smaller (≅1.47) value of the B parameter was obtained with it. Therefore, a lower selectivity, accompanied by a higher conversion, was expected with V10Al with respect to V10Si, at least under anaerobic conditions, i.e. when the dispersion of the active sites, and not the presence of unselective O species, controls the selectivity of the process. This has been indeed observed [9], confirming the reliability of the V^{4+}-EPR data to enlighten the physico-chemical fundamentals of this catalytic process. Furthermore, the formation of V^{4+}-based ferromagnetic domains was observed with VO_x/Al_2O_3 samples even at very low V concentrations, at difference with VO_x/SiO_2. This further confirms that weak out-of-plane V^{4+} - O bonds, as with V10Al, are accompanied by ferromagnetic domains formed of V^{4+} paramagnetic centres tightly interacting with each other. These centres, on the other hand, come from the reduction of V^{5+}-based active sites. Therefore, in these cases also the V^{5+}-based active centres must be close to each other or grouped into clusters.

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HYDRODYNAMICS OF GAS-SOLID FLUIDIZED SPOUTED BEDS USING OPTICAL PROBES AND GAMMA RAY COMPUTED TOMOGRAPHY

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Gas-solid fluidized spouted bed has been used widely in various applications that include both chemical and physical processes, including chemical vapor deposition (CVD) coating. Unfortunately, the scale-up and design of the current processes using gas-solid spouted beds have been based on empirical approaches and are operated as «black boxes» due to lack of fundamental understanding of the hydrodynamics of spouted beds. Hence, in this work a new optical probe has been developed to study the solids and gas holdup profile and solids velocity in gas-solid spouted beds. The technique has been used to investigate these parameters in two spouted beds of 3 inch and 6 inch diameter using solids that give match and mismatch in hydrodynamics similarity. Gamma ray computed tomography has been used to evaluate and validate the measurements of the newly developed optical probe and to investigate the time averaged cross sectional distribution of both solids and gas holdups.

In this presentation, the results and findings will be discussed.

CFD-CALCULATION OF MALDISTRIBUTION OF EFFECTIVE HEAT CONDUCTIVITY COEFFICIENT IN A REGULAR PACKING OF SPHERICAL PARTICLES

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Primary results of computational investigation of fundamental regularities of transversal heat transfer in a simple-packed beds of balls in a slab are presented. Balls are situated in the nodes of cubic or rhombic or mixed cubic-rhombic lattices and are non-zero heat conductivity. Relative heat conductivity of the balls $\Lambda = \lambda_{cat} / \lambda_{gas}$ was varied from 0.01 to 100. Number of balls layers from one wall of a slab to another one was set as 1, 2, or 4 at a constant slab width. Porosity of each of the packing is equal to ca 0.62.

One wall of a slab was hot, and another one – cold. Gas flow direction is parallel of cubic edges or of rhomb diagonals. At such statement, flow pattern is symmetrical, but temperature field is anti-symmetrical. By this, total heat flux throw the input and output boundaries of the computational cell is idem, and total heat flux throw the arbitrary wall-parallel section of the computational cell is idem too.

Calculations were carried out at ANSYS FLUENT 6.3.26 program package at cluster system NCS-160 of Siberian Super-Computer Center. Four processors were used. Tasks discrete dimension were depended on lattices structure and were from about 2500000 to about 5000000 control volumes for computational cell.

Some results of modeling are adduced on a figure below.

Coefficient of effective transversal heat conductivity λ_{eff} is defined from equation:

$$(\lambda_{gas} + \lambda_{eff}) \frac{\partial < T >}{\partial y} = Q_{wall} / S_{wall}, \quad \text{where}$$

$Q_{wall} = \int\limits_{S_{wall}} \lambda_{gas} \frac{\partial T_{gas}}{\partial y} ds$ – integral wall heat flux;

$< T(y) >= \frac{1}{S(y)} \int\limits_{S(y)} T ds$ – averaged temperature profile;

y – dimensionless transversal coordinate (normal to slab walls).

Integral convective heat flux is defined as $Q_{conv}(y) = \int\limits_{S(y)} V_y \cdot (\rho C_p \cdot T)_{gas} ds$.

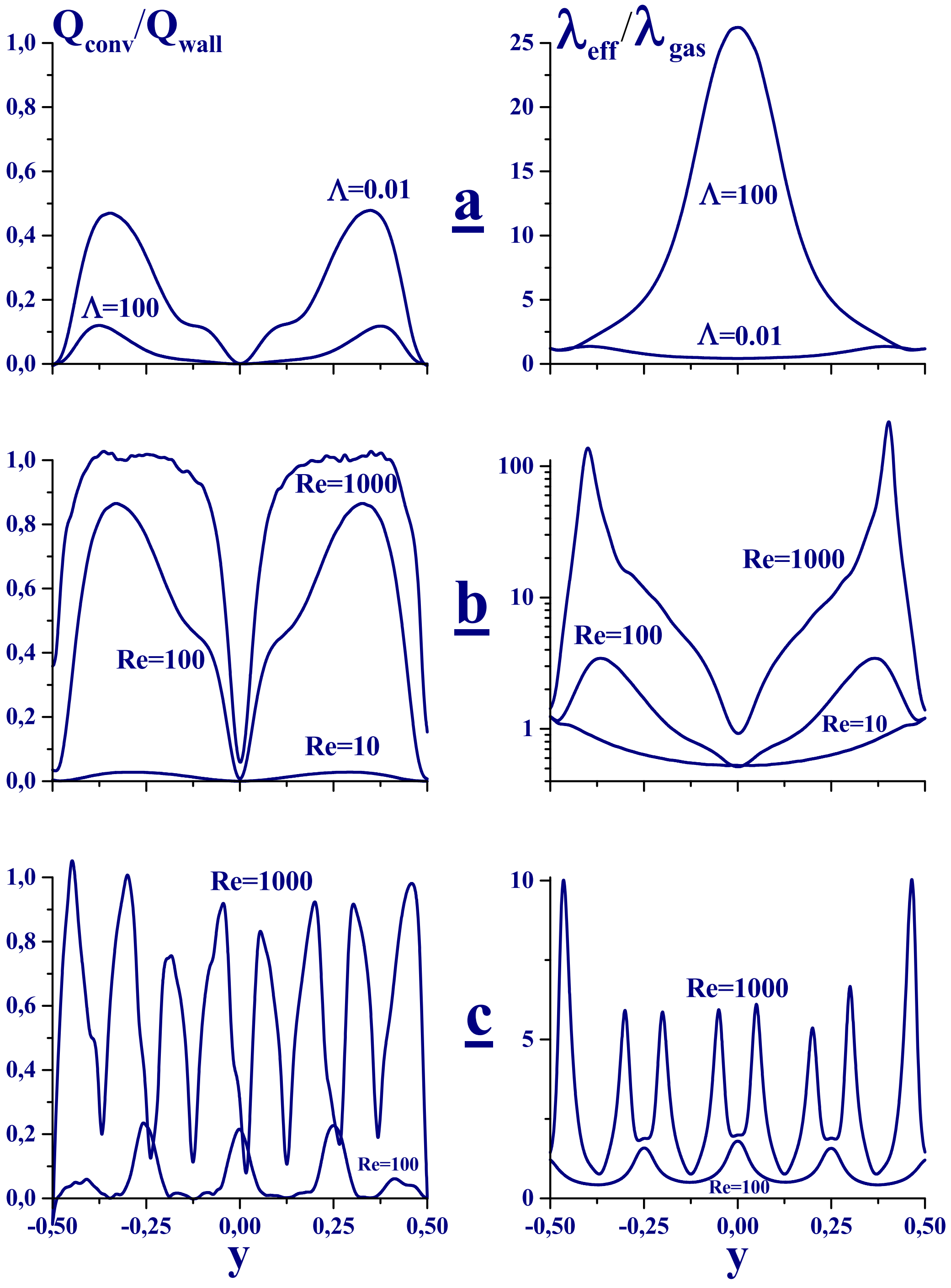

Fig. 1. Dimensionless maldistributions of convective heat flux (left plots) and effective transversal heat conduction coefficient (right plots).
a – single-layer cubic packing, $\mathrm{Re} = 100$;
b – single-layer rhombic packing, $\Lambda = 0.01$;
c – four-layer mixed cubic-rhombic packing, $\Lambda = 0.01$.

PP-II-8

INVESTIGATION OF NONLINEAR PATTERN FORMATION IN CATALYTIC CO OXIDATION BY MEANS OF PARAMETER CONTINUATION AND JACOBIAN-FREE NEWTON-KRYLOV METHODS

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Heterogeneously catalyzed reactions on single-crystal surfaces exhibit a rich variety of nontrivial spatiotemporal patterns [1]. The well-known example of relatively simple reaction system demonstrating chemical wave propagation and spatial pattern formation is the $CO+O_2$ reaction over platinum group catalysts. Great importance in the industry and ecology provides a strong motivation for analysis of the reaction dynamics subject to external conditions.

A number of strategies can be used to analyze typical spatiotemporal phenomena in heterogeneous catalysis as functions of driving parameters. The first approach is a dynamic modeling of evolution processes by means of stochastic or deterministic simulators. The second approach includes fixed-point and path-following computations of steady state equations and bifurcation analysis.

The only dynamic simulations do not allow one to determine the complete set of possible spatiotemporal patterns and construct the bifurcation diagrams showing the regions of different structures on a plane of model parameters. Here we present the combined strategy, which allows us to perform comprehensive analysis of propagating reaction fronts, traveling pulses, motionless localized structures and other spatiotemporal patterns in surface chemical reactions. It is based on the modern numerical methods such as an arclengh continuation, Jacobian-free Newton-Krylov-GMRES method with time-stepper based preconditioning [2]. Our approach allows us to study the large-scale systems of non-linear equations in efficient way.

Deterministic approach. We focus on reaction-diffusion equations (RDEs) for catalytic CO oxidation, which contain mean-field rate equations for local chemical kinetics and Fick's law for transport of mobile species:

$$\frac{\partial \mathbf{и}}{\partial t} = \mathbf{D}\frac{\partial^2 \mathbf{и}}{\partial x^2} + \mathbf{f}(\mathbf{и}). \tag{1}$$

Here, $\mathbf{и}(x,t) = \left[\theta_{CO};\theta_{O};\theta_{O_V}\right]^T$ – concentrations of CO_{ads}, O_{ads} and subsurface oxygen; $\mathbf{D} = \mathrm{diag}(d_i)$, $(i = 1,2,3)$ – diffusion coefficients of adsorbed species; $\mathbf{f}(\mathbf{и})$ describes the adsorption, desorption, and reaction kinetics in terms of subsurface oxygen model [3]:

$$\begin{cases} f_1(\mathbf{и}) = k_1 P_{CO}\left(1 - \theta_{CO} - \theta_{O} - \theta_{O_v}\right) - k_{-1}\theta_{CO} - 4k_3\theta_{CO}\theta_{O} - 4k_5\theta_{CO}\theta_{O_v}, \\ f_2(\mathbf{и}) = 4k_2 P_{O_2}\left(1 - \theta_{CO} - \theta_{O} - \theta_{O_v}\right)^2 - 4k_3\theta_{CO}\theta_{O} - k_4\theta_{O}, \\ f_3(\mathbf{и}) = k_4\theta_{O} - 4k_5\theta_{CO}\theta_{O_v}. \end{cases} \qquad (2)$$

Two types of solutions are of interest: spatially homogeneous steady states and localized structures. Since localized structures (pulses) do not change their shape and propagate with constant velocity, they are described by the following equation:

$$0 = \mathbf{F}(\mathbf{и}, v) = \mathbf{D}\frac{\partial^2 \mathbf{и}}{\partial \eta^2} + v\frac{\partial \mathbf{и}}{\partial \eta} + \mathbf{f}(\mathbf{и}), \qquad (3)$$

subject to specific boundary conditions. Here, $\eta = x - vt$ is a new coordinate in a co-moving frame, v – velocity of pulse propagation. If $v=0$, the immobile localized structures are described.

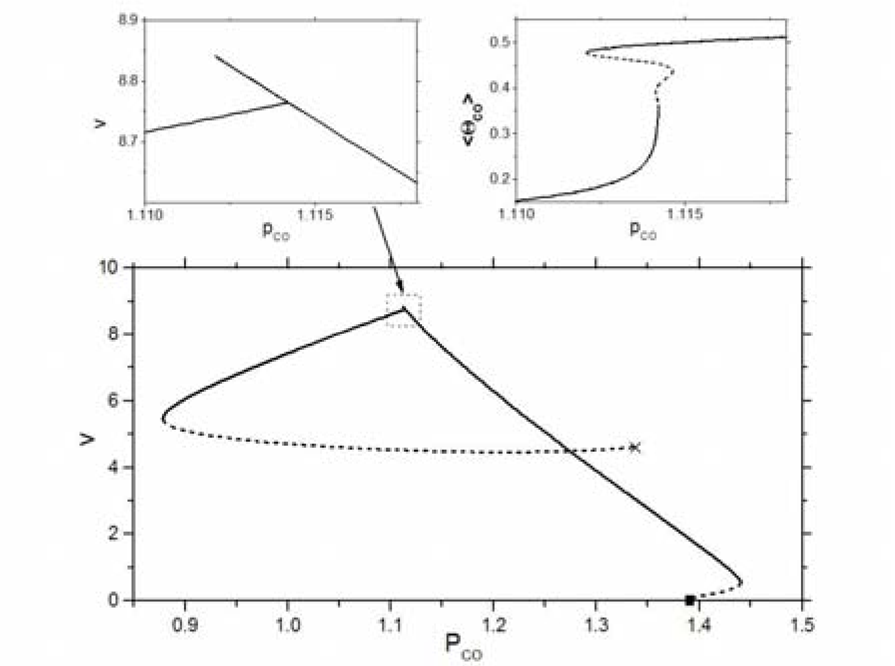

Fig. 1. Dependence of the pulse propagating velocity on CO partial pressure;
$k_1=1$; $k_{-1}=0.2$; $k_2P_{O2}=0.5$; $k_3=250$; $k_4=0.03$; $k_5=0.02$; $d_1=100$, $d_2=d_3=0.01$

Figure 1 shows an example of parameter continuation using P_{CO} as a bifurcation parameter. Here, the stable (unstable) branches are shown by solid (dashed) curves. Two main types of stable traveling pulses were found. The first type, existing at relatively low CO pressures ($P_{CO}<1.113$), is represented by a CO-rich zone moving along an O-covered background. The second one is represented by a predominantly oxygen covered region which is able to exist and propagate on an CO-covered background. In both cases, the traveling pulses give a region of enhanced reaction rate as compared to the background phases with low reactivity. There is a small range of P_{CO} values where the different stable pulses coexist, as demonstrated on the upper insets of Fig. 1. One can see that a transformation from the pulses of the type-1 to the pulses of the type-2 occurs via a cascade of bifurcations.

Upon P_{CO} increasing, the pulse solution loses its stability via a saddle-node bifurcation and, eventually, it is transformed to an unstable immobile solution via a «drift-pitchfork» bifurcation (marked by a solid square).

Upon P_{CO} decreasing, the traveling pulse solution also loses its stability via a saddle-node bifurcation at $P_{CO} \approx 0.88$. The unstable branch is visually «terminated» in a point marked by cross. Actually, this point is also a turning point, but the new branch cannot be seen on the $v(P_{CO})$ dependence because the new unstable solution has the same propagating velocity as the previous one. The new unstable branch is represented by a bound state of two pulses.

In summary, using the modern «matrix-free» computational technology, we were able to construct the detailed bifurcation diagrams showing the regions of different spatiotemporal patterns in dependence upon the model parameters.

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A REACTOR FOR DYNAMIC HIGH PRESSURE-TEMPERATURE REACTIONS IN GAS PHASE

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Construction of reactor for gas reactions at high pressures and temperatures in dynamic regime is proposed. Novelty of the construction consists in several items. The reactor represents a system «cylinder-piston» made from aluminium alloys, work surfaces of which covered by chemically, mechanically and thermally stable aluminium oxide Al_2O_3 prepared by thermo-electrochemical oxidation technology. The piston remains static whereas the cylinder is a moving part; this allows to control the technological regimes easily by means of regulation of pressure in reaction chamber. Necessary air-tightness of system is reached thanks to size and surface fitting of cylinder and piston without a use of traditional sealing rings. High antifriction characteristics of work surfaces from aluminium oxide allow to refuse oiling of system «cylinder-piston»; this not only prevents a contamination of reaction products but also allows to raise the temperature of process without a fear of carbon smut. The design makes provision for efficient system of maintenance of steady-state conditions by means of control of basic parameters of process. The simplicity of the construction may be an advantage in the case of use of similar reactors in the processes of petrochemical synthesis, especially in «field» conditions, for example, at processing of casing-head gas on oil well.

PP-II-10

CALCULATION OF INDUSTRIAL CATALYTIC REACTORS FOR THE SYNTHESIS OF NON-OZONE-DEPLETING SUBSTANCES

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The Montreal Protocol on Substances that Deplete the Ozone Layer (ODS) issued a new challenge on the processes for non-ozone-depleting substituents (NODS) manufacture.

In cooperation with other Russian institutions FSUE «Russian Scientific Center «Applied Chemistry» (RSC ACh) carried out a lot of work on changeover of industrial sector to such novel chemicals. This research resulted in a new family of hydrofluorocarbons produced under Russian trademark «hladon»: HFCs 134a (CF_2CFH_2), 152a (CF_2HCH_3), 125 (CF_3CF_2H), 32 (CH_2F_2) etc.

The applied method was that of gas-phase hydrofluorination catalyzed with chromium-magnesium fluoride catalyst (CMFC).

The major steps of the work were follows:

1. Optimization of the supported catalyst composition.

Our search for suitable CMFC formulations was accelerated considerably thanks to a newly developed computational method for forecasting of CMFC activity depending on active component (AC) concentration on the catalyst surface. According to our calculations CMFC activity hits its maximum when the support specific area is $95 m^2.g^{-1}$ and Cr (III) concentration is 9,4 %. Our tests confirmed both the calculation results and the applicability of the proposed mathematical model.

2. Mathematic model for the process of gas-phase catalytic hydrofluorination.

The kinetic principles of CMFC-catalyzed hydrofluorination of trichloroethylene and 1,1,1-trifluorochloroethane in a continuously operated laboratory-scale plant were studied in detail. Our mathematical model represented the gross process through 21 stages. The related kinetic model described variations in both feedstock and intermediates concentrations under isothermal conditions. LSODA method was used for numerical integration of the ordinary differential equations system. The search for constant values was considered as the task of regression analysis. The functional minimization was carried out using Gauss-Newton method.

Our tests confirmed the mathematical model adequacy.

3. Design of industrial reactors.

Starting with the obtained results we proposed the flow diagram for gas-phase synthesis of 1,1,2-tetrafluoroethane from trichloroethylene.

The above industrial process optimization method proved to be also applicable in updating of processes for other NODS synthesis.

TRICKLE-BED CATALYTIC REACTOR DESIGN. MATHEMATICAL MODELING AND MODEL VERIFICATION

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Multiphase catalytic processes are now widespread in industrial practice. They are usually implemented within two reactor types, i.e. trickle-bed reactors and slurry reactors. In the former catalysts with grain dimension 2-4 mm are used, in the latter – finely dispersed catalysts with grain dimension 50 mkm and less [1].

In spite of multiphase processes wide spreading, design and development of reactors for their implementation usually cause significant difficulties [1 - 3].

The present work proposes a mathematical model for trickle-bed reactors, which describes main physico-chemical processes occurring in such reactors, i.e. mass transfer from gas to liquid and from liquid to solid surface, diffusion in catalyst pores, chemical reactions on catalyst active surface, taking into account incomplete wetting of catalyst grain surface and liquid phase volume changes during the reaction. In order to calculate the diffusion rate inside the catalyst pores, a quasi - homogeneous model of catalyst pellet is accepted.

Taking benzene hydrogenation on Pt/C catalyst with the kinetics described in [4] as the model reaction, mathematical modeling of a trickle-bed reactor is performed. Influence of temperature, pressure, liquid flow rate per cross-section unit, gas flow rate, catalyst grains dimension and susceptibility towards diffusion on the reaction rate and on the catalyst effectiveness factor has been investigated.

It has been established that in broad range of parameters' values the mode of reactor operation approaches the external diffusion regime due to the limitations of mass transfer rate from liquid to solid. Rates of heat and mass transfer from gas to liquid and from liquid to solid surface were calculated using conventional correlations [5-8].

In addition, regimes of catalyst action have been investigated with the assumption of non-complete grain impregnation with an active component. It has been established that in such type of reactors a catalysts with small impregnation depth should be used, because in the conditions of three – phase process internal part of the grain is not available for the reactants. It was also shown that optimal catalyst impregnation depth exists, at which maximal possible conversion is achieved in all positions along the bed height.

The methodic has been proposed which allows to verify the reactor's mathematical description using some test (model) reaction. The nitrobenzene hydrogenation on Pd/C catalyst was chosen as such test reaction. Kinetic characteristics and catalyst activity were determined using «spinning-basket» reactor and then compared with the results of experiments in a «multiple-sphere string reactor». Results of comparison allowed us to adjust empirical dependences of mass transfer rate coefficient from liquid to solid $k_{\mathrm{L\text{-}S}}$ on temperature, pressure, liquid flow rate per cross-section unit and gas flow rate in the reactor.

This work has been accomplished with the financial support of ISTC project № 2995.

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INITIAL CONDITIONS OF NON-CATALYTIC PARTIAL METHANE OXIDATION PROCESS IN ADIABATIC REACTOR

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Moscow State Academy of Fine Chemical Technologies named by M.V. Lomonosov, Moscow

There are some factors, which have an influence on kinetics conditions for high-temperature methane conversion. One of those is spontaneous combustion characterized by induction period, which depends of process pressure and temperature of reagents. Non-catalytic partial methane oxidation process is carried out in millisecond residence time. In that case conversion goes by in adiabatic conditions, and process temperature depends of reagents initial temperature and adiabatic heating of mixture. Different data of induction period dependencies is given in literature. In [1] suggested carrying out the process with initial temperature equal 400°C at pressure 1 MPa. In [2] process was investigated at pressure 3 MPa, initial temperature of methane equal 350-450°C and initial temperature of O_2 equal 120°C. Besides, there are some sources [3,4] suggested heating of reagents mixture up to 500°C. To predict of spontaneous combustion it is necessary to create conditions with residence time extremely less than induction period. The process parameters dependence of reagents initial temperature was calculated in research work for optimal reagents ratio and pressure 5.0 MPa. Reported that rise of initial temperature provokes increase of adiabatic heating temperature, increase of CO content, decrease of CO_2 content and H_2/CO ratio. Calculated optimal value of initial temperature equals 227°C, adiabatic heating temperature equals 1313°C, CO_2 content is 4.8 % vol.

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PP-II-13

MATHEMATTICAL MODELLING OF THE PROCESS OF OBTAINING ARTIFICIAL DRYING OIL

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Polymerisation and copolymerization processes are complicated processes of chemical transformations, they last for long periods of time forming various intermediate compounds. Kinetics of such processes is complicated and can be simplified by means of various assumptions.

The offered system of copolymerization consists of four components and includes cis - and trans-isomers of piperylene, butadiene and vinylacetylene. While working out the mathematical description of kinetics for the investigated system the principle of stationary concentrations was applied and the assumption about insignificant influence of the length of a material chain on reactivity of a macroradical is made.

The accepted mechanism of radical copolymerization of divinyl, vinylacetylene, cis - and trans-isomers of piperylene consists of the following elementary stages: decomposition of the initiator, initialization, chain growth, chain interruption.

Also as an assumption we take that the rate of chain breakage does not depend on the type of reactions ($k_{22} = k_{23} = k_{24} = \ldots = k_{31}$).

The rate of initiator consumption:

$$\frac{dI}{dt} = -k_0 \cdot I - k_1 \cdot I^2$$

The rate of monomer consumption is described by the system of the differential equations:

$$\frac{dR^*}{dt} = -R^* \cdot (k_2 \cdot M_1 + k_3 \cdot M_2 + k_4 \cdot M_3 + k_5 \cdot M_4) + k_0 \cdot I + k_1 \cdot I^2$$

$$\begin{aligned}\frac{dM^*_1}{dt} &= M_1 \cdot (k_2 \cdot R^* + k_6 \cdot M_1^* + k_{10} \cdot M_2^* + k_{14} \cdot M_3^* + k_{18} \cdot M_4^*) - M_1^* \cdot (k_6 \cdot M_1 - \\ &- k_7 \cdot M_2 + k_8 \cdot M_3 + k_9 \cdot M_4) - k_{22} \cdot M_1^* \cdot (M_1^* + M_2^* + M_3^* + M_4^*)\end{aligned}$$

$$\begin{aligned}\frac{dM_2^*}{dt} &= M_2 \cdot (k_3 \cdot R^* + k_7 \cdot M_1^* + k_{11} \cdot M_2^* + k_{15} \cdot M_3^*) - M_2^* \cdot (k_{10} \cdot M_1 - \\ &- k_{11} \cdot M_2 + k_{12} \cdot M_3 + k_{13} \cdot M_4) - k_{22} \cdot M_2^* \cdot (M_1^* + M_2^* + M_3^* + M_4^*)\end{aligned}$$

$$\frac{dM_3^*}{dt} = M_3 \cdot (k_4 \cdot R^* + k_8 \cdot M_1^* + k_{12} \cdot M_2^* + k_{16} \cdot M_3^*) - M_3^* \cdot (k_{14} \cdot M_1 - \tag{1}$$
$$- k_{15} \cdot M_2 + k_{16} \cdot M_3 + k_{17} \cdot M_4) - k_{22} \cdot M_3^* \cdot (M_1^* + M_2^* + M_3^* + M_4^*)$$

$$\frac{dM_4^*}{dt} = M_4 \cdot (k_5 \cdot R^* + k_9 \cdot M_1^* + k_{13} \cdot M_2^* + k_{17} \cdot M_3^*) - M_4^* \cdot (k_{18} \cdot M_1 -$$
$$- k_{19} \cdot M_2 + k_{20} \cdot M_3 + k_{21} \cdot M_4) - k_{22} \cdot M_4^* \cdot (M_1^* + M_2^* + M_3^* + M_4^*)$$

$$\frac{dM_1}{dt} = -k_2 \cdot R^* \cdot M_1 - k_6 \cdot M_1^* \cdot M_1 - k_{10} \cdot M_2^* \cdot M_1 - k_{14} \cdot M_3^* \cdot M_1 -$$
$$- k_{18} \cdot M_4^* \cdot M_1$$

$$\frac{dM_2}{dt} = -M_2 \cdot (k_3 \cdot R^* + k_7 \cdot M_1^* + k_{11} \cdot M_2^* + k_{15} \cdot M_3^* + k_{19} \cdot M_4^*)$$

$$\frac{dM_3}{dt} = -M_3 \cdot (k_4 \cdot R^* + k_8 \cdot M_1^* + k_{12} \cdot M_2^* + k_{16} \cdot M_3^* + k_{20} \cdot M_4^*)$$

$$\frac{dM_4}{dt} = -M_4 \cdot (k_5 \cdot R^* + k_9 \cdot M_1^* + k_{13} \cdot M_2^* + k_{17} \cdot M_3^* + k_{21} \cdot M_4^*)$$

$$\frac{dP}{dt} = k_{22} \cdot M_1^* \cdot M_1^* + k_{22} \cdot M_1^* \cdot M_2^* + k_{22} \cdot M_1^* \cdot M_3^* + k_{22} \cdot M_1^* \cdot M_4^* +$$
$$+ k_{22} \cdot M_2^* \cdot M_2^* + k_{22} \cdot M_2^* \cdot M_3^* + k_{22} \cdot M_2^* \cdot M_4^* + k_{22} \cdot M_3^* \cdot M_3^* +$$
$$+ k_{22} \cdot M_3^* \cdot M_4^* + k_{22} \cdot M_4^* \cdot M_4^*$$

where I – a molecule of hydroperoxide of ethylbenzene; R^* – primary initiating radical; M_1 – a molecule of cis- piperylene; M_2 – a molecule of trans- piperylene; M_3 – a molecule of divinyl; M_4 – a molecule of vinylacetylene; M^*_1, M^*_2, M^*_3, M^*_4 – growing (increasing) radicals; P – a molecule of polymer; k_0, k_1 – reaction rate constants of initiator consumption; k_2, k_3, k_4, k_5 – reaction rate constants of initialization; k_6, k_7, …, k_{21} – reaction rate constants of chain growth; k_{22}, k_{23}, …, k_{31} – reaction rate constants of chain interruption.

The system (1) is the mathematical description of kinetics of copolymerization of the transe-cis-isomers of piperylene with divinyl and vinyl acetate.

It is known that while solving an inverse problem of kinetics one of the challenges is the definition of the parametres which values can be found for the accepted kinetic scheme on the basis of the available experimental information. As parametres of the model of kinetics of copolymerization constants K_2, ..., K_{31} were accepted. For the quantitative assessment of the divergence of experimental data and the results of calculations the functional of the type was accepted:

$$Q = \sum_{i=1}^{7} \left[(I_{\text{Э}} - I_P)^2 + (M_{1\text{Э}} - M_{1P})^2 + (M_{2\text{Э}} - M_{2P})^2 + (M_{3\text{Э}} - M_{3P})^2 + (M_{4\text{Э}} - M_{4P})^2 \right]$$

where $I_{Э}$, $M_{1Э}$, $M_{2Э}$, $M_{3Э}$, $M_{4Э}$ – experimental values of the concentration of initiator and monomers; I_P, M_{1P}, M_{2P}, M_{3P}, M_{4P} – rated values of the same components; i – the number of the experiment.

As an identification algorithm the "complex" of Box method [1] was applied, this method belongs to nongradient search methods and is noted for high efficiency while solving a large number of problems of nonlinear programming.

The system (3) was integrated by the method of Runge-Kutt [2] having initial conditions: $[I]_0 = 0{,}254$ *mol/l*; $[M_1]_0 = 1{,}58$ *mol /l*; $[M_2]_0 = 3{,}36$ *mol /l*; $[M_3]_0 = 2{,}12$ *mol /l*; $[M_4]_0 = 0{,}64$ *mol /l*.

As a result of the calculations the following values of rate constants were obtained:

1. $k_0 = 0{,}473\cdot 10^{-4}$
2. $k_6 = 0{,}499\cdot 10^{-4}$
3. $k_{12} = 0{,}516\cdot 10^{-4}$
4. $k_{18} = 0{,}220\cdot 10^{-3}$
5. $k_1 = 0{,}861\cdot 10^{-3}$
6. $k_7 = 0{,}506\cdot 10^{-4}$
7. $k_{13} = 0{,}515\cdot 10^{-4}$
8. $k_{19} = 0{,}483\cdot 10^{-3}$
9. $k_2 = 0{,}413\cdot 10^{-3}$
10. $k_8 = 0{,}511\cdot 10^{-4}$
11. $k_{14} = 0{,}499\cdot 10^{-4}$
12. $k_{20} = 0{,}358\cdot 10^{-3}$
13. $k_3 = 0{,}537\cdot 10^{-3}$
14. $k_9 = 0{,}510\cdot 10^{-4}$
15. $k_{15} = 0{,}506\cdot 10^{-4}$
16. $k_{21} = 0{,}310\cdot 10^{-3}$
17. $k_4 = 0{,}436\cdot 10^{-3}$
18. $k_{10} = 0{,}498\cdot 10^{-4}$
19. $k_{16} = 0{,}511\cdot 10^{-4}$
20. $k_{22} = 0{,}249\cdot 10^{-2}$
21. $k_5 = 0{,}450\cdot 10^{-3}$
22. $k_{11} = 0{,}508\cdot 10^{-4}$
23. $k_{17} = 0{,}511\cdot 10^{-4}$
24.

The calculation of kinetic curves led to a good agreement with the experiment, at the same time the value of goodness of fit amounted to $Q=0{,}0008$.

PP-II-14

LIGNOSULPHONATE TOTAL ORGANIC CARBON TREATMENT USING ELECTROCHEMICAL OXIDATION

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Introduction

Lignin derivatives account for a significant fraction of the biorefractory content in the wastewaters coming from the pulp and paper industry. Biological activated sludge processes do not allow the treatment of biorefreactory organic carbon. Advanced oxidation processes (AOP) such as electrochemical oxidation have been described as an efficient alternative due to the removal of dissolved organic matter by electro-generated oxidations (1). Lignosulphonate was selected as specific compound to describe the biorefractory fraction of the wastewaters. Total Organic Carbon (TOC) will be studied in the effluent.

Experimental results and discussion

The Lab-scale electrochemical treatment plant is based on a conventional two-parallel boron-doped diamond (BDD) electrodes flow cell DiaCell 106.101® (Adamant Technologies) operated in a batch mode under isothermal conditions and constant flowrate. TOC removal was studied until 90% reduction was obtained.

In order to study the effect of selected variables (initial TOC ($[TOC]_0$), current density (j) and supporting electrolyte concentration ($[Na_2SO_4]$)) in the electrochemical oxidation of lignosulphonate, the experimental design and kinetic modelling shown in table 1 was performed. According to experimental TOC time profiles, a first order kinetics was used to describe experimental results in the form of dimensionless TOC:

Table 1. Experimental design and kinetic constants

Exp. run	$[TOC]_0$ ($mgC\cdot L^{-1}$)	j ($mA\cdot cm^{-2}$)	$[Na_2SO_4]$ ($g\cdot L^{-1}$)	$k\cdot 10^3$ (min^{-1})*	r^2	$k_I\cdot 10^3$ (min^{-1})*	r_I^2	$k_{II}\cdot 10^3$ (min^{-1})*	r_{II}^2
1	150	30	5	3.92±0.29	0.988	3.78±0.17	0.989	3.78±0.17	0.989
2	150	30	2.5	3.64±0.20	0.993				
5	450	30	5	2.93±0.15	0.993	2.98±0.13	0.988	2.98±0.13	0.988
6	450	30	2.5	3.03±0.26	0.985				
3	150	60	5	4.39±0.22	0.994	4.52±0.16	0.993	4.42±0.12	0.991
4	150	60	2.5	4.65±0.25	0.994				
7	450	60	5	4.07±0.25	0.992	4.32±0.20	0.989		
8	450	60	2.5	4.59±0.24	0.994				

*Confidence range=95%

$$TOC\cdot TOC_0^{-1} = \exp\left(-k\cdot t\right)\ \forall t \geq 0\,,$$

where TOC_0 is the initial TOC ($mgC\cdot L^{-1}$), t is time (min) and k is the first order kinetic constant (min^{-1}). Results of the experimental fitting with PolyMath® v5.0 for k lead to a correlation coefficient $r^2 > 0.985$ in all individual runs as it is shown in table 1.

From table 1, overlapping of experimental results is observed in the experimental runs where only sulphate concentration was modified. These experimental results can be described as it is shown in table 1 (k_I) and one value of the kinetic parameter independent of the electrolyte concentration has been obtained. Kinetic parameters for high current density (60 $mA\cdot cm^{-2}$) were later lumped together, as summarized in table 1 (k_{II}) showing the negligible influence of the initial lignosulphonate concentration at high current densities.

Conclusions

Kinetic results summarized in table 1 show that the concentration of sodium sulphate supporting electrolyte between 2.5 and 5 $g\cdot L^{-1}$ at each level of initial TOC and applied current density does not show any influence on the kinetic parameter and therefore this influence can be neglected in the studied range of variables. At high current density (60 $mA\cdot cm^{-2}$) there is not an influence of the initial TOC in the kinetic parameter ($k\cdot 10^3 = 4.42\pm0.12\ min^{-1}$); at low current density (30 $mA\cdot cm^{-2}$) kinetics is faster at low initial TOC (at 150 $mgC\cdot L^{-1}$, $k\cdot 10^3 = 3.78\pm0.17\ min^{-1}$) when compared to high initial TOC (at 450 $mgC\cdot L^{-1}$, $k\cdot 10^3 = 2.98\pm0.13\ min^{-1}$). Previous studies with phenol oxidation in sulphate media gave higher values of the first order kinetic constant ($k\cdot 10^3 = 11.94\pm0.62\ min^{-1}$) operating at low current density (2).

Acknowledgments

This research is financially supported by the Spanish Ministry of Science and Technology (Project CONSOLIDER CTM2006-00317).

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MATHEMATICAL MODELING OF FRACTIONATION STAGE OF REACTIVE DISTILLATION PROCESS FOR THE PRODUCTION OF ETHYLENE GLYCOL

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In the conference «Chemreactor-17» [1] we presented the contribution concerning the analysis of the work of chemical stage of reactive distillation process, in this report we present the work of the fractionation stage. Rectification process as a rule is calculated by models of static on the base of conception of theoretical tray which ensure improvement of equilibrium between vapor and liquid passed in definite time. Six version column working for receiving ethylene oxide of high purify were examined.

The calculation of the ethylene oxide hygrolysis process was fulfilled at 493 K and ratio water : ethylene oxide (in initial time of reactions) as 30:1 and more.

Ethylene oxide of high purify can be produced only in the case when the qualitative ethylene glycol is aside as side product from reactive distillation column.

The adequacy of the combined mathematical model of column is proved by indirect testify.

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PP-II-16

AUTOCATALYTIC REACTION FRONTS PROPAGATION IN A PACKED-BED REACTOR

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Introduction: The phenomenon of autocatalytic reaction fronts is a striking example of the coupling of a chemical reaction and diffusion transport demonstrating that the reaction can occur not only in a time but also in a space. The presence of macroscopic non-diffusive fluxes like advection or convection in the reactive media can lead to even more fascinating effects of the interaction between transport and chemical reactions. For instance the stationary Belousov-Zhabotinsky (BZ) reaction fronts arise in the wide range of advective flow velocities in a packed-bed [1]. From the other side the theory for reactive fluids is incomplete, and unable to describe the number of events arising in the flowing reactive media. The work presents theoretical and experimental investigation of non-oscillating autocatalytic reaction fronts propagation in flowing liquid reactive media.

Results and discussion: It has been demonstrated that behavior of autocatalytic Fe^{2+} and Co^{2+} oxidation reactions can not be described in terms of plug-like flow approximation in a packed bed, since the fronts propagation does not obey expecting translation of the front by the advective flow. At the same time stationary fronts was not observed. To gain better understanding of this we have performed theoretical analysis of advection influence on reaction fronts based on comparison of the flow characteristics in simple geometries (two parallel plates with the gap between them – Hele-Show cell and cylindrical tubes) and the flow in a packed-bed. Corresponding numerical calculations of two-dimensional reaction-diffusion-advection model oriented to BZ stationary fronts were performed. According to the obtained results the parameters that control front velocity in the advective flow are ratio of gap (pore) half-width to the width of front in the absence of the flow, η, and ratio of the maximum flow velocity $U_{\max}$ to the average flow velocity U in the flow field. Larger values of these parameters increase the deviation of front velocity from simple translational behavior, which is assumed by the plug-like flow approximation in a packed-bed [2]. As we have found, the porous media flow geometry is favorable for achieving limiting behavior of reaction front characterized by zero value of front propagation velocity in the adverse flow (V_f^-, stationary front), because of much larger $U_{\max}/U$ ratio as compared to the flow in a gap (Hele-show cell) or a cylindrical tube.

In this work, we have increased the concentration of the key reactants in the thiosulfate oxidation reaction by chlorite to achieve the limit of large η. This allowed us, for the first time, to achieve experimentally zero value of non-oscillating reaction front propagation velocity in a wide rage of adverse flow velocities. This corresponds to the observation of stationary fronts for a range of adverse flow velocities, similar to the observations made for the BZ reaction in a bed of glass beads. This can be rationalized as follows. The transport mechanism which governs reaction front propagation is diffusion. When flow is turned on, the diffusion in axial direction is essentially quenched, since diffusion along bead walls implies a dramatically increased tortuosity factor and possibly a significantly reduced connectivity for the diffusion path. This quenching of implies that in the adverse flow reaction front propagates with the velocity $V_f^- \approx 0$, as confirmed by the calculations.

We also demonstrate that it is not appropriate to substitute the dispersion coefficient for diffusivity in the reaction-diffusion-advection equation when describing of the concentration fronts in autocatalytic reactions in a wide range of flow velocities, in particular if both supportive and adverse flows are to be explained. Such substitution completely fails to account for the behavior of the reaction front in the case of the adverse flow, at least in the limiting case described above. Therefore it can be concluded that, an adequate description of a reaction front behavior in the presence of advection therefore requires that the flow velocity field is taken into account explicitly.

Conclusions: In this work we studied mechanisms of the formation of stationary reaction fronts in continuous flow packed-bed reactors. It has been demonstrated that stationary fronts in not the exclusive feature of Belousov-Zhabotinsky reaction, but also can be observed in non-oscillating reactions. Corresponding numerical calculations and experimental evidences show that such uncommon dynamic behavior of reaction fronts can be explained in term of specific influence of the advective flow in a packed-bed.

Acknowledgements: Authors are grateful for a support of the presrnt work by the grants from RFBR (05-03-32472 and 07-03-12147), SB RAS (integration grant # 11) and RAS (5.1.1 and 5.2.3).

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Section 3.

Catalytic processes' development and reactors design: modeling, optimization, new catalyst application

VARIANTS OF THE CATALYST BED WITH CONTROLLED TEMPERATURE PROFILE IN TUBULAR DEVICE FOR THE SINGLE-STAGE WATER GAS SHIFT PROCESS

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Conversion of the natural gas, basically consisting of methane, is the main industrial method of hydrogen production for its further use in ammonia synthesis, hydrogenation of petroleum products (hydrotreating, hydrocracking and etc) and other organic compounds, and as a fuel for ecologically clean energy production in fuel cells [i,ii].

The extent of carbon monoxide conversion by water gas shift reaction (WGSR) is determined by thermodynamic equilibrium and depends on the temperature in the catalyst layer. High carbon monoxide conversion extent can be only achieved at low temperatures.

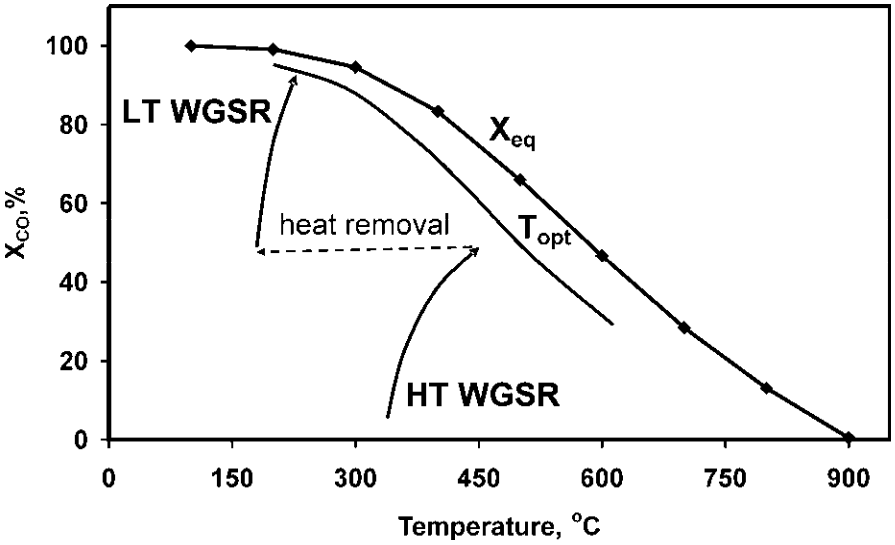

Figure 1. Temperature dependence of the carbon monoxide conversion extent in the course of the water gas shift reaction.
X_{eq} – equilibrium conversion extent (the initial gas composition: CO (6.3%), CO_2 (4.7%), H_2 (44%), H_2O (45%));
T_{opt} – optimal temperature profile under continuous heat removal along catalyst bed (for the hypothetical catalyst, which is thermostable in a wide temperature range);
HT WGSR – LT WGSR – typical temperature profile of the traditional WGSR process.

Figure 1 shows temperature dependence of equilibrium CO conversion in the WGSR starting from the reaction mixture composition: CO (6.3%), CO_2 (4.7%), H_2 (44%), H_2O (45%), the optimal temperature profile along the catalyst bed for the process operation with use of the hypothetical catalyst, which is thermostable in a wide temperature range, and that for the traditional scheme of the industrial process organization: two adiabatic stages and intermediate heat removal.

Novel schemes of the heat-transfer with use of the heat-conducting composite catalytically active materials [iii,iv] may allow approaching the optimal temperature field in fixed catalyst bed and improving the process performance. The application of such schemes requests new high-performance catalysts, which can stably operate in a wide temperature range, e.g. those described in recent patents [v,vi].

The topic of the present study is considering the variants of the catalyst layer organization with controlled temperature profile close to optimal for the WGSR process. The results permit concluding that the use of high-performance catalysts in apparatuses with controlled temperature profile can greatly increase efficiency of the WGSR stage of the natural gas utilization in the schemes of ammonia syntheses and hydrogen production as well as in schemes of electric power production using the fuel cells.

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MATHEMATICAL MODELING OF PENTANE-HEXANE FRACTION ISOMERIZATION PROCESS ON SI-2 CATALYST

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Last years the consumption of isomerizates as high octane number motor fuels component essentially increased. The maintenance of optimal activity of isomerization catalyst and prevention of its deactivation is a very important problem.

The aim of this work is to create mathematical description of pentane-hexane fraction isomerization process and computer modeling system for estimating the main values of the process, controlling the catalyst state, its deactivation rate, finding optimal activity.

The analysis of possible mechanism of pentane-hexane fraction isomerization process reactions was done, the formalized scheme of hydrocarbons transformation was formed (figure 1).

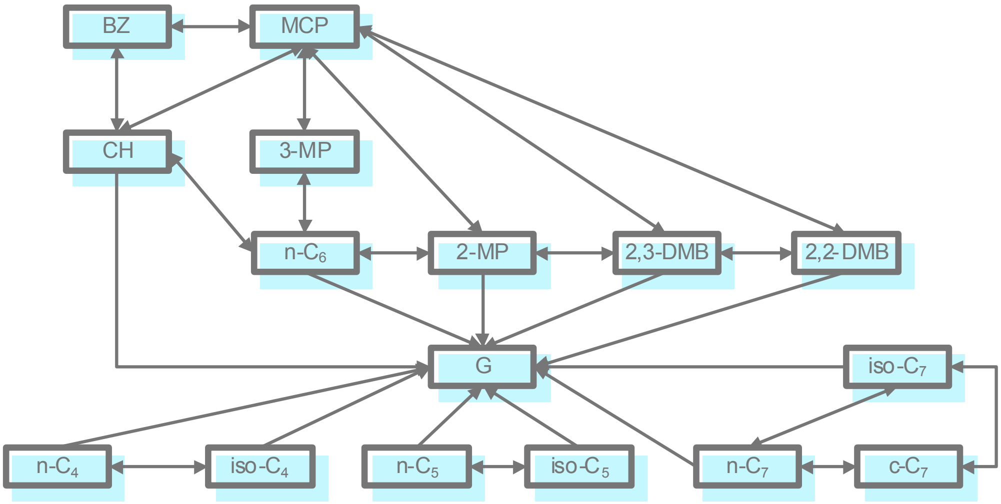

Figure 1 – Formalized scheme of hydrocarbons transformation
BZ-benzene; MCP-Methylcyclopentane; MP-methylpentane CH-cyclohexane; DMB-dimethylbutane; G-gas; n-normal; iso-isomer; c-cyclo;

The mathematical model of isomerization process consists of material and heat balance equations, and it also is completed with equations considering aging, agglomeration, coking of catalyst.

$$\begin{cases} \dfrac{dC_i}{d\tau} = \sum_{j=1}^{n} \pm W_j \\ \dfrac{dT}{d\tau} = \dfrac{1}{\rho * Cp} \sum_{j=1}^{n} (\pm \Delta H_j) * W_j \end{cases}$$

PP-III-2

Initial conditions: $C_i(0)= C_{i,0}$; $T(0)= T_{en}$,

where C_i – i-component concentration [mol/м^3]; T – temperature, °К; ρ - mixture density, [kg/м^3]; Cp – mixture heat capacity, [кJ/mol*К]; ΔH_j – j-hydrocarbon enthalpy, [кJ/mol]; W_j – j-hydrocarbon reaction rate.

During the investigations the inverse kinetic problem was solved and rate constants of main reactions going in pentane-hexane fraction isomerization process were obtained. For calculations we used experimental data from L-35-11/300 unit of «Kirishinefteorgsintez» Ltd. The program realization of the model was done in integrated environment Delphi 7.

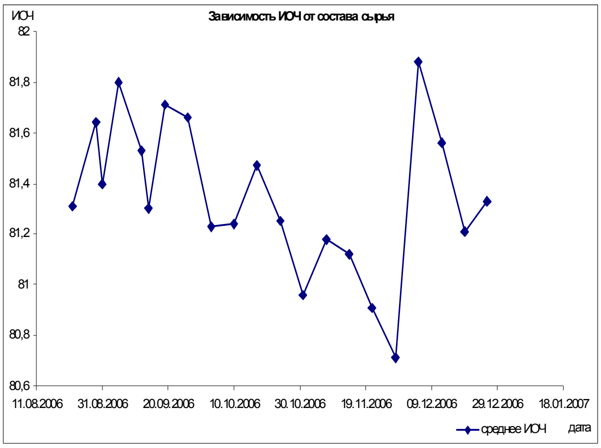

Figure 1 – The octane number dependence on raw material composition

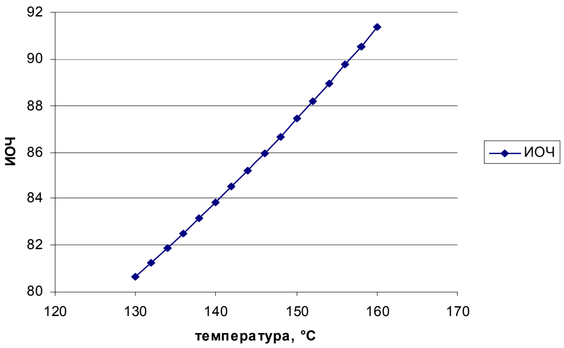

Figure 2 – The octane number dependence on process temperature

The influence of raw material composition on octane number was examined with constant technological parameters. The change of octane number has chaotic character within quite large interval of 1.0-1.5 points (figure 1) while all other parameters are constant. Elaborated computer modeling system allows to detect raw material composition influence on isomerizate octane number.

Temperature increase provides obtaining of isomerizate with higher octane number. At the same time it leads to decrease of catalyst service cycle because of coking reaction rate increasing, also the fraction of side hydrocracking reactions increases. The obtained results agree with theoretical ideas. Moreover temperature selection allows to change the isomerizate octane number in a wide range.

Using mathematical modeling method it is possible to find the optimal conditions of process running, to calculate and to design reactor blocks for isomerization process.

PHOTOCATALYTIC SELF CLEANING SURFACES FOR HOUSEHOLD COOLING APPLIANCES

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Introduction

Household refrigerators are meant to store and preserve food at low temperatures. The refrigerator cabinet is a closed environment, where organics releases from stored food represents the main concern and harm for users. Hygiene perception is a primary value for potential customers: colour and shapes of inside surfaces are designed to communicate and provide ease of cleaning. Nevertheless, cleaning of inside cabinet is still a major issue for customers. The work described in the present paragraph represents a novel approach to refrigerator cleaning. The potential of photo-catalysis as a self cleaning process is investigated. The well known oxidative properties of titanium dioxide (anatase form) is worthwhile to be investigated. TiO_2 commercial availability and cost make it suitable for white goods market.

A low temperature in-situ synthesis was adopted to obtained a catalytic layer that was characterised by Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD), to verify layer integrity and morphology. Photocatalytic activity towards organic dirt decomposition was measured through the oxidation of various organic dyes, as the perceivable decolouring of the dirt can be a clear activity indicator for users.

Experimental

The refrigerator-grade polystyrene liner requires a tailored TiO_2 deposition process. The investigated TiO_2 substrate was polystyrene (PS) extruded in sheets, being the typical material used as liner for the refrigerator internal cabinet. For this purpose, a low temperature coating process was applied to achieve a photocatalytic layer, based on the production of an amorphous type titanium hydroxide gel, to be used as a coating precursor [1,2]. The preparation method described in literature uses, as precursor, a titanium tetrachloride aqueous solution, to be reacted with an ammonium hydroxide solution in an acidic range of pH 2 to 6. Being $TiCl_4$ a quite dangerous and difficult compound to handle in an industrial process, the authors decided to modify the process, by using an organic titanium oxide precursor, namely titanium isopropoxide $Ti(OC_3H_7)_4$, in the same conditions.

Afterward, a 30% aqueous hydrogen peroxide solution was gradually added to the so obtained white aqueous $Ti(OH)_4$ gel, to induce the formation of a yellow titanium peroxide solution. PS sheet samples, previously cleaned with diluted nitric acid, ethanol and deionizer water, were coated by dipping them into the obtained titanium hydroxide gelified solution. Both a room temperature and a mild heat treatment have been applied, to allow TiO_2 formation, confirmed by XRD analysis. The photocatalytic performance of the obtained coatings was benchmarked vs. a coating of γ-Al_2O_3 powders obtained by Aldrich (99,8% purity). To achieve controlled and repeatable exposure conditions, a UV test cell was used, equipped with a 300W UV-A lamp. To avoid excess of substrate heating up, forced ventilation of the samples was ensured by a fan. Organic dyes were used as chemical compounds to be degraded by the photocatalythic activity of titania coating [3-6]. The selected dyes, used in different concentrations (0.4% w/w solution, further diluted 100 and 1000 folds), were Methylene Blue, Methyl Red, Ortho-Cresole Red, Rhodamine-B, Eosin, Bengal Rose. Samples were soiled by equal dyes solution volumes (1 cm^3). The results were evaluated by colorimetric analysis: RGB pixel values were averaged over sample image, and normalized using a standard sample (uncoated PS) as baseline; higher colorimetric indexes indicate color whitening, hence dye decomposition. Clear photocatalytic effect (dye discoloring) was detected on coated samples, comparable with anatase powder ones, and significantly higher than alumina reference; such effect was quantified by colorimetric data as shown in Fig. 1, where titania coating compared with γ-Al_2O_3 effectiveness over Eosin and Rhodamine B is shown. Slight discoloring in alumina coated samples can be related to direct UV light action on dyes.

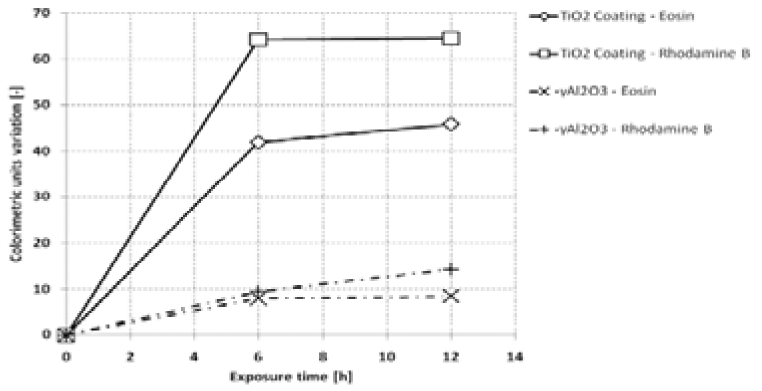

Fig. 1. Colorimetric analysis of photocatalytic effects on Eosin and Rhodamine-B; TiO_2 and γ-Al_2O_3 coating performance comparison

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OPTIMIZATION AND SCALING UP OF THE RECIPROCAL FLOW REACTORS OF FILTRATION COMBUSTION FOR THE TASKS OF PARTIAL OXIDATION OF METHANE AND VOCS OXIDATION

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Gas filtration combustion in a porous media [1] may be utilized for realization of practically important processes: hydrocarbons conversion to syngas, vent gas purification by VOCs oxidation, granular solids purification etc. Working parameters optimization and scaling up should be performed for practical implementation of the technology. The results of numerical investigation, optimization and scaling up of the reciprocal flow filtration combustion reactor (RFR), Fig. 1, for the tasks of methane partial oxidation and vent gases oxidative purification are presented in this report.

Methane conversion to syngas in the reciprocal flow porous media reactor is one of the promising technologies [2] deserving intensive investigation.

An overall three-step six-component chemical kinetics model is elaborated for simulation of partial oxidation of methane in inert porous media. Procedure of the model adjusting to the experimental data is described. The applicability of the model to the tasks of methane conversion in the porous media is discussed.

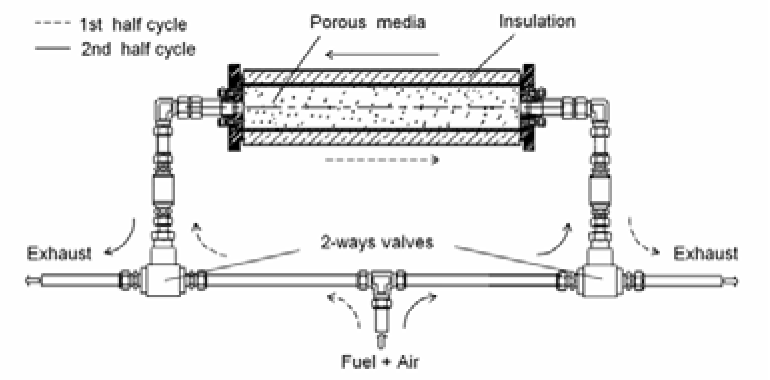

Fig. 1. Schematic of Reciprocal Flow Reactor.

The influence of RFR scaling up (flow rate ranging from G=1 to 1000 m^3/h) on the process of partial oxidation of methane in the filtration combustion reciprocal flow reactor is investigated numerically. It is demonstrated that the residence time increase with the reactor length is compensated by decrease of the maximum temperature. It is shown that the experimentally observed temperature growth saturation is caused by pressure growth in the reactor.

The parametric study of the RFR (G=100 м^3/ч) with reduced aspect ratio geometry is performed. It is shown that given geometry provides better efficiency for the high flow rates regimes, although the minimum length is determined by the limitations on front stability. The optimal fuel to air equivalence ratio providing maximum methane conversion ratio is determined Ф=2.7.

The influence of the water vapor addition to the methane – air mixture on the conversion ratio and hydrogen concentration is investigated, Fig. 2. It is shown that hydrogen concentration in the gas obtained may be increased by 0.5-1 percent and the methane conversion ratio may be improved by 10-15 % by adding steam to a working mixture. The optimum equivalence ratio remains the same as in the water free case. The steam concentration, that maximizes H_2 differs from that which maximize the conversion ratio. Some intermediate concentration may be recommended for practical operation depending on technological requirements.

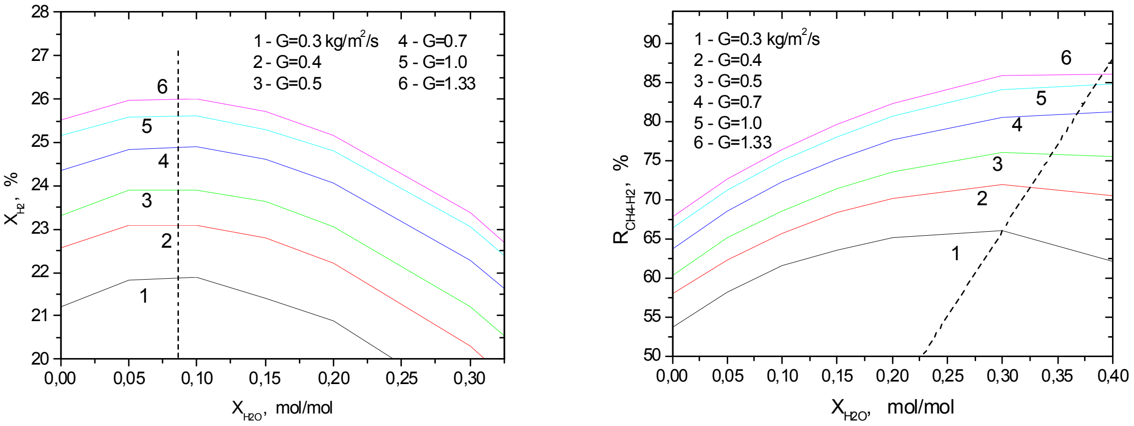

Fig. 2. Hydrogen output concentration (left graph) and methane conversion ratio (right graph) as a function of added water. The specific mass flow rates are given in the legend. The dashed line joins maxima. Φ=3.

Another task explored in the work is VOCs oxidation in the RFR. The critical question for the application of this technology is lean combustibility limit (LCL): LCL determination and extension [3,4]. Analytical and numerical investigation of the LCL for the extra lean methane –air mixture in the reciprocal flow filtration combustion reactor is performed. New quantitative results on LCL dependence on the reactors length, porous media porosity, packed bed particles size, thermal insulation and other parameters are reported. Simulation show that packed bed particles size is the most important parameter determining LCL, while the pressure plays a negligible role.

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WASHCOATS FOR STRUCTURED REACTORS IN PROPANE OXIDATION. V_2O_5 SUPPORTED ON TiO_2 WASHCOAT DEPOSITED ON METALLIC PLATES AND FOAMS

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Introduction

Microreactors or structured reactors (including heat exchanger-type reactors) offer a potential to conduct mass or heat transfer-demanding reactions under safe conditions while maintaining and/or increasing selectivity and productivity. In the case of reactions of selective oxidation of hydrocarbons the whole mass of the transition metal oxide is reacting in usual reactors (fixed or fluidized beds) and it is not so straightforward to get high catalytic activity/selectivity in a thin layer. The goal is therefore to obtain high surface area when covering a low, geometric area of the metallic substrate, while maintaining a high mechanical and chemical stability [1,2]. The coating of aluminum and of stainless steel plates by VO_x/TiO_2 catalysts for oxidative dehydrogenation of propane [2-4] was studied using dip-coating and sol-gel methods, which provided high mechanical stability but poor chemical stability as revealed by the iron poisoning of the catalyst. Another way of coating using a plasma-assisted chemical vapor deposition (PACVD) had already been explored in the case of silica supported cobalt for Fischer-Tropsch synthesis of clean fuels [4-6]. In the present paper the parameters to control PACVD during the coating of metallic plates by VO_x/TiO_2 catalysts for ODH of propane are studied. The same PACVD technique was applied to metallic foams for the first time.

Results and Discussion

PACVD of tetramethyldisiloxane used for silicon [6,7] was adapted to coat metallic substrates (here called S). A typical rate of increasing thickness of films of polymers is 300 nm·mn^{-1}. A new sample holder was designed to allow the coating of metallic foam (Cr-Ni from Metafoam). After mineralisation in O_2-N_2 plasma, a calcination step was applied to stabilize the layer of silica primer onto S. Titania was further deposited on the SiO_2/S plate or foam by using an alcoholic/aqueous suspension of titania (anatase) powder (Aldrich).

Vanadium oxide was grafted on $TiO_2/SiO_2/S$ by means of vanadyl isopropoxylate. Raman spectroscopy, scanning electron microscopy and XPS were used to characterise the deposits on various substrates at each step of preparation. Tests of adhesion and of reducibility in propane up to 550 °C (metallic substrates) or 450 °C (glass) showed that the SiO_2 primer film (thickness 5 μm) was stable while SEM showed that its surface has an irregular, more or less glazy aspect. XPS analysis on SiO_2/S shows the presence of some remaining carbon while no metallic element of S is detected. The textural analysis of titania shows that its surface area and particle size is retained.

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CATALYTIC SELF CLEANING PROCESS FOR DOMESTIC OVEN

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Household ovens cleaning process is an issue both for customers and manufacturers, today performed by apposite caustic detergents or via high temperature (> 500°C) incineration cycles. Oven soiling is mainly constituted by fatty acids splatters, thermally degraded by the prolonged exposure to oven wall temperatures (up to 300 °C), strongly adhered to wall themselves. The present work aimed to provide oven walls with self cleaning properties, via catalytically enhanced thermal oxidation of soil at temperatures within the available range of standard ovens.

First, representative organic compounds were identified to be used to test possible catalyst formulations: for this purpose saturated fatty acids, as myristic (tetradecanoic), palmitic (hexadecanoic), stearic (octadecanoic) acid were selected. In a second step it was also tested the olive oil and the butter as real compounds present in a domestic oven. A preliminary thermal degradation behavior of such compounds were characterised via TGA (Thermo Gravimetric Analysis), in different conditions (partially thermally degraded) and atmospheres (air, 5% O_2 and 0,5% O_2 with the N_2 balance).

Three oxidative catalyst types were selected: Spinels ($CoCr_2O_4$, $MnCr_2O_4$, $MgFe_2O_4$ and $CoFe_2O_4$), Perovskites ($LaFeO_3$ and $LaCrO_3$) and Lanthanoids Oxides (La_2O_3 and CeO_2). All the catalysts were prepared by Solution Combustion Synthesis method, a fast and self-sustaining chemical reaction between metal nitrate precursors and urea or glycine as sacrificial fuel [1]. The catalytic activity has been tested in a temperature programmed oxidation (TPO) apparatus. This equipment consists of a fixed bed inserted in a quartz microreactor (i.d.:4 mm). The fixed bed was prepared by mixing 50 mg of a 1:9 by weight mixture of fatty acid and catalyst in powder. The TPO runs were performed increasing the temperature from room temperature to 700 °C at a 5 °C/min rate, under an air flow of 100 N ml/min. This experiment was set up to evaluate the activity of pure catalyst towards selected fatty acids oxidation, monitoring CO_2 and CO concentration resulting from organic compounds oxidation and using concentration peaks as term of comparison for identifying maximum activity temperature. The temperature corresponding to the CO_2 concentration peak

(T_p) was taken as an index of the catalytic activity of each tested catalyst. CeO_2, $LaFeO_3$ and $MnCr_2O_4$ catalysts showed the best performances with a lowering of the T_p of about 150-200°C, from 500°C to about 300°C (a temperature easily reached in real conditions) compared to the uncatalytic runs. Moreover, a very high selectivity towards CO_2 conversion was observed for the catalytic runs respect to the uncatalytic one.

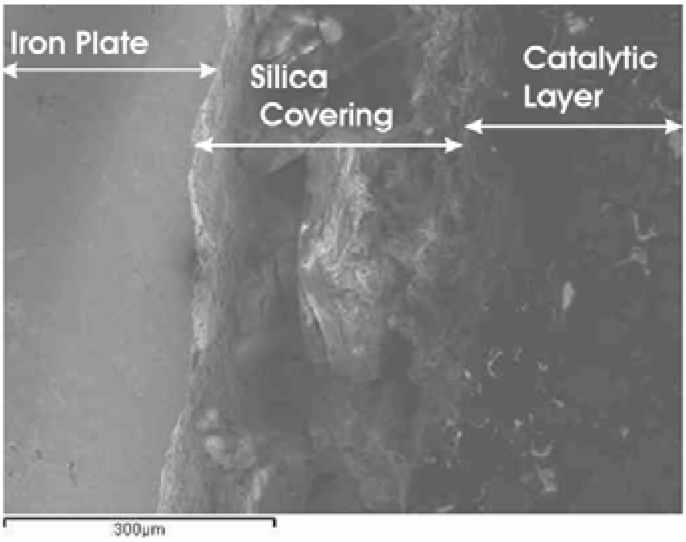

Fig. 1. SEM view of the ceria catalytic layer deposited by *in-situ* SCS onto the Ferro enamel - Perc^{TM} sheet.

The best tested catalysts were then deposited on an appropriate substrate: vast majority of oven muffle liners are made by carbon steel sheets protected by enamel, typically made by ore aluminosilicates. Samples of steel sheet coated by commercial Ferro enamel - Perc^{TM} - were used as support for catalyst deposition experiments. Both in-situ spray pyrolysis and SCS were selected for the deposition of the catalyst on enamel. Obtained catalytic layers were characterized by SEM (Scanning Electron Microscopy) and XRD (X-Ray Diffractometer), to assess integrity, adhesion on enamel and obtained phases (Fig. 1).

Catalytic layer activity towards reference fatty acids oxidation was investigated via TPC experiments using an appropriate reactor: fatty acids were deposited on catalyzed enameled steel sheet strips, using bare enamel as a reference. Also, catalytic efficiency towards natural fat substances (olive oil, pork lard, butter) was tested: solid and liquid natural fats are subjected to significant variance and natural degradation, hence comparative test were performed on samples from a common stock.

Finally, 50 mm wide square samples were coated by the most promising catalysts and located on a drip pan, to perform a cooking cycle simulation (250 °C for 60'; soiling by olive oil at target temperature reach) in a standard oven; weight loss, aesthetic appearance, cleanability were benchmarked versus bare drip pan enamel surface. Significant positive differences, resulting in a clearly perceivable self cleaning effect, were observed on the catalyzed samples.

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ALKYLATION REACTOR MODELING IN LINEAR ALKYLBENZENES PRODUCTION

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Alkylation of benzene with long-chained olefines is a part of LAS (linear alkylbenzene sulfonates) production, which are known as widespread surfactants. Biodegradability and detergent properties of these surfactants strongly depends on production conditions and raw materials composition. Since serious interference in functioning of a real industrial unit in order to investigate influence of different factors is an inexpedient, computer simulation of the reactor process is an efficient instrument in improving existent technology.

The developed mathematical model is based on experimental data of hydrofluoric alkylation process at Kirishi industrial LAB-production unit and contains description of kinetic and hydrodynamic aspects of this process.

Kinetic model of this process is built upon the following kinetic scheme:

$C_nH_{2n}+C_6H_6\xrightarrow{k1}C_6H_5(C_nH_{2n+1})$ (linear alkylbenzene (LAB) formation)

$i-C_nH_{2n}+C_6H_6\xrightarrow{k2}i-C_6H_5(C_nH_{2n+1})$ (non-linear alkylbenzene (NAB) formation)

$C_6H_5(C_nH_{2n+1})+C_mH_{2m}\xrightarrow{k3}C_6H_4(C_nH_{2n+1})(C_mH_{2m+1})$ (dialkylbenzene (DAB) formation)

$C_kH_{2k}+C_6H_4(C_nH_{2n+1})(C_mH_{2m+1})\xrightarrow{k4}C_6H_3(C_nH_{2n+1})(C_mH_{2m+1})(C_kH_{2k+1})$ (polyalkylbenzene (PAB) formation)

$C_nH_{2n-2}+2C_6H_6\xrightarrow{k5}C_nH_{2n}(C_6H_5)_2$ (diphenylalkane (DPA) formation)

Where n, m, k – carbon numbers; linear alkylbenzenes – desired products with high biodegrability; non-linear alkylbenzenes – by-products with low biodegrability, dialkylbenzenes, polyalkylbenzenes, diphenylalkanes – by-products, which are often aggregated under name «heavy alkylate».

Plug-flow model was proposed to describe the hydrodynamic conditions in the reactor because of its geometrical characteristics. This assumption was checked by calculation of Pekle’s number, which is equal 576. So, diffusion flows in the reactor can be neglected.

Taking into account kinetic and hydrodynamic parts, the mathematical model of the alkylation process reactor has the following form:

$$\frac{dC_{\text{LAB}}}{d\tau} = k_1\, C_{\text{olefines}} - k_3 C_{\text{LAB}} (C_{\text{olefines}} + C_{\text{i-olefines}})$$

$$\frac{dC_{\text{NAB}}}{d\tau} = k_2\, C_{\text{i-olefines}} - k_3 C_{\text{NAB}} (C_{\text{olefines}} + C_{\text{i-olefines}})$$

$$\frac{dC_{\text{olefines}}}{d\tau} = -k_1\, C_{\text{olefines}} - k_3 C_{\text{olefines}} (C_{\text{LAB}} + C_{\text{NAB}}) - k_5 C_{\text{olefines}} (C_{\text{aromatics}} + C_{\text{DAB}})$$

$$\frac{dC_{\text{i-olefines}}}{d\tau} = -k_2\, C_{\text{i-olefines}} - k_3 C_{\text{i-olefines}} (C_{\text{LAB}} + C_{\text{NAB}}) - k_5 C_{\text{i-olefines}} (C_{\text{aromatics}} + C_{\text{DAB}})$$

$$\frac{dC_{\text{diolefines}}}{d\tau} = -k_4 C_{\text{diolefines}} C_{\text{benzene}}^{\;2}$$

$$\frac{dC_{\text{benzene}}}{d\tau} = -2k_4 C_{\text{diolefines}} C_{\text{benzene}}^{\;2} - k_1 C_{\text{olefines}} - k_2 C_{\text{i-olefines}}$$

$$\frac{dC_{\text{DPA}}}{d\tau} = k_4 C_{\text{diolefines}} C_{\text{benzene}}^{\;2}$$

$$\frac{dC_{\text{PAB}}}{d\tau} = k_5 (C_{\text{olefines}} + C_{\text{i-olefines}})(C_{\text{aromatics}} + C_{\text{DAB}})$$

$$\frac{dC_{\text{DAB}}}{d\tau} = k_3 (C_{\text{olefines}} + C_{\text{i-olefines}})(C_{\text{LAB}} + C_{\text{NAB}}) - k_5 (C_{\text{olefines}} + C_{\text{i-olefines}}) C_{\text{DAB}}$$

$$\tau = 0 \quad C_{\text{i}}(0) = C_{\text{i},0}$$

Where τ – contact time, sec; C_{i} – concentration of *i*-component, mol·m^{-3}.

Estimation of rate constants for these reactions $(k_1 - k_5)$ was carried out based on available information from different sources [1, 2, 3] and experimental data from real industrial unit at Kirishi LAS-production plant.

Another input data were processed with the use of mathematical model and the calculated output data (yield and biodegradability factor of the target product) were compared to the experimental ones.

As the results of product yield and quality calculation conform to similar experimental figures, the model can be used for estimation of alkylation process efficiency under different technological conditions.

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PEROVSKITE CATALYSTS FOR NO REDUCTION WITH H_2

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Introduction

Road transport is a major contributor of hydrocarbons (HC), nitrogen oxides (NO_x) and particulate matter (PM). The prevalent technology available to control NO_x emission is indeed the selective catalytic reduction (SCR) by NH_3. In the last years, the use of hydrocarbons, co-existing in the vehicle exhaust, as reducing agents has been extensively studied [1]. Hydrogen could be the most likely candidate as a reducing agent in the SCR reaction to abate NO_x emissions in an excess oxygen environment, such as diesel engine exhaust; this possibility has been reported by several researchers [2]. The high performance of H_2-SCR reaction can justify the employment of a reformer for H_2 generation from diesel fuel.

In the present paper, the activity of perovskite catalysts belonging to the $LaFeO_3$ family was investigated for the H_2-SCR technology. On the basis of the obtained results, the suitability of the mentioned catalysts for application in the treatment of the diesel exhausts will be finally discussed.

Experimental Campaign & Results

A series of perovskite catalysts ($La_{0.8}Sr_{0.2}FeO_3$, $La_{0.8}Sr_{0.2}Fe_{0.9}Pd_{0.1}O_3$, $La_{0.7}Sr_{0.2}Ce_{0.1}FeO_3$, $Pd/La_{0.7}Sr_{0.2}Ce_{0.1}FeO_3$) have been prepared by Solution Combustion Synthesis (SCS) from an aqueous solution of metal nitrates precursors and urea (acting as a sacrificial fuel). According to this method an easily-crumbling foam of nano-sized particles (see Fig. 1) with high specific surface area was obtained. Pd was then deposited via IWP [3] employing an aqueous solution of Palladium nitrate. The prepared powder was dried in oven at 120°C for 12 hours, then calcined in air at 500°C for 5 hours in order to decompose the nitrate and obtain small and well dispersed Palladium clusters on the perovskite surface.

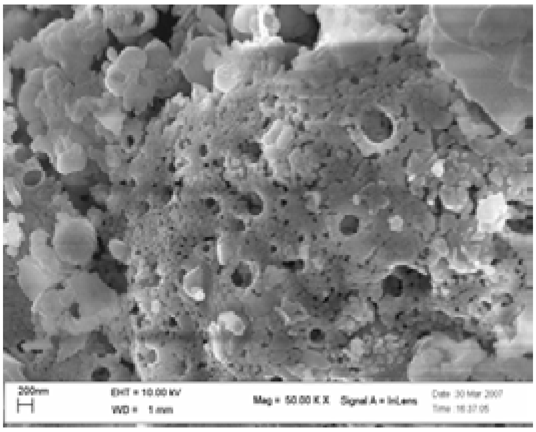

Fig. 1. FESEM picture of $La_{0.7}Sr_{0.2}Ce_{0.1}FeO_3$.

The catalysts were characterized (XRD, FESEM, BET) and tested in a fixed-bed quartz microreactor under an atmosphere of 1000 ppmv NO, 4000 ppmv H_2, with 10% or without

O_2, balanced by He, at a rate of 300 ml/min^{-1} over 100 mg catalyst (W/F = 0.02 g·s· cm^{-3}, GHSV ≈ 30,000 h^{-1}). The maximum NO conversion and the corresponding temperature were taken as an activity index of each tested catalyst. Fig. 2 shows that the most promising catalyst was $Pd/La_{0.7}Sr_{0.2}Ce_{0.}FeO_3$. The latter entailed a T_{50} of just 117°C (the lowest measured value, see Fig. 2) as opposed to the 590°C of non-catalytic reaction.

Therefore this catalyst was deposited over a honeycomb support (cylindrical cordierite honeycombs diameter 35 mm, length 25 mm, 200 c.p.s.i., CTI). The catalytic converter was prepared by a preliminary deposition of a layer of γ-alumina (5 wt% referred to the monolith weight) by *in situ* SCS; then the deposition of 15 wt% (referred to the γ-alumina weight) of catalyst and finally the Pd deposition by wet impregnation with a $Pd(NO_3)$ aqueous solution followed by calcinations at 500°C for 2 hours so as to obtain 1 wt% of Pd referred to alumina. A monolith calcination step at 700°C for 3 h in air was finally performed [3].

The quite promising performance of the supported catalyst was also confirmed (Fig. 3).

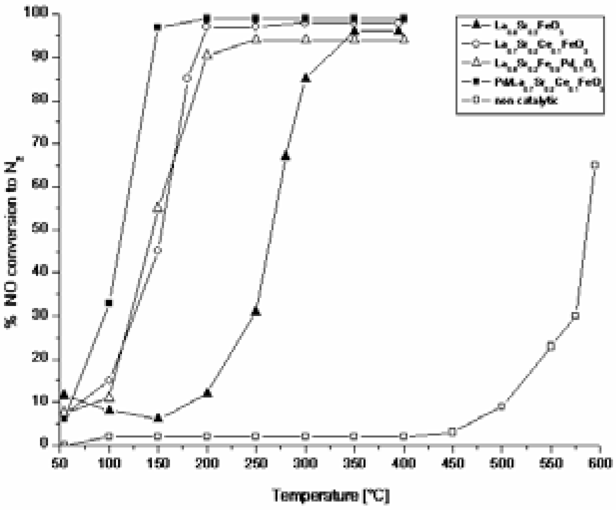

Fig. 2. NO conversion to N_2; conditions:1000 ppmv NO, 4000 ppmv H_2, GHSV 30000 h^{-1}.

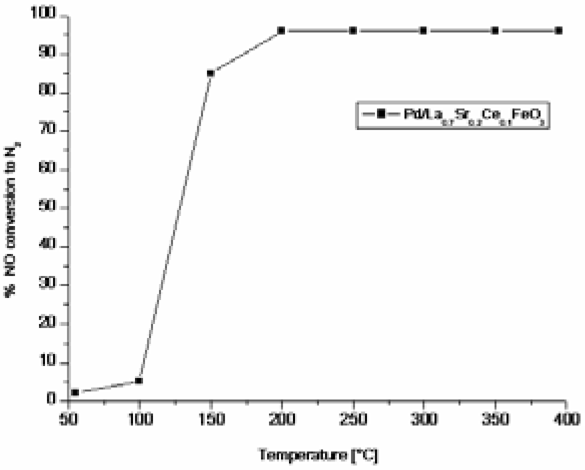

Fig. 3. NO conversion to N_2 in $NO+H_2$ reaction over $Pd/La_{0.7}Sr_{0.2}Ce_{0.1}FeO_3$ deposited on a honeycomb cordierite monolith (same conditions as in Fig. 2).

When oxygen is present in the feed stream, the T_{50} shift is negligible. A deep understanding of this occurrence is being gained through ad-hoc temperature programmed desorption/reduction and XPS analyses. No oxidation products (N_2O, NO, NO_2) were in any case detected. Wide details about these the last experiments will be given in the full paper.

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COMPARISON OF IRREVERSIBLE GAS-SOLID REACTION BEHAVIOR IN PLUG-FLOW AND GRADIENT-FREE REACTORS

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Plug-flow reactors are widely used both in industry and researches. As for gradient-free reactors they are mainly intended for kinetics studies. While the description of steady-state catalytic reactions in gradient-free reactors is widely known, that for unsteady gas-solid reactions seems not to be. Besides the case of gas-solid reaction kinetics study where the gradient-free flow may be created deliberately, following situations are also of interest. Test reactor may contain only few granules of solid reagent in a flat bed, so it is hard to expect any gradient of gaseous reagent along the gas flow. Or, the gradient of gas composition may smooth out because of longitudinal diffusion or convection.

So the model (or models) of absorbent or solid reactant behavior in a gradient-free reactor may be of interest especially in comparison with that for plug-flow reactor, particularly, the way to distinguish these types of flow mode in some reactor under study.

The obvious material balance for the reaction of minor gas admixture in a gradient-free reactor can be expressed as follows:

$$\left(c_{in}-c\right)G=w_b V_R,\ dP/dt=-w_b \tag{1}$$

where c_{in} – inlet gas admixture content; c – gas admixture content inside the reactor; G – total gas volume flow rate; w_{b} – reaction rate per unit reactor volume; V_{R} – solid reactant volume; P – instant content of the solid reactant per unit reactor volume; t – current reaction time.

Assuming irreversibility of the reaction and first order of the reaction rate with respect to gas admixture content, following [1], we have

$$w_b=cf_m\left(P\right), \tag{2}$$

function $f_{\text{m}}(P)$ being determined by the nature of gas-solid reaction and mass transfer involved. Functions $f_{\text{m}}(P)$ (m is a model number) for various reaction models are given in ref. [2].

Substituting (2) to (1), finally we get after some transformations:

$$\nu=\left[\tau_{ac}f_m\left(P_0\eta\right)+1\right]^{-1},d\eta/dt=-\left(c_{in}/P_0\right)\left[\tau_{ac}+f_m\left(P_0\eta\right)^{-1}\right]^{-1}, \tag{3}$$

where $\nu = c/c_{\text{in}}$; $\tau_{\text{ac}} = V_{\text{R}}/G$ – contact time; $\eta = P/P_0$; P_0 – initial content of the solid reactant per unit reactor volume.

Solution of system (3) for all models described in ref. [2] can be obtained in closed form. The first feature of this solution is that solid-phase conversion *vs.* time dependencies differ significantly from those for single granule [3], especially at large contact times τ_{ac}.

The results for the case of both diffusion and reaction on the core interface being limiting, the latter being first-order with respect to gas impurity content (Model 3[2]), are shown on figs. 1 and 2. Bed parameter values were chosen as in ref. [2], $\tau_{ac} = 4$ s that is typical for laboratory test.

It was found [2] that time-dependent data concerning the impurity content in the gas flow leaving an absorbent bed rather than solid-phase conversion vs. time data are those sensitive to the gas-solid reaction model choice.

In practice, this method of testing was elaborated by Dantsig *et al.* [4] for the case of gas desulfurizing using ZnO granules.

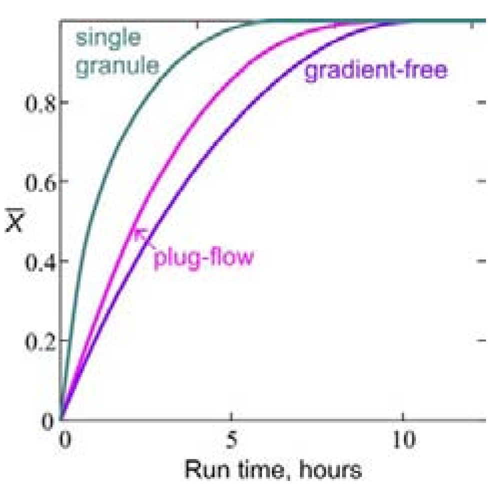

Fig. 1. Solid-phase conversion *vs.* time dependencies.

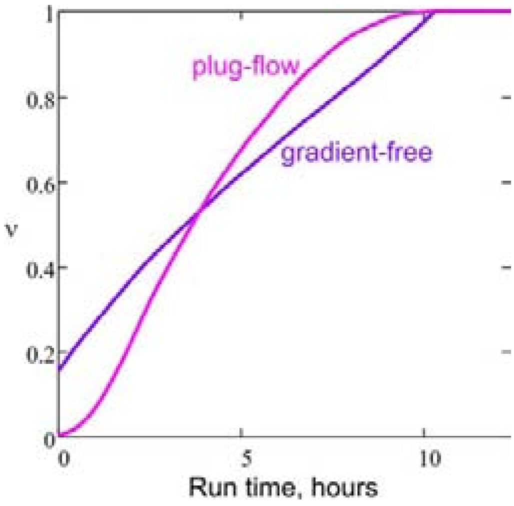

Fig. 2. Gas content *vs.* time dependencies.

When comparing the behavior of plug-flow and gradient-free reactors we have exactly the same case. Curves for these two types of reactors in the Fig. 1 do not merge, but lie close together. On the contrary, gas content *vs.* time dependencies (Fig. 2) differ qualitatively. The main difference is that the minimal possible breakthrough value v ($t = 0$) is much less in the case of plug-flow reactor, as it can be seen in the Fig. 2. Besides that, it decreases exponentially for plug-flow reactor when τ_{ac} increases, the decrease being much more slow for gradient-free reactor. So the latter seems not to be suitable to sweeten gas in industry.

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SIMULTANEOUS HYDROGENATION OF SULFUR, NITROGEN AND AROMATIC COMPOUNDS IN HEAVY PETROLEUM FRACTIONS OVER NiMo/γ-Al_2O_3 CATALYSTS

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Hydrotreating processes (HDT) have long been broadly investigated for upgrading of petroleum fractions all over world, and its role grew in importance recently because of the use of heavier feedstocks as a consequence of decreasing in light reserves and international prices increasing. Particularly, hydrodesulfurization (HDS) and more recently hydrodenitrogenation (HDN) and hydrodearomatization (HDA) are becoming a key target for the research in specialized scientific community [1, 2]. The three processes have been separately matter of many investigations, and therefore many phenomena seem clear for the scientists [3]. However, no extensive work has been done in research of simultaneous HDS, HDN and HDA carried out in heavy feeds at industrial process condition. To respond to this situation, this work deals with the analysis of the simultaneous behavior of sulfur, basic nitrogen, non-basic nitrogen and aromatic families compounds, in real heavy feeds oils during the hydrotreating process [4]. In this research, heavy vacuum gas oil (VGO) and demetalized oil (DMO) were selected as main feedstocks. By fractioned distillation, each one of the feeds were split in four fractions (lowest to heaviest) and each fraction was analyzed and underwent to the HDT process in a pilot plant, employing a combination of catalysts NiMo/γ-Al_2O_3 and under temperatures of 330, 350 and 370 °C, pressure of 10 MPa, liquid hourly space velocity of 1.1 h^{-1}, and gas/oil ratio of 6.24 [5]. The employed methodology is shown in Figure 1. The hydrotreating of full VGO and DMO was denominated «Direct Pathway», whereas the hydrotreating by cuts was denominated «Indirect Pathway». The analytical techniques used in this work were: ultraviolet-visible spectroscopy for analysis of aromatics families, nuclear magnetic resonance (H-NMR) for total aromatic hydrogen content, and standard methods (ASTM) for the determination of total sulfur, total nitrogen, basic nitrogen, boiling point distribution, density, API, refraction index, and distribution in saturates, aromatics, resins.

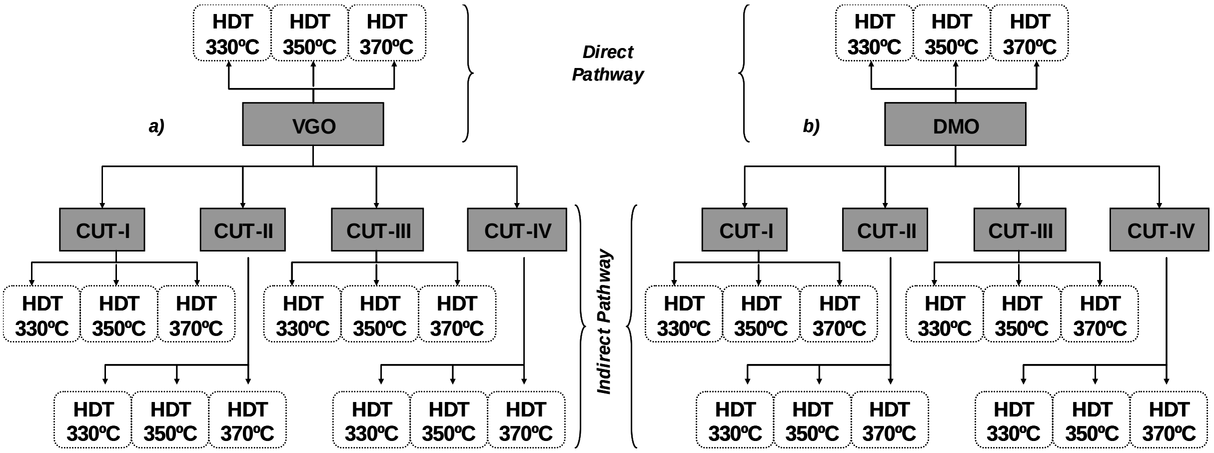

Figure 1. Metodology for hydrotreating of VGO and DMO.

In general, it was observed that sulfur, basic nitrogen, non-basic nitrogen, and total aromatics contents increased with the boiling point of each fraction, whereas the product oil became more purified by the removal of undesirable contaminants with increasing temperature of HDT. The reactivity order for hydrotreating of heavy vacuum gas oil (VGO) was established as HDS > HDA(PA) > HDA(TA) > HDNBN > HDA(DA) > HDBN = HDA(MA) following the relationship 3.0/2.0/1.8/1.6/1.5/1.0=1.0. Moreover, the reactivity order for hydrotreating of demetalized oil (DMO) was established as HDS>HDA(PA)>HDA(TA)>HDNBN> HDA(DA)>HDBN=HDA(MA) following the relationship 5.0/2.5/1.8/1.5=1.5/1.3/1.0. Additionally different correlations for eleven measured physicochemical properties were explored, finding that a linear function satisfactorily correlated the sulfur content with nitrogen content in the feed oil and the product oil. Therefore, the nitrogen content could be used to determinate the reactivity of different feedstocks. Likewise was observed that the calculated composition obtained by theoretical mixing the four hydrotreated cuts using the same mass proportions is better than composition obtained by direct hydrotreating of complete feedstock. Therefore new schemes for HDT of heavy petroleum fractions could be proposed in order to produce fuels with higher quality.

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PP-III-11

LOW TEMPERATURE OXIDATION OF CARBON MONOXIDE ON POTASSIUM PROMOTED GOLD DISPERSED ON Fe_2O_3, TiO_2, Al_2O_3 SUPPORTS

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Despite the intensive efforts the nature of gold catalyst active sites and the mechanism of low temperature carbon monoxide oxidation $CO + O_2 \rightarrow CO_2$ remains unresolved and the mode of oxygen activation is one of the least understood reaction step. In this work the role of potassium ions deposited on Au/support (Fe_2O_3, TiO_2, Al_2O_3) catalysts was investigated.

Supported catalysts 0.5 – 10% Au/support (Fe_2O_3, TiO_2, Al_2O_3) were prepared by two methods: conventional impregnation and deposition precipitation. In the case of impregnation method commercial supports were impregnated in aqueous solution of $HAuCl_4$ (pH ≈ 2). After water evaporation catalyst samples were dried at 60 °C in air. A fraction of samples were additionally impregnated with aqueous solution of KOH (pH > 13) and finally catalysts were dried at 60 °C. In deposition precipitation method aqueous solution of Na_2CO_3 was used as precipitation agent for $HAuCl_4$ solution to achieve pH value in the range 7 – 8 and then appropriate amount of commercial support was admixed and the obtained catalysts were dried at 60 °C in air. The physicochemical properties of supported catalysts were investigated by: low temperature nitrogen adsorption – BET(N_2), temperature programmed reduction – TPR H_2 and diffraction method – XRD, second ions mass spectrometry – ToF-SIMS and electron spin resonance spectroscopy – ESR. The catalysts were tested in CO oxidation reaction using a fixed bed quartz reactor. Typically, CO (3% in He) and O_2 (6% in He) were mixed and fed to the reactor at controlled flow rate (usually 50 cm^3/min) through the catalyst sample (0,20 g) in appropriate temperature range, and the products were analysed at every 50 °C temperature interval, using on-line gas chromatography. The applied molar ratio O_2 : CO being about 4 : 1 reflects the oxidative conditions commonly experienced in industrial practice of carbon monoxide removal.

Acid-base character of Au/support catalyst surface can play important role in catalytic performance. Different acidity in preparation procedure: impregnation (pH = 2) in comparison with precipitation-deposition (pH = 7 – 8), and KOH addition (pH > 13) results in the hydrolysis of chlorine ions and their re-adsorption taking place on support surface:

$[AuCl_4]^- + 4\,OH^- \rightarrow [Au(OH)_4]^- + 4\,Cl^-$.

The activity of Au/support catalysts in CO oxidation and WGS reaction is as follow: $TiO_2 > Fe_2O_3 > Al_2O_3$.

The beneficial role of the addition of potassium hydroxide in such oxidation reaction like $CO + O_2$ or $CO + H_2O$ seems to be governed by the nature of basic hydroxyl groups which can be engaged into chemical cycling via potassium hydro-peroxide and bicarbonate group formation: $2K^+ + 2OH^- + O_2 \rightarrow 2KHO_2 + 2CO \rightarrow 2KHCO_3 + 2OH^- \rightarrow 2K^+ + 2OH^- + 2CO_2$. Such interpretation allows to avoid the dissociation of oxygen molecule what seems to be a case in proposed high temperature mechanism. Thus, the addition of KOH, even to a non-active or poorly-active impregnated Au/support (Fe_2O_3, TiO_2) catalysts result in 100% CO conversion at room temperature. The promotional effect was attributed to hydro-peroxide groups formation on support surface as a result of direct O_2 molecules non-dissociative activation with basic potassium originated hydroxyl groups: $OH^- + O_2 + 2e \rightarrow HO_2^- + O^{2-}$. The possible sources of electrons responsible for this reaction may originate from metal ions oxidation $M^{n+} \rightarrow M^{n+1} + e$, where M can represent transition metal atoms: Fe^{2+}, Ti^{3+} or Au^0 being in direct vicinity of potassium ions. The formation of super-oxide or hydro-peroxide surface species resembling those experimentally verified compounds like: KO_2, KHO_2, KFe_2O_5, $KTiO_4$ or $KAuO_3$ favours the postulated mechanism of CO oxidation at low temperature.

Acknowledgements

The financial support of this work by the Polish Scientific Research Council supports (Grant No. 4T09 146 25 and partially No. PBZ-2/2006) is gratefully acknowledged.

IMPROVING THE PROCESS OF HIGHER PARAFFIN DEHYDROGENATION ON THE BASIS OF NONSTATIONARY KINETIC MODEL

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The potential demand of domestic market of synthetic detergents in a raw material base, which is linear alkyl benzenes (LAB) and linear alkyl benzene sulphanates (LABS), is about 100 thous. tons per year. One of the possible ways of the set productivity improvement is inclusion of the second dehydrogenation reactor in parallel operation.

At present, only one dehydrogenation reactor is included into set operation, while the second reactor being a reserve one. Technical staff supposes that the reserve reactor inclusion into parallel operation allows increasing the volume of released production without fundamental reconstruction of operative equipment.

Forecasting operation of such variant of scheme of the operative set may be performed the most efficiently applying the kinetic model developed by the authors, describing sufficiently the industrial process of higher paraffins dehydrogenation, and technological modeling system created on its basis (TMS) [1].

Mathematical description of dehydrogenation process is taken as a principle of the technological modeling system, which contains the following issues: current and prognostic calculation of higher paraffins dehydrogenation processes and by-products hydrogenation, material balance calculation of the set in whole, visualization of the obtained results (curves, tables).

Using the developed TMS the prognostic calculations set indexes operation were carried out at the following invariable initial data: molar ratio H_2/hydrocarbons = 7:1; n-paraffins volume flow for both reactors 75 m^3/h; LAB generation – 180 t./day.

At parallel operation of dehydrogenation reactors the main factor, defining the change of efficiency indexes of this process, is raw materials load reduction per one reactor, and therefore, decrease of volumetric feed rate, i.e. increase of contact time of agents and catalyst. Reduction of volumetric raw materials feed rate allows decreasing temperature profile of the process, on the one hand, and as a result, increasing catalyst service life (Fig. 1).

On the other hand, it does not allow increasing LAB capacity (this index remains almost at the same level or it will be a little bit higher due to a longer contact time).

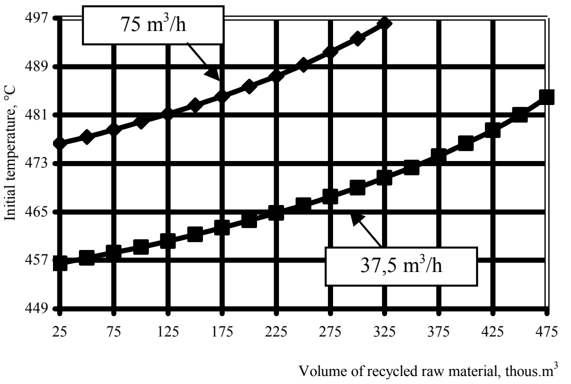

Fig. 1. Dependence of temperature of input into dehydrogenation reactor on raw material consumption (prognostic calculation by mathematic model)

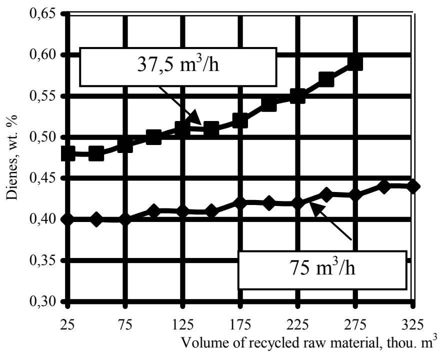

Fig. 2. Dienes concentration depending on raw material consumption (prognostic calculation by mathematical model)

Therefore for increasing process intensity the initial temperature of input into dehydrogenation reactor should be retained at prior level (as at raw material load 75 m^3/h per a reactor). Because of contact time increase, and also high temperature of input into reactor the concentration of by-products (diene hydrocarbons) increases at an average on 15 wt. % and by the end of operation cycle to 50 wt. % (Fig. 2). It results inevitably in formation of such high-molecular compounds as tetralin and indan homologues, polyalkylaromatic compounds, di-and more phenylalkanets and others (at LAB generation about 200t/day) and deterioration of a desired product biological decomposability that is inadmissible.

The transition to two-reactor scheme provides the decrease of total pressure in the system due to reduction of raw material load to one dehydrogenation reactor. It gives the additional reserve for increasing hydrogen feeding into the system. Therefore it would be reasonable in this case to increase molar ratio H_2/hydrocarbons.

Prognostic calculation by the model showed that the average content of desired and by-product components at ratio H_2/hydrocarbons, equal 8:1, will be reduced to the level, when the set was operating at raw material load 75 m^3/h per a reactor.

Though LAB generation does not exceed the level 180 t/day but the duration of catalyst operation cycle increases in 1,5…1,7 times, that balances the dead time at reactors overloading.

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POTENTIAL OF WOWEN FIBROUS CATALYTIC CLOTHS IN FLOW REACTOR

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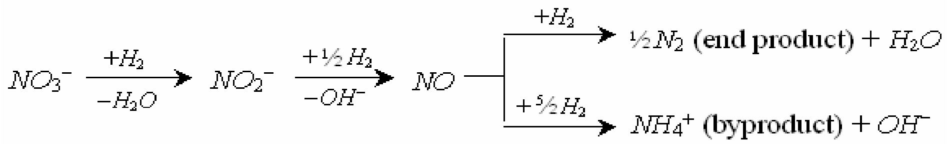
Fibrous woven catalytic cloths[1] form a special category of structured catalysts and with their unique ability to combine an open macrostructure with mechanical flexibility would be suitable for design of new kinds of reactors. A novel flow reactor with rolled fibrous catalytic cloth was proposed to carry out a gas-liquid reactions with hydrogen pre-dissolved in the liquid-phase at elevated operating pressure prior to entering into catalytic reactor[2].

The hydrogenation of nitrate in water (reaction 1) over most active 2wt%Pd-0.6wt%Cu catalyst supported on activated carbon cloths (ACC, Figure 1a) in this reactor (Figure 1b and c) at 25 C, shows selectivity up to 84% toward nitrogen at nitrate conversion up to 93%.



$$NO_3^- \xrightarrow[-H_2O]{+H_2} NO_2^- \xrightarrow[-OH^-]{+\frac{1}{2}H_2} NO \begin{cases} \xrightarrow{+H_2} \frac{1}{2}N_2 \text{ (end product)} + H_2O \\ \xrightarrow{+\frac{5}{2}H_2} NH_4^+ \text{ (byproduct)} + OH^- \end{cases} \qquad (1)$$

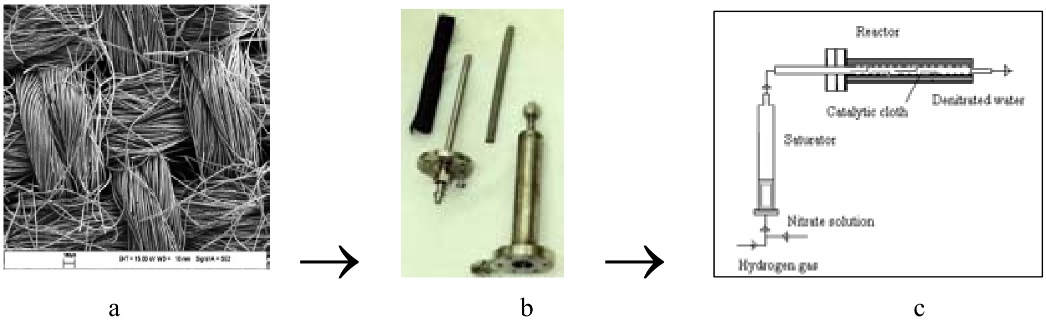


Figure 1. Typical SEM image of ACC (a), radial flow reactor with catalytic cloth (b) and schematic diagram of the experimental nitrate hydrogenation test unit (c).

The aim of this work is to highlight the potential benefits of novel radial-flow reactor with fibrous catalytic cloths as compared to pellet or monolith for water treatment. To compare woven cloths with pellets or monoliths, we use a merit index that accounts for a tradeoff between mass transfer and pressure drop performances:

$$-\ln(1-X)/\Delta P/(\rho u^2) = dS_v\, Sh/2f\, ReSc = dS_v k_m/2fu \qquad (2)$$

where k_m – liquid/solid mass-transfer coefficient for liquid reactant (m/s); ΔP – pressure drop (Pa), X – nitrate conversion; ρ – bulk density of catalytic bed (g/cm^3); S_v – external surface area per unit volume of bed (m^{-1}) and u – superficial flow velocity (m/s).

Woven cloths have a specific geometric structure (Figure 1a), containing tows, which are bundles of arrays of aligned filaments with pores (openings) results from the interlacing of two adjacent warp and weft tows. Results of experimental measurements of pressure drop through one layer of ACC with different pore sizes were used to calculate opening diameters *(d_o)* and correlations for dimensionless friction factors (*f*). Liquid-solid mass transfer coefficients k_m for Pd-Cu/ACC catalysts with different pore sizes were determined under mass-transfer-limited operation according to a simple one-dimensional model of the test reactor.

For beds of spheres and monoliths with square cells classical literature expressions have been adopted and relevant variables were expressed in dimensionless form by calculating the Sherwood (*Sh*), Schmidt (*Sc*), and Reynolds (*Re*) numbers, using pore diameter as the characteristic length, specific for each support (d_p for pellets, d_h for monolith). (Table 1).

Table 1.

	pellet	*monolith*	***woven cloth***
characteristic dimension	d_p	d_h	d_o
relationship between S_v and bed porosity *e*	$d_pS_v=6(1- e)$	$d_hS_v=4 e$	$d_oS_v= e (1- e)$
mass-transfer coefficient	$Sh=aRe^bSc^{1/3}$	$Sh=2.977[1+0.095(Re/\varepsilon)Sc(d/L)]^{0.45}$	$Sh=0.24Re^{0.56}Sc^{1/3}$
friction factor	$2f=(1- \varepsilon)/ \varepsilon^3[1.75+150((1-\varepsilon)/Re)]$	$f=14.23/ \varepsilon Re$	$f=2.66+0.75/Re$

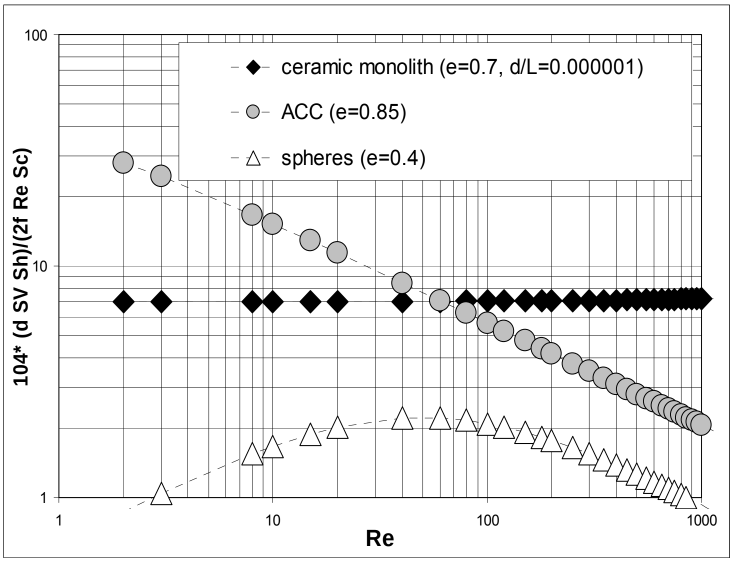


Figure 2. Conversion–pressure drop tradeoff index for different catalysts.

The obtained results of tradeoff index calculations (Figure 2) demonstrate that reactor with woven cloths perform much better than those with packed beds of spheres, whose index is strongly penalized by the high pressure drop across the bed. On the other hand, the advantage of cloth over monolith increases at lower liquid velocities (lower Re).

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A REACTOR FOR PHOTOELECTROCATALYTIC OXIDATION OF AROMATIC ALCOHOLS

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In heterogeneous photocatalysis the charge recombination between the photogenerated electrons and holes is often a main limiting factor lowering the quantum yields of the processes. Recently, several efforts have been made to enhance the photocatalytic efficiency of titanium dioxide, such as noble metal deposition, ion doping and electrochemically assisted method. Concerning this last opportunity, an external anodic bias is applied to force the photogenerated electrons and holes in different directions so that the charge recombination is reduced to a large extent.[1-3]

Photoelectrochemical technology with external field appears to be a novel emerging research front in photocatalytic degradation of organic pollutants. As for any hybrid technology, it is significant to take into account the advantages coming from higher oxidation rates and synergic factors coming from the combined system. The experimental phenomenon is considered as an indicator of synergetic effect originated from the interaction between the single technologies.

It was recently developed by us a new photoelectrochemical reactor, used in the oxidation of p-methoxybenzyl alcohol. The Pyrex reactor is of cylindrical shape and graphite rods (diameter: 3 mm) play the role of anodes, while a gold sheet, that of cathode. A 125 W medium pressure Hg lamp (Helios Italquartz, Italy) was axially positioned inside the reactor; it was cooled by water circulating through a Pyrex thimble. The six anodes were placed axially with respect to the lamp (Figure 1). The annulus of reactor was filled with Pyrex beads, of 3 mm diameter. TiO_2 thin layers, obtained through a sol gel method from $TiCl_4$, were deposited either on the glass beads or on the graphite rods.

Photoelectrocatalytic runs (with a constant bias in the 0-4 V range) were performed in recirculation mode, with or without irradiation. The photoelectrocatalytic conversion for all the runs was always higher than the single photocatalytic and electrocatalytic reaction rates. Figure 2 shows runs performed with TiO_2 covering glass beads (thickness 1μm).

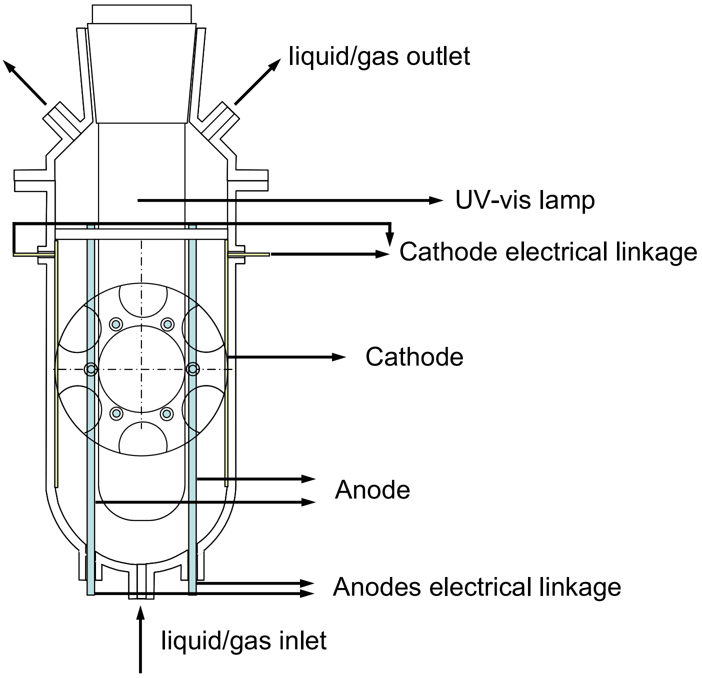

Figure 1. Scheme of the photoelectrochemical reactor.

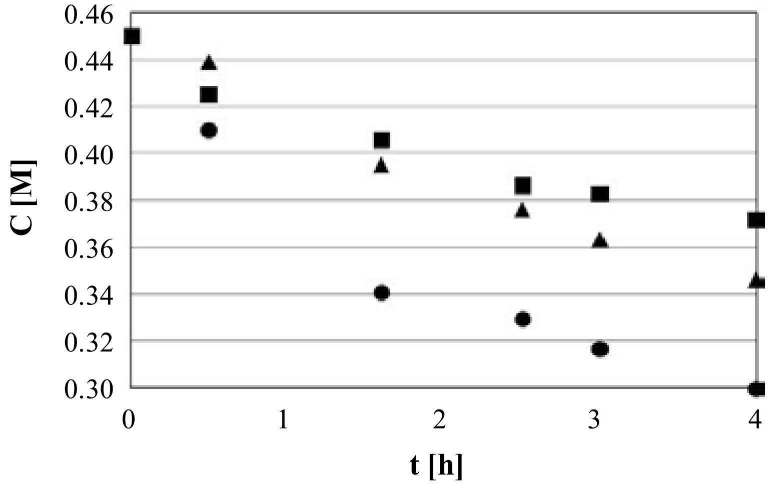

Figure 2. Alcohol concentration *versus* irradiation time for 2 V bias.
▲, photocatalysis; ■, electrocatalysis; ●, photoelectrocatalysis.

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COMPUTER MONITORING OF CATALYTIC REFORMING PROCESS IN SEMI-REGENERATIVE CATALYTIC REFORMER

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Catalytic reforming is considered as a complex multi-component chemical-engineering process the main purpose of which appears to be the production of gasoline with a high octane level and individual aromatic hydrocarbons for the petrochemical requirements. The process is affected by a great number of different parameters such as temperature, pressure, feedstock composition and consumption, catalyst surface condition, therefore it is very important to maintain the optimal behavior of the system. Therefore the continuous monitoring of the process becomes important because it allows engineer to estimate the deviations of the process from the optimal regime and to indicate the probable reasons for these deflections. Thus the objection of the work appears to be the catalytic reforming process monitoring to investigate the changes in optimal behavior of the system and to indicate the probable causes of that.

To begin with, by way of criterion for optimal behavior of the system an optimal activity was chosen. Catalytic reforming is known to be conducted on the surface of platinum containing catalyst which tends to reduce in its activity due to carbonaceous coke deposition and chloride loss. The optimal activity represents the catalyst activity when the equilibrium of coke deposition and hydrogenation reactions takes place. The deviation of catalytic activity from the optimal activity results in the more intensive accumulation of the coke on the catalyst surface hence reducing the time of catalyst exploitation. The activity of the catalyst can be periodically regenerated or restored by in situ high temperature oxidation of the coke followed by chlorination. Semi-regenerative catalytic reformers are regenerated about once per 6 to 24 months.

For calculating the optimal activity of the catalyst the special simulator “Catalyst control” was used. This simulator is based on the not stationary mathematical model of the adiabatic reactor with a fixed bed of the catalyst taking into account the physicochemical regularities of the process. The mathematical model of the reactor is represented by a number of material balance equations, thermal balance equation supplemented with the equation of catalyst deactivation [1].

The experimental data for catalytic reforming monitoring was obtained from refinery reforming unit L-35-11/1000 (Kirishi, Russia). Using the feedstock composition, octane level of the product and technologic data the optimal activity was calculated. The results of calculation followed by the values of the main technologic parameters are presented (table 1).

Table 1. Catalyst optimal activity change with cumulative coke and feedstock refined

Date	Optimal activity, relative units	Cumulative coke, mass fraction	Feedstock refined, thousand tons
01.05.2007	0,93	5,11	608940
01.06.2007	0,87	5,79	700995
01.07.2007	0,87	6,32	780816
01.08.2007	0,84	6,82	858781
02.09.2007	0,86	7,55	956173
30.09.2007	0,82	8,10	1031549
02.11.2007	0,88	8,59	1094079
30.11.2007	0,80	9,07	1163462

The table shows that the optimal activity of the catalyst reduces with increasing of feedstock refined and the quantity of cumulative coke. However, it could be noticed that the reduction of the optimal activity seems to be not linear having the local increase in September. Making the attempt to explain the optimal activity curve behavior it was supposed that the value of catalyst activity is affected by the current feedstock consumption (figure 1).

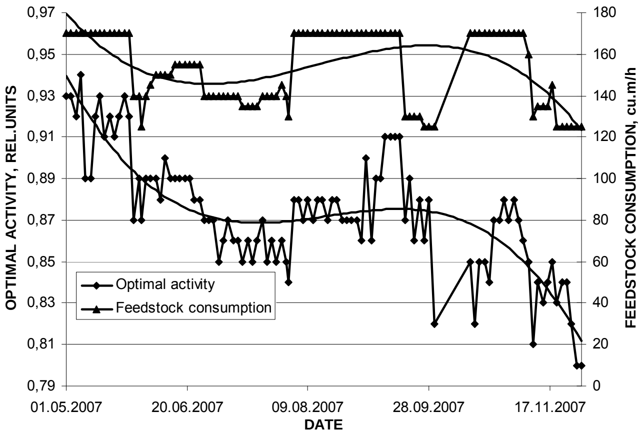

Figure 1 shows that the good correlation between catalyst optimal activity and the current feedstock consumption can be observed. It also seems to be approved that the catalyst activity depends on the feedstock composition hence on the feedstock type used.

Thus computer monitoring allows engineer to design the optimal technologic regime on the basis of feedstock composition and consumption and the required quality characteristics of the product to be produced.

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NANOSTRUCTURED POLYMERIC METAL-CONTAINING NANOCOMPOSITES AS EFFECTIVE NANOCATALYSTS IN REACTIONS OF FINE ORGANIC SYNTHESIS

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Introduction. Industrial processes of fine organic synthesis using catalytic technologies continue to receive significant attention due to the importance of pure and cheap intermediates in the manufacture of vitamins, pharmaceuticals and medicines. One of the most complicated problems is the achieving of high affectivity and stability and at the same time the use of mild conditions of catalytic stage conduction.

Earlier the nanostructured polymers containing noble metal nanoparticles (MNPs) were shown to have increased activity, selectivity and stability of active phase in various organic reactions in comparison to traditional catalysts [1, 2]. Thus, in this study several types of polymers were investigated: (i) amphiphilic block-copolymers; (ii) polyelectrolytes (PE); (iii) polymeric matrices. Catalytic properties of the synthesized nanocomposites were studied in selective hydrogenation of triple bond, enantioselective hydrogenation, direct selective oxidation of monosaccharides and full oxidation of phenols.

Experimental. Homo- and heterogeneous mono- (Pd and Pt) and bimetallic (Pd-Au-, Pd-Pt- and Pd-Zn) catalysts of (i) type were prepared using poly (ethylene oxide)-block-polyvinylpyridine (PEO-b-P2VP) and polystyrene-block-poly-4-vinylpyridine (PS-b-P4VP). In case of (ii) type catalysts, PEs (polydiallyldimethyl ammonium chloride (PDADMAC), chitosan (CS) and poly(sodium 4-styrenesulfonate) (PSS)) were deposited on alumina using two methods: monolayered and "layer-by-layer" deposition. Thus Pd-PDADMAC and Pd-PSC (multilayered) were synthesized. Hypercrosslinked polystyrene (HPS) was used to obtain the (iii) type catalysts: Pd-, Pt-, Ru-, Pd-Zn- and Pd-Pt-HPS.

The oxidation reactions were conducted batchwise in PARR 4890 apparatus. The analysis of reaction mixture was performed by SpectraPhysics HPLC chromatograph. All the oxidation reactions were performed in an aqueous reaction medium. Enantioselective hydrogenation of activated ketones was conducted also batchwise in PARR 4307 apparatus.

Catalytic hydrogenation of triple bond of acetylene alcohols was conducted batchwise in glass reactor equipped with shaker at ambient pressure. In the case of catalytic hydrogenation different solvents and their mixtures were used. The analysis of reaction mixture for all the hydrogenation reactions was performed by gas chromatograph «Kristallux 4000».

It is important to note that catalytic oxidation of monosaccharides was also conducted continuously using fixed bed pilot reactor.

Kinetic investigations of both oxidation and hydrogenation reactions were conducted at variation of substrate to catalyst ratio, pressure and temperature. Pressure was varied in the range of 0.1 – 7 and 0.1 – 2 MPa, and temperature was varied in the range of 25 – 150 and 0 – 95 °C in the case of catalytic oxidation and hydrogenation reactions, respectively. Physicochemical (TEM, AFM, XRD, FTIR, XPS, BET, NMRS) investigations of the nanocatalysts were conducted and the hypotheses of reaction mechanisms were proposed.

Results and discussion. On the base of physicochemical investigations for (i) catalysts it was assumed that bimetallic NPs have different structure. In case of (ii) nanocatalysts the use of «layer-by-layer» preparation method was found to provide the higher stability of catalytic system than monolayered one. HPS was found to effectively control the MNPs growth due to the existence of nanosized microvoids. For all investigated catalysts the interaction of active component of the catalyst with the solvent, support, modifier and substrate was found to take place. The diameter of MNPs was determined to be equal to 2 – 3 nm.

Investigated methods for nanocatalysts synthesis allowed to develop highly active, selective (selectivity reached up to 99% at 100% conversion) and stable catalytic systems.

Conclusion. High active, selective (selectivity reached up to 99% at 100% conversion) and stable catalytic systems of hydrogenation, enantioselective hydrogenation and direct oxidation were developed and investigated in different reactors and conditions.

Acknowledgements

We sincerely thank to Sixth framework programme N 506621-1 and NATO science for peace programme Sfp 981438 for financial support.

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GAS PHASE OXIDATION OF FORMALDEHYDE INTO FORMIC ACID ON A V/Ti CATALYST: 2. DESIGN OF A TUBULAR REACTOR BY MATHEMATICAL MODELING

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Introduction

Boreskov Institute of Catalysis has developed a catalytic route of formic acid production by direct oxidation of formaldehyde by air oxygen in a gas phase. Thus, formic acid can be produced from methanol, the well established technology of methanol oxidation into formaldehyde on the oxide catalyst being the first stage:

$$CH_3OH \xrightarrow{O2} HCHO \xrightarrow{O2} HCOOH$$

The key component of the technology is the appropriate V/Ti oxide catalyst providing high selectivity of formaldehyde oxidation at temperature range 100-130 °C. The goal of this work was a choice of catalyst particle shape and sizing of a commercial cooled tubular reactor for oxidation of formaldehyde into formic acid based on comprehensive mathematical modeling of the reactor tube.

Mathematical model

A two-dimensional quasihomogeneous model of a catalyst bed incorporating a dusty-gas model of a catalyst particle was used. Intrinsic reaction kinetics was studied and established in [1], effective diffusivities being determined from special experiments with full-size catalyst pellets. Heat transfer parameters of the model are defined by correlations valid for different holed particles [2, 3].

Optimization procedure

For each catalyst shape, reactor residence time (catalyst volume at fixed capacity) was minimized under restrictions imposed on formaldehyde conversion, pressure drop, hot spot temperature, hot spot temperature sensitivity and quality catalyst packing. The last restriction is evaluated quantitatively according to [4] as a) minimum allowable ratio of reactor tube to particle diameters and b) allowable ratio of catalyst particle longitudinal and diametrical dimensions. Temperature sensitivity is defined as hot spot temperature rise at increase of cooling agent temperature by one degree. In some cases constraints can be put on catalyst particle wall thickness due to a strength issue.

The following parameters are changed and optimized during a calculation procedure: gas velocity, a tube diameter, cooling agent temperature, catalyst particle dimensions, catalyst activity (within a potential range).

Results

The following catalyst shapes were considered and used in the above described optimization procedure separately: cylindrical pellets, Raschig rings and holed trilobes. At the first stage, the catalyst properties were assumed invariable along the catalyst bed. It was shown that the catalyst shaped as a trilobe is preferable in this case.

At the second stage, a multi-layer catalyst bed loading was considered. The layers could differ in catalyst shape, dimensions and activity. It was shown that multi-layer loading has significant advantages in comparison with uniform one.

As a result, catalyst bed configuration, main design reactor and process technological parameters of a commercial reactor were chosen.

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DEVELOPMENT OF INDUSTRIAL CATALYST SELECTIVITY IN THE HYDROGENATION PROCESS OF DIENES C_9–C_{14}

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Traditionally increase of catalyst efficiency for the oil refining processes requires laboratory and pilot research. The ways of Ni-catalyst development which we propose are based on a calculation with use of a mathematical model for higher diolefines hydrogenation process.

For the most part diolefines are hydrogenated to olefins, which, in their turn, can be hydrogenated to paraffins and thus the process selectivity and the yield of desired product are reduced.

The main peculiarity of this process is a selective catalyst poisoning with a sulfur-bearing substance in order to raise catalyst selectivity.

The mathematical model of hydrogenation process is based on a scheme of chemical transformations. Sulfur-bearing substance (DMDS) takes part in the following reactions:

$$CH_3-S-S-CH_3+1.5H_2+1.5Ni \rightarrow 1.5NiS+2CH_4+0.5H_2S \qquad (1)$$

$$Ni+H_2S \rightarrow NiS+H_2 \qquad (2)$$

Reaction (2) leads to desorption of Ni from catalyst surface. In the presence of water the deactivation of catalyst is very probable:

$$NiS+H_2O \rightarrow NiO+H_2S \qquad (3)$$

Thermodynamic analysis shows that reaction (1) is irreversible, and so quantity of poisoning substance on the catalyst surface depends on the reaction (2) equilibrium. Catalyst activity reduces as a result of this reaction. Quantity of sulphide, in its turn, increases with the rise of sulfur-bearing substance consumption, with rise of equilibrium constant (2) and decrease of hydrogen quantity in the system.

As the dependences of hydrogenation reaction rate on the catalyst activity are different for olefins and diolefines, the determination of optimal catalytic activity is rather complex problem.

The following dependence of the DMDS residual quantity on the temperature in reactor was discovered while analyzing experimental data (Fig. 1).

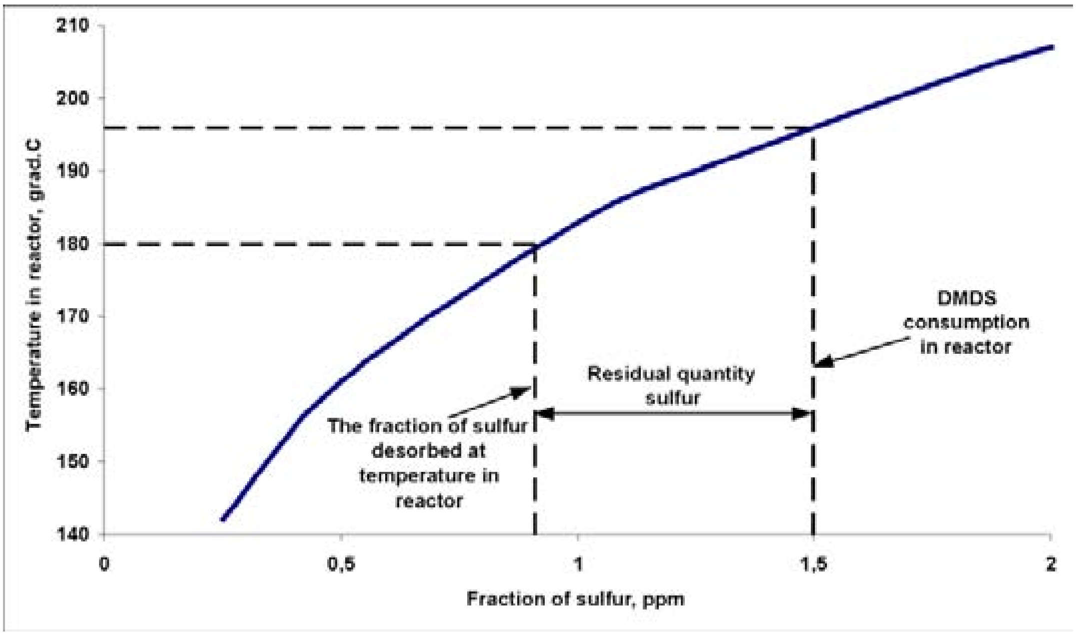

Figure 1 – Dependence of the DMDS residual quantity on the temperature in reactor

Every point at this diagram corresponds to the quantity of sulfur-bearing substance and temperature which set off the effect of each other and lead to the total desorption of sulfur from the catalyst surface. If temperature in reactor is lower then it is needed for the full compensation of sulfiding, then there is a residual quantity of sulfur on the catalyst surface.

An optimal consumption of DMDS at different temperatures is calculated with use of the mathematical model of hydrogenation process.

As a result of investigations for Ni-catalyst of hydrogenation which is used at LAB production plant, it was revealed that in order to get an optimal quantity of sulfur on the catalyst surface DMDS consumption should be kept at the present level (1,5 ppm) and the temperature should be decreased from 180–190 °C to 140–150 °C. But this will cause unavoidable decrease in hydrogenation reaction rate. The second way is to keep present temperature conditions along with increase in DMDS consumption from 1,5 ppm to 2–3 ppm.

PP-III-19

NEW HOMOGENEOUS CATALYTIC SYSTEMS FOR ARYL- OR ARYLALKYL ACIDS PRODUCTION AND UTILIZATION OF PERSISTENT ORGANIC POLLUTANTS - POLYCHLOROBIPHENYLS VIA CARBONYLATION

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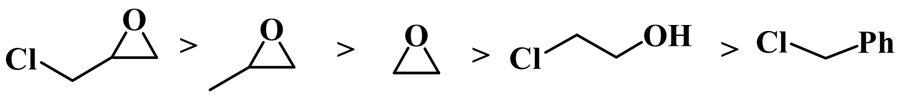
Synthesis of mono- and poly-alkylaromatic and aromatic acids represents the big practical interest. Besides the traditional areas of application: drugs, dyes, lubricants, herbicides, at present, the use of these compounds in high-tech applications, such as liquid crystal materials and thermoplastics, polyester fibers, and electroluminescent and nanomaterials, intensively expands.

We have suggested universal method and developed flexible economical technology of aryl- and arylalkyl acids (ethers, salts, amides) production via the halides carbonylation with use of catalysts on the base of cobalt carbonyl [1-3]:

$$\mathbf{ArHal + CO} \xrightarrow[\text{ROH + B}]{\text{Co}_2\text{(CO)}_8\text{+A}} \mathbf{ArCOOR}$$

The carbonylation reactions are carried out under very mild conditions, at a CO pressure not higher then 3 atm and a temperature up to 65 °C in a methanol medium in the presence of alkali metal hydroxides or carbonates as bases (B):

New highly active catalytic systems based on modified carbonyl cobalt were developed for low-activity aryl halides activation and involvement into the carbonylations reaction. We proposed and investigated a number of modifiers (cocatalysts) (A) (alkyl halides and epoxides) formed «in situ» active «true» carbonylation catalyst:



Epoxides are the most active cocatalysts and benzyl chloride was the most active among alkyhalides. The best as industrially available is propylen oxide.

With the purpose of perfection of the production technology of the key products aromatic and alkylaromatic acids we designed and constructed an original pilot installation for carbonylation of halides with installed capacity of 10 tons a year. (The volume of carbonylation reactor is 100 l). This setup was used for production of experimental batches of the products in amount from 10 to 50 kg.

Our method has some advantages and merits over traditional multistep ways for synthesis of these acids:

- high yields (> 95 %) and selectivity (> 98 %),
- low energy and feedstock consumption,
- greater ecological cleanness,
- **Versatility**.
  1. the possibility of the wide range acids production using the same equipment, under the same very mild conditions with the same cobalt carbonyl catalyst,
  2. the possibility of the extension of range and types of obtaining acids as necessary, (an example, synthesis of heteroarylcarboxilic acids [3]),
  3. extension of the fields of application this method and technology, as an example for utilization of persistent organic pollutant (POP) – polychlorobiphenyls (PCBs).

PCBs are widespread stable dielectric fluids that have previously been produced on a large scale and are used mainly in transformers. At present it is well known that PCBs are dioxin-like POPs, which pose the serious hazard to the environment and humans. The necessity of their destruction or utilization is put forward by the Stockholm International Convention on POPs. Since PCBs are very resistant to biological or chemical degradation, the problem of their involvement in chemical reactions presents a real challenge. The cobalt carbonyl – epoxide – base catalytic system turned out to be useful for reactions with especially inert substrates such as PCBs. Our experiments with specially synthesized individual PCB congenrrs and commercial PCB –Sovtol-10 speciments relevant that all these objects can be involvedwell into the carbonylation reaction, yielding new products – bi- and- three-biphenylcarboxylic acids.

This work was supported by RFBI (RF-0803-90104-Mol_a).

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MODELLING OF PERIODIC OPERATION IN TRICKLE BED REACTORS: INFLUENCE OF THE UNSTEADY STATE HYDRODYNAMICS

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Keywords: liquid flow modulation, trickle bed reactors, modeling at the reactor scale

Abstract

Trickle Bed Reactors (TBRs) provide flexibility and simplicity of operation, as well as high throughputs and low energy consumption. They are widely used in the chemical, petrochemical and petroleum industries, in biochemical and electrochemical processing and in waste water treatments. In most of the applications, the reaction is gas-limited, therefore steady-state operation of TBRs is usually controlled by mass transport of the gaseous reactant. Reactor performance may be enhanced by an appropriate liquid feed strategy such as ON-OFF Liquid Flow Modulation (LFM). In this Process Intensification technique, the liquid flow rate is periodically interrupted while the gas phase passes continuously during the entire period. Therefore, the external surface coverage of the catalyst particles varies periodically, so the supply of the gaseous reactant is enhanced. Pulsation of the liquid phase can be imposed with a simple modification of the existing plant at very low costs and benefits could be quite profitable. For this reason, in the last few years, many researchers are exploring this alternative. (Silveston and Hanika, 2002).

Performance enhancement in terms of production capacity and/or conversion and hydrodynamic studies has been reported by several authors. However, a cycling strategy is still not being applied commercially mainly due to the lack of an established methodology of design. Hence, rigorous experimental and modeling efforts are still necessary to understand the phenomena underlying periodic operation before commercial implementation.

In this context, Ayude et al. (2005) have formulated and solved a comprehensive model, aimed at the particle scale, to describe the course of a gas liquid reaction taking place within an isothermal porous catalyst subjected to ON-OFF cycling. The model allows deciding a priori if a cycling strategy would modify TBR performance for a given reaction system.

Furthermore, Ayude et al. (2007) has carried out a systematic characterization of the time evolution of the liquid holdup at different axial positions within a mini-pilot scale cold mock up of a trickle bed reactor operated with ON-OFF liquid flow modulation.

The objective of the present contribution is to include the acquired hydrodynamic information into the model at the particle scale for examining the response of an isothermal TBR to a liquid flow modulation ON-OFF strategy. Additionally, we proposed to extend the model towards the reactor scale for analyzing the actual reactor output and to validate the model robustness and capability of prediction against experimental results reported in literature.

Slow ON-OFF modulation is described in the model as induced by a cyclic square-wave of the liquid velocity in the top of the reactor. The model assumes that, during the ON cycle, the external surface of the particle is completely wet. Likewise, once the liquid flow rate is cut off, the liquid drains and the liquid holdup diminishes progressively up to the static holdup value, if the dry time is long enough. External wetting efficiency and mass transport coefficients are linked to the liquid holdup value obtained during each operation stage, ON cycle or OFF cycle.

Total internal wetting is considered during the whole cycle. The kinetic is assumed to be first order with respect to both, gas and liquid reactants. Non steady state mass balances for the gas and liquid reactants inside an spherical catalyst particle and for the bulk liquid are formulated and solved by the alternating direction implicit method.

Reactants radial and angular profiles within the catalyst, as well as axial variation in the reactor can be evaluated with the model for any moment during the cycle.

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REACTOR DESIGN OF THE DIISOBUTYLPHTHALATE MANUFACTURE

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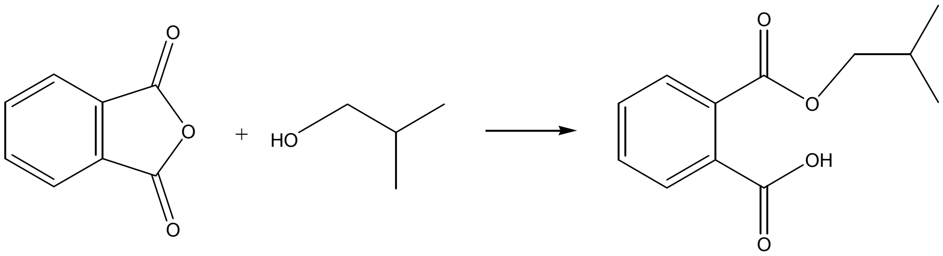
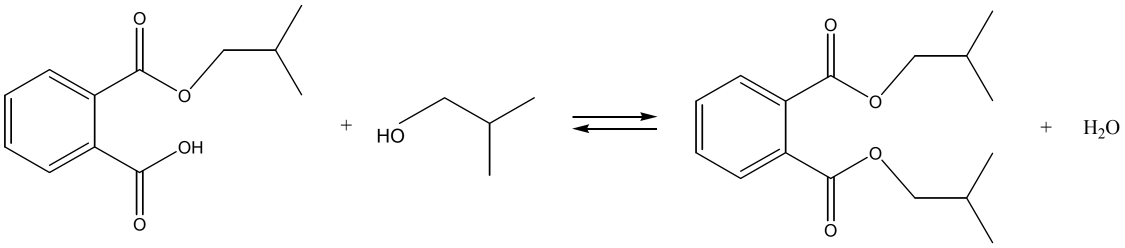
Phthalate esters are used as plasticisers, solvents and perfumery compounds. A continuous synthesis of diisobutylphthalate from phthalic anhydride and isobuthanol is carried out. The first reaction step, alcoholysis of phthalic anhydride with the monoester formation, is rapid and goes to completion. The reaction starts at moderate temperature and proceeds exothermically.



Second step is the conversion of the monoester to a diester with the formation of water.



This is a reversible reaction and proceeds much more slowly than the first. To shift the equilibrium towards the diester the reaction water is removed by azeotrope formation with the alcohol. The azeotrope can be removed from reaction vessel by rectification of water- alcohol mixing and, after purification steps, the alcohol can be recycled. Reaction rate is accelerated by usage of ion exchange resin Amberlyst A-70 as a catalyst in the temperature range of 120 – 140 °C. Both reaction and rectification processes are performed in a closed system consisted of a tube reactor filled with the ion exchange resin and the vessel with a rectificated column. The reaction mixture via a circulation pump is passed through both apparatus. Two another pumps feed and pump out the end-reaction mixture.

PP-III-22

OPTIMIZATION OF THE METHANOL OXIDATION OVER IRON-MOLYBDATE CATALYSTS

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Introduction

It is well known that the iron-molybdate catalysts used in practice have good activity and relatively high selectivity [1]. Despite that, several issues still remain open for discussion and in search of new solutions. They are mostly connected with the requirements of current technologies for production of adhesives and plastics that need formaldehyde free of residual methanol (< 0.5 %), and are also connected with decreasing the quantity of side products and lowering the prime cost of production. In order to meet these requirements it is necessary to search for conditions to implement the process, during which the total level of methanol transformation is over 98.5%, and the selectivity – over 92%. To reach these indicators the manufacturers use an additional adiabatic layer or an additional reactor, situated under the main one [2]. Although this approach is widely popular in practice, there is a complete lack of research in this direction in scientific literature.

This research aims to shed more light on the possibilities to optimize the process of selective oxidation of methanol over oxide catalysts using an adiabatic layer by determining border values of basic parameters of the process in the adiabatic layer that ensure a maximum rate of transformation of methanol at high selectivity.

Experimental

All laboratory experiments were carried out on a flow apparatus for estimation of oxide catalysts for methanol oxidation, using a stainless steel pseudo-isothermal reactor as a “main” reactor and a glass adiabatic reactor, also acting as an adiabatic layer. The content of the gas mixture entering the main reactor, space velocity, and temperature regime allow the experiment to be carried out at conditions closest to the industrial ones. The outlet gas mixture was analyzed for methanol, CO, dimethyl ether (DME), and CO_2 content in the analytical section. Industrial catalyst produced by Neochim SA [3] was used.

Results and discussion

Laboratory experiments were performed to clarify the influence of the most important parameters of the process (temperature, space velocity and methanol concentration) on the efficiency of the adiabatic layer. An industrial experiment was carried out to verify the results obtained.

Laboratory experiments

Studies were carried out on the influence of methanol concentration and temperature of the gas flow entering the adiabatic reactor on the operation efficiency of the adiabatic layer at a space velocity of the gas flow of 6000, 8000, 14000 and 24000 h^{-1}. Analyzing the results presented we can conclude that the influence of the temperature, methanol concentration and space velocity of the feed gas entering the adiabatic layer on the total methanol oxidation and selectivity of the process is complex. Methanol concentration and space velocity are the most important factors. Their increase leads to rapid decrease of the borders of applicability of the adiabatic layer. Temperature influence is limited by the operating conditions of the main reactor. At low inlet temperatures the limiting factor is methanol conversion, while at higher temperatures the selectivity is more important.

Industrial experiment

A fifteen months' industrial experiment was carried out. The industrial installation monitored consists of two pseudo-isothermal reactors. An adiabatic layer with a thickness of 50 – 60 mm was located under the reactors.

Mössbauer spectrometry, XRD and chemical analysis were used to characterize fresh and post reaction iron molybdate catalyst. Catalytic measurements were performed too. No differences were found between sample of fresh catalyst and samples discharged from the adiabatic layer.

Conclusions

1. Using an adiabatic layer under the main reactor leads in all cases to a loss of formaldehyde due to its secondary oxidation to CO. Carefully controlling the process parameters allows full compensation of these losses by the oxidation of the methanol entering from the main reactor and the secondary oxidation of DME, mainly to formaldehyde.
2. The results from the Mössbauer spectroscopy, XRD and the chemical analyses reveal no irreversible change in the chemical and phase content of the catalyst. The catalytic properties of the catalyst used in the adiabatic layer remain virtually unchanged.

Acknowledgement

This work is supported by Bulgarian Ministry of Education, Project VU- X-305/07.

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PP-III-23

EXPERIMENTAL INVESTIGATION OF NO YIELD VERSUS MONOLITHS GEOMETRY IN AMMONIA OXIDATION PROCESS

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Ammonia oxidation process in nitric acid production ($4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$) is realized on Pt gauzes in different plants under atmospheric, medium and high pressure. Due to high temperature operation conditions, Pt losses occur. At that, the last gauzes in the catalyst layer polish ammonia conversion while still lose a sound portion of noble metals. Therefore, an idea to replace them by less expensive oxide catalyst was evident. In 1960th the two stage catalytic system (1 gauze + layer of palletized oxide catalyst) was developed by GIAP for normal pressure plants [1]. In 1990th BIC-42-1 honeycomb catalysts was developed at Boreskov Institute of Catalysis for UKL-7 high pressure plant [2, 3]. It is shaped as a 70x70x50 mm monolith with square cannels (5x5 mm) and wall thickness 1.8-2.2 mm. Its application (9 gauzes and 1 layer) results in 25-30% saving in gauzes loading and 15-20% reduction of Pt losses at near the same product yield and longer gauzes life time [4]. Honeycomb catalyst seems to be more attractive providing uniformity of gas flow, low pressure drop and low dust formation.

Mathematical modelling of a two-stage catalytic system for medium pressure plant AK-72 (operation pressure – 3.5 Bar) was performed as well [5]. This reactor is normally loaded by 7 woven Pt gauzes with an initial fibre diameter of 0.092 mm. The mathematical model applied presumes mass transfer limitation of the reaction both on Pt gauzes and a honeycomb catalyst. It was calculated that system consisting of 4 Pt gauzes and 1 layer of honeycombs with 50 mm height and not less than 50 cpsi should provided ammonia conversion as for 7 woven Pt gauzes [5]. Strong requirement to catalyst for application in AK-72 is its high selectivity. It is also known that catalyst geometry may influence not only on the ammonia conversion, but also on the NO yield due to possibility of different secondary reactions.

The main goal of this investigation is experimental investigation of NO yield for honeycomb monoliths of different chemical composition and geometry for application at medium pressure plant. For such investigation the lab-size monoliths with 2 types of geometry (Table 1) were prepared using modified frame structured cordierite-like materials, perovskite-like oxides and iron oxide.

Ammonia oxidation process was carried out in a bench scale quartz tubular reactor with inner diameter of 26 mm at temperature 700-900 °C and atmospheric pressure. Samples of honeycomb catalysts in the form of fragments with diameter of 21-22 mm and length of 50 mm were tested with and without one Pt sheet. Before the reaction starts up, catalysts were preheated at 700 °C in air for 30 minutes. Then reaction gazes (5% ammonia in the air preheated at 450 °C in a quartz mixer) were flowed through the catalyst with 7.6 l/min flow rate (standard gas velocity 0.33 m/s). The ignition of the catalyst was determined by temperature increase. Ammonia, NO and NO_2 concentrations were analyzed by the on-line spectrophotometer analysis [6, 7].

Table 1. Honeycombs geometry

	Channels form	d, mm	δ, mm	D, mm	S, m^2/m^3	N cpsi	ε
1	triangular	2.5	0.4	***1.53***	***1520***	180	0.63
2	triangular	4.0	1.2	***2.27***	***890***	56	0.41

All as prepared catalysts provide 100 % ammonia conversion degree even without Pt gauzes at temperature higher 850 °C that is in agreement with our calculations for lab reactor. NO yield for monoliths and in the two-stage system (with one Pt gauze) was shown to depend on the temperature and chemical composition of monoliths (with the same geometry) as well as on the channel density [3]. Monoliths with 56 cpsi have revealed the NO yield not higher than 86% at 900 °C most probably due to the influence the homogeneous reactions. NO yield increases with increase of channel density only for Fe_2O_3-based catalysts and for BIC-42-1 honeycombs with 180 cpi nearly 90% NO yield was revealed. The best data (NO yield higher 95%) at 830-900 °C were obtained for modified BIC-42-1 iron oxide-based monolith with 180 cpsi.

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CATALYTIC REACTORS WITH HYDROGEN MEMBRANE SEPARATION

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Hydrogen - the main energy carrier of the future - will find wide application only after solving the problem of low-cost recovery of hydrogen from hydrogen-containing sources such as water, natural gas, oil, coal, biomasses, timber, and industrial waste [1]. Utilization of hydrogen permits one to avoid the problem of direct electrification, which is accompanied by large electric losses and impossibility of energy storage. Besides, hydrogen recovery provides no harmful substances as methane or carbonic acid exhausts. Note that the hydrogen meant for fuel cells including a proton-exchange membrane should have high purity grade and CO concentration not higher than 10 ppm. This can be provided by dividing hydrogen containing gases into a pure hydrogen flow and by-product gases using hydrogen-permeable membranes.

The work describes the main catalytic hydrogen generation processes in which it is expedient to use hydrogen-permeable membranes. Different solid membranes serving hydrogen isolation from gas mixtures and the methods of their preparation are considered.

Thus, the researchers of the Boreskov Institute of Catalysis are deeply involved in the preparation of thin composite palladium membranes by a chemical method with following reduction. These works result from a number of successful designs associated with the methods of synthesis of layered catalysts and their anchoring on the metal supports. The preliminary experimental results are very encouraging. Porous stainless steel (average pore size is 5 μm, porosity is 57 %) was used as a membrane support. A palladium membrane was prepared in two steps: activation of the support surface and deposition of palladium from a solution (as palladium complex) on the activated surface. The support surface was prepared by detonation spraying of corundum with following deposition of highly porous γ-Al_2O_3 using a gel-sol method, which was then activated by small amounts of salt Pd(II). The resulting support was thermally treated at 500 °C in hydrogen to reduce palladium. The experiments showed that the first corundum layer supported by detonation spraying prevents exfoliation of the palladium membrane from the support. During the next step, palladium was deposited from the ammonium palladium solution on the pre-activated support, which was successively reduced by hydrazine and hydrogen at 500 °C. Structural properties of the as-prepared membrane were studied by scanning tunnel microscopy, XRD, X-Ray fluorescence analysis and the specific surface (area) was measured by BET etc. The considered method permits deposition of thin (1-10 μm) layers of Pd on the complex-surface membranes used in the catalytic reactors.

The work exemplifies designs of catalytic reactors with an integrated membrane module and compares their properties with the traditional reactors with a fixed catalyst bed.

Catalytic membrane reactors, having small dimensions, provide high power efficiency (≥ 80%), good dynamic characteristics, low temperature of hydrocarbon conversion, generation of high-purity hydrogen during one step, and conversion exceeding the equilibrium value.

Thus, a methane conversion of ~100 % can be obtained in a catalytic membrane reactor at ~500 °C. The generated hydrogen does not contain CO and can be utilized in low-temperature fuel cells. The reactors with integrated membrane modules for separation of hydrogen from the reaction mixture and feeding of oxygen into the reaction zone provide an eight times higher hydrogen output than the traditional tubular reactors. The authors review the mathematical models of the reactors using membrane hydrogen feeding and present some modeling data. The prospects of catalytic membrane integrated reactors in hydrogen energy and in transport vehicles are analyzed [2, 3]. The work includes more than 90 references.

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PP-III-25

ACTIVITY OF Cu/ZSM-5 CATALYSTS FOR THE OXIDATION OF PHENOL WITH HYDROGEN PEROXIDE

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Introduction

Organic compounds, e.g. phenol and its derivatives which are extremely toxic and refractory in nature, are common pollutants in many industrial wastewaters. In the last years, the treatment of phenols in aqueous solutions was generally carried out by oxidation with molecular oxygen or air, at elevated pressure (1-10 MPa) and temperature (373–573 K) in the presence or absence of catalysts thus increasing the treatment cost. An alternative process which allows performing oxidation reaction at ambient or close to ambient conditions, limiting the investment costs is the use of hydrogen peroxide in so-called catalytic wet peroxide oxidation (CWPO). Great number of different catalysts, as example different metals supported on metal oxides, clays, graphite, polymers, and carbon, supported and unsupported metal oxides and so on.

The main objective of this work is to evaluate the activity and stability of copper species incorporated within zeolite support. The catalytic performance has been monitored in terms of phenol and TOC conversions.

Experimental

The kinetic experiments and activity tests were carried out in stainless steel Parr reactor in batch operation mode at temperature between 50 °C and 80 °C and atmospheric pressure. The mass ratio of the active metal component on the zeolite was in the range of 1.62-3.24 wt. %, and the initial concentration of phenol and hydrogen peroxide was 0.01 mol dm^{-3} and 0.1 mol dm^{-3}, respectively. The catalyst samples (Cu/ZSM-5) were prepared by direct hydrothermal synthesis. Characterization of the catalysts extends to X-ray diffraction (XRD) and scanning electron microscopy (SEM), while the adsorption techniques were used for the measurement of the specific surface area.

Results and discussion

Preliminary experiment showed that phenol oxidized with hydrogen peroxide without catalyst, but its conversion after 3 h was only 10% [1]. No catalyzed homogeneous phenol oxidation was characterized by an induction period followed by a faster reaction phase, typical for the reactions governed by free-radical mechanisms.

Fig. 1 shows the influence of copper loading on phenol removal, hydrogen peroxide consumption, and TOC reduction after 180 min of reaction. It is well known that CWPO of phenol is very complex process consisting of a set of parallel and series reaction in which many types of intermediates and final products are involved. These consisted of aromatic compounds, mainly benzoquinone, hydroquinone and cathecol, carboxylic acids (acetic, maleic, oxalic and fumaric acids) and other oxygenated compounds such as aldehydes and ketones. Looking at phenol conversion presented in Fig. 1, all catalyst samples were able to oxidize the parent pollutant, phenol to an extent of 92-97 % depending upon the copper loading on zeolite. Meanwhile, the TOC reduction is in all cases, significantly lower that phenol conversion indicating formation of different intermediates and final results is far from complete mineralization of phenol. It can be also evidenced that the TOC removal enhanced with the increase in the copper loading on zeolite. Deeper removal of the organic load was impeded, by the accumulation of refractory organic byproduct acids that were stable in the reaction medium because they were already highly oxidized molecules. The low pH found after 180 min of reaction confirm the presence of organic carboxylic acids as by products of phenol oxidation.

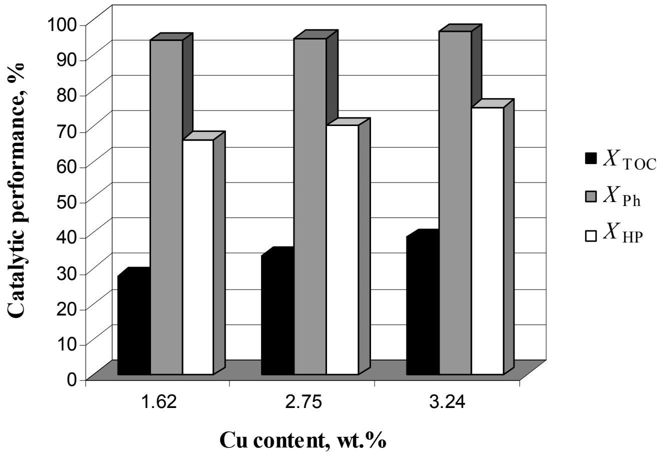

Fig. 1. Influence of copper loading on TOC, phenol and hydrogen peroxide conversion.

Conclusions

The experimental results indicate that in the space of 180 min, the use of these catalysts allows almost total elimination of phenol and significant removal of chemical oxygen demand, without significant leaching of Cu ions from zeolite. The best candidate was Cu/ZSM5-DHS3 catalyst containing the highest copper loading.

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PP-III-26

SIMULATION AND OPTIMISATION OF SEMIBATCH REACTOR OF ANIONIC POLYMERIZATION OF PROPELENE OXIDE

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Introduction

At present polyethers of glycerol made by co-polymerization of ethylene and propylene oxides are of great importance as a component of demulsifiers for water-oil emulsions. Generally such polyethers have molecular weight in a range of 3000 – 6000. The common procedure includes two stages – addition of propylene oxide to glycerol and then addition of ethylene oxide. Process is carried out in a semibatch reactor in such a way as firstly glycerol with catalyst are loaded into reactor then they are heated up to reaction temperature and then feeding of propylene oxide is starting. The inlet flow of propylene oxide must be so as the temperature in the reactor is maintained on an optimal level. The problem is that the reaction is high exothermic (about 85 kJ/mol) and overheating of reaction mixture leads to loss of quality of final product.

Results and conclusions

The aim of presented work was optimization functioning regime of semibatch reactor for producing of polyoxipropylated glycerol in order to increase throughput without loss of product quality. Reactor has volume of 2 m^3 and is meant for producing of polyethers with molecular weight about 670 – 4300. It is supplied with anchor stirrer and internal coil for removing of exothermic heat. Initially reactor was working with propylene oxide feeding in a range 0.01 – 0.09 kg/(m^3 h).

The mathematical model of this reactor based on known kinetic data was built. The model includes equations of material and heat balances. Furthermore the model describes changing of effective heat-exchange surface during process that is due to continuous growth of level of reaction mixture.

Parameters of obtained mathematical model were determined by treating of data on temperature and propylene oxide flow in different synthesis. As a result the model adequately describing the process was obtained. This model allowed optimization of functioning regime of reactor. The optimal regime consists in stepwise increase of propylene oxide feeding during synthesis from 0.5 kg/min to 4.5 kg/min.

SIMULATION OF LARGE-SCALE FATTY AMINE ETHOXYLATION REACTOR

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Introduction

Non-ionic surfactants based on ethylene oxide and fatty amines are widely used as detergents, cleaning agents, they are also applied in textiles, oil recovery, etc. Non-ionic surfactants in question are commercially produced by the reaction of ethylene oxide and fatty amine. Kinetic studies in the model system butyl amine-ethylene oxide showed the identity of rate laws for hydroxide ethoxylation of alcohols and aminoalcohols:

$$RNH_2 \xrightarrow[C_2H_4O]{k_0} RNHC_2H_4OH \xrightarrow[C_2H_4O]{k_1} RN(C_2H_4OH)_2 \xrightarrow[C_2H_4O]{k_2} RN((C_2H_4O)_nH)_2$$

where R is alkyl C12-C16, n = 3-18.

Only products with 3-12 mol of ethylene oxide per mole of fatty amine have the practical applications.

The industrial ethoxylations are carried out mainly in a batch-wise manner at low concentrations of ethylene oxide in the reaction mixture. The significant exotherm (83.8 kJ/mol of added ethylene oxide) makes heat removal a crucial issue, especially due to limitations caused by the product quality deterioration at higher temperatures (products tend to be coloured). There are different ways of carrying out this reaction in the batch reactor. Usually the process is carried out in a semi-batch system with ethylene oxide being fed into the reactor equipped with the mixer and a cooling coil. As the reaction proceeds the reaction mixture gets more viscous lowering the efficiency of mass transfer and, subsequently, the reaction rate. The reaction time is 12-15 h.

This process is more complicated than ethoxylation of alcohols due to the presence of autocatalysis. The aim of this work is the building of the computer model of the plug flow reactor for amine ethoxylation that will be of enormous help in the designing of a large scale process.

Results

The kinetics of fatty amine ethoxylation was investigated and the kinetic equations for as catalytic and noncatalytic reactions were obtained. The kinetic model was put on a base of model of plug flow reactor. The final model includes mass and energy balance, kinetic description, description of hydrodynamics and changing of physical properties.

The values of reactor temperature and ethylene oxide conversion were obtained by the numerical integration of the model. Molar ratio fatty amine:ethylene oxide was 1:2, heat carrier temperature 100 °C (boiling water), initial temperature of the reaction mixture 100 °C. The integration was run up to 99% conversion degree. Results are listed in Table 1. The maximum reactor temperature is limited by the product quality requirements (at high temperatures the product becomes coloured). It is clearly seen that in the framework of the model the range of reactor diameters when the reaction temperature does not exceed 480 K. Model predicts severe constrains in the choice of diameter and length of reactor tubes. The acceptable range of tube diameter is 0.032-0.04 m and length 50-100 m. The sensitivity of the temperature profile to the variation of parameters depends on their starting set. In our case the model stability is increased with decreasing the pipe diameter and molar ratio ethylene oxide-fatty amine. The stability is also increased with growth of the heat carrier temperature and reactants' feed linear rate. The model is most sensitive to the variations in heat carrier temperature. Under certain conditions the change of heat carrier temperature on 1 °C could result in great variations in the reactor temperature (up to 100 °C). The analysis of the model behaviour with the following constraints: heat carrier temperature variation ±5 °C and reactor temperature variation ±50 °C revealed that at pipe diameter 0.045 m the model sensitivity exceeds the acceptable limit of 10°C/1°C. The results demonstrated that when all ethylene oxide is fed at the reactor inlet the acceptable range of process parameters is very narrow.

Table 1

Reactor temperatures ad different pipe diameters

d(m)	*w* (m/min)	Reactor length (m)	T-max (K)
0.019	13.9	300	390
0.032	8.25	100	470
0.04	6.6	50	480
0.049	5.4	35	553
0.068	3.9	30	607
0.079	3.33	27	617
0.1	2.65	15	620
0.125	2.10	10	637
0.15	1.8	8	650

Conclusions

The model of the plug flow reactor for amine ethoxylation describing adequately experimental data was built. It was shown how this model can be used to predict the performance of a real reactor, i.e. the product distribution and the temperature profile.

DEHYDROGENATION OF C_1–C_5 PARAFFINS ON Cr_2O_3/Al_2O_3 CATALYSTS IN FLUIDIZED AND FIXED BED REACTORS

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Qualified processing of C_3–C_5 paraffins, entering into gas condensate, associated petroleum gas (APG) or natural gas liquids (NGL), is a very important problem of the oil-and-gas industry of Russia. One way to process the above substances is catalytic dehydrogenation resulting in the production of olefin and diolefin hydrocarbons. In the present report we consider both theoretical and experimental feasibility of dehydrogenation of C_1–C_5 mixtures without preliminary separation of individual components.

The work includes thermodynamic calculations of the equilibrium conversion degrees upon dehydrogenation of model C_1–C_5 paraffin mixtures and NGL.

It is common knowledge that dehydrogenation conversion degree is determined by a thermodynamic equilibrium. At the similar temperature and pressure values, the equilibrium dehydrogenation degree (reactivity) increases in the paraffin series with an increase in the number of carbon atoms and the degree of paraffin branching [1]:

$$C_2 \ll C_3 \ll n\text{-}C_4 < i\text{-}C_4 < n\text{-}C_5 < i\text{-}C_5.$$

Thermodynamic calculations of the dehydrogenation process of the above mixtures indicate a complex mutual effect of the components on the equilibrium yield of olefins. Each component of the mixture can simultaneously act as a diluent providing a shift of the dehydrogenation equilibrium of the rest mixture components to the desired olefin and as an additional supplier of hydrogen to the reaction zone that shifts the dehydrogenation equilibrium to the left. Summary input will depend on the position of a component in the reactivity series regarding the other components position. Thus, for example, propane stands to the left of iso-butane and n-butane in the thermodynamics reactivity series. For this reason, propane is difficult to dehydrogenate as compared to the mentioned paraffins. Therefore, the propane involved in the above paraffins mixture acts as a diluent and increases dehydrogenation level to iso-butylene or n-butenes. Since propane undergoes dehydrogenation first-hand and evolves hydrogen, its effect is lower than that of inert diluents, the concentration being similar in the reaction mixture. In view of the fact that iso-butane and n-butane are more easily dehydrogenated than propane, these components, as follows from the calculations, cause an overall decrease in the equilibrium dehydrogenation level of propane. However, an adverse effect of iso-butane or n-butane is lower than that observed upon dilution of propane by pure hydrogen.

Calculations were experimentally verified on the dehydrogenation of model paraffin mixtures in the presence of novel catalysts Cr_2O_3/Al_2O_3 for fluidized and fixed beds developed at the Institute of Catalysis (Novosibirsk, Russia) [2]. The catalytic experiments confirmed in full the thermodynamic calculations for dehydrogenation of iso-butane or n-butane and in part for propane.

Thus, during the dehydrogenation of a mixture of propane and iso-butane, the yield of iso-butylene increases in accordance with the thermodynamic calculations, whereas the selectivity to isobutylene holds approximately constant. An absolute value of the yield increase depends on: dehydrogenation temperature, propane/iso-butane ratio in the initial mixture and type of the dehydrogenation reactor. Thus, for the volume ratio $C_3 : C_4 = 1:1$, an increase in the yield of iso-butylene can be about 3–5 wt.%. It should be noted that we did not observe a significant decay in the propylene yield predicted by thermodynamic calculations. Evidently, an additional amount of propylene, resulting from the side cracking reaction of C_4 paraffins, partially compensates the decay. The calculated selectivity towards propylene essentially increases and can exceed 100%.

For propane, efficient dilutants are ethane or methane that is inert in this process. During dehydrogenation of the model methane-propane mixtures (the ratio of the components approximates that in APG), a marked increase in the propylene yield, 3–7 mass.%, was accompanied by a slight increase in its selectivity. The beneficial action of methane dilution (as well as ethane) is even higher for dehydrogenation of C_4 paraffins.

Thus, the experiments and thermodynamic calculations of the dehydrogenation of model mixtures C_1–C_5 suggest that if it is necessary to direct dehydrogenation at producing either butenes or iso-amylenes, it is wise to perform dehydrogenation of NGL C_3–C_5, which is accompanied by generation of propylene. To obtain high propylene yields, it is efficient to utilize APG or its mixtures with NGL (in definite proportions).

Both versions will provide:

- High summary conversion of C_3-C_5 paraffins into olefins;
- An increase in the summary selectivity of the process towards olefins;
- No need in double separation of hydrocarbons (before and after dehydrogenation);
- An increase in the total amount of propylene in the end product. Since concentration of propylene (by-product of cracking on the dehydrogenation of individual C_4–C_5) is low in the mixture and its isolation is not profitable, the existing industrial schemes utilize propylene and C_1-C_2 hydrocarbons as a flue gas.

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A STUDY ON THE ACTIVITY OF A Pd/(Cu or Sn) CATALYST FOR THE DENITRIFICATION OF NATURAL WATER IN DIFFERENT REACTOR SYSTEMS

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Introduction

Nitrate concentration in water supplies has experienced an important increase in the last years, mainly caused by the use of fertilizers necessary for an intensive agricultural production. The increasing control of the drinking water quality standards, generates the urgent need to develop a new technology for the nitrate removal from aqueous solutions. Conventional techniques for ground water denitrification are relatively costly and they need in some cases a secondary post-treatment of the effluent and the sludge generated. Recently, it has been shown that the most adequate way to remove nitrates, from the environmental point of view, is to convert them into N_2 by liquid phase nitrate hydrogenation on noble metal catalysts [1-5]. However the catalyst has to be selective to avoid the production of NO_2^- and NH_4^+. Typically, metal-oxide supported bimetallic catalysts, combining a noble metal, usually Pd or Pt, and another metal, such as Cu, Sn or In, supported on alumina have been applied for this reaction [4-6]. Nevertheless, the kinetics and the selectivity of the process are severely limited by mass transfer problems [2, 7, 8]. The diffusion of the reactants towards the active centers is very influenced by the nature of the support and by the reactor, for this reason it is necessary an adequate selection of them to design an active catalyst.

In the present work, we have studied the influence of different reaction systems on the activity of a Pd/(Cu or Sn)-Al_2O_3 catalyst for the nitrate removal, using natural water from different polluted aquifers.

Experimental

The supports used for the catalysts were hydrotalcites, synthesized in our laboratory and γ-Al_2O_3 supplied by Merck. Palladium and copper or tin were added to the support by standard impregnation methods in order to have a metal concentration of 5 % and 1.5 % respectively. The sample was calcined in air at 500 °C for 1 hour and reduced in hydrogen flow at the same temperature. Powder catalyst was tested in different reactor systems: batch, continuous and pressurized reactors, using hydrogen as a reducing agent. The NO_3^-, NO_2^- and NH_4^+ concentration in the aqueous-phase samples was determined by UV/VIS spectroscopy.

Results and discussion

From our previous studies it was observed that in order to obtain a good activity and selectivity it is necessary an adequate contact of the three phases present (the optimized solid catalyst, the liquid media containing the nitrates and the gaseous hydrogen) [9]. This can be easily obtained in a batch reactor, where the nitrates present in one liter of a natural water containing 90 ppm of NO_3^- are completely removed in 30 minutes, producing 15 ppm of ammonia.

Nevertheless when the reaction is made in a continuous reactor, the results obtained are not so good, indicating some mass transfer limitations and some deactivation of the catalyst. Comparing the different continuous reactors, it was observed that in the flow piston reactor, a fast decrease on the nitrates concentration is observed during the first 5-10 minutes, stabilizing the conversions at 60% after 1 hour reaction. This conversion is stable during 5 hours reaction, when the catalyst starts to deactivate. In the stirred flow tank reactor, better results were obtained, obtaining 100% conversion during 5 hours. Afterwards, just as in the piston flow reactor, the catalyst starts to deactivate. The deactivation is due to the deposition of calcium salts and to the oxidation of the reduced active sites It is also interesting to indicate that with both reactors the formation of ammonia and nitrite is lower than with the batch reactor, presenting a maximum during the first minutes of the reaction but stabilizing around 5 ppm of ammonia after 1 hour reaction.

The use of a pressurized reactor at different pressure conditions do no improve the results obtained with these catalysts in the nitrate conversion, neither in its selectivity.

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THE WAY OF METHANOL AND HIGHER ALCOHOL PRODUCTION: PROCESS MODELLING AND INTENSIFICATION

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Process improvements can produce significant financial benefits if large volume chemicals are involved [1-2]. The aim of the work is to ascertain the reaction mechanisms of methanol and higher alcohol synthesis, to construct corresponding kinetic models, catalyst grain models and models of catalytic reactors. The use of these models makes it possible to calculate the regimes of an industrial reactor operation providing significant energy-saving and low raw material consumption. It is shown that new regimes of reactor equipment operation for methanol and higher alcohol syntheses allow us to increase drastically selectivity and profitability of the processes.

While constructing the mechanism of the catalytic reaction it is postulated that the formation of methanol and higher alcohols takes place on different sites of the catalyst [3-5]. The growth of alcohol chain proceeds sequentially as a result of addition of low molecular species to alcohol intermediates. According to these statements we offer two-centered reaction mechanism of combined methanol and higher alcohol synthesis. Due to this mechanism the initial stages of the reaction (formation of low molecular species and initiation of the chain growth) occur with the formation of trimolecular surface species. This scheme agrees with the isomeric composition of the reaction products.

The reactions on the catalyst surface are slow stages and the stages of adsorption and desorption are fast and reversible. For the mechanism obtained, 36-dimentional vector of stoichiometric numbers and (36×11) – dimensional matrix of overall equations for the routs are calculated.

The kinetic model containing 21 constants is developed for this stepwise reaction scheme. Sequentially planned experiments were carried out in the single-row laboratory catalytic reactor. The maximal numbers of constants admitting estimation were established by statistic methods developed by authors.

The next stage is to verify the adequacy model results to experimental data. The hypothesis on the equality of the covariance matrices of the vector of measurement errors Σ_2 and the vector of residues Σ_1 calculated within the model is used. Methods to verify the adequacy of multistage model were developed for arbitrary degrees of freedom of Σ_1 and Σ_2 and were proved to be efficient.

The following stage is process modeling in the catalyst grain. The equations of diffusion stochiometry and invariant relations for the efficiency factors of grain operation are derived. The latter substantially simplifies the procedures for calculating temperature and concentration profiles of the reactants in the catalyst grain.

The next step is modeling of industrial adiabatic reactor operation. The productivity of the process is 8 tons of raw material per hour. The process is carried out in four sectional reactor with height of 14 m; diameter of 1.2 m. The composition of feed gas stated to be: CO_2 – 6 % vol.; CH_4 – 8% vol.; N_2 – 17 % vol.; H_2 &CO – the rest; with variation of molar ratio H_2/CO in a wide range from 1.2 to 2.1. The reactor model was chosen and its macrokinetic parameters were estimated due to the results of pilot plant experiments. The adequacy of the model results to experimental data was proved.

The most favorable way of process performance is: volumetric flow rate – 5000 hr^{-1}, inlet temperature – 340 °C, molar ratio H_2/CO – 2.05-1. The overall conversion of carbon oxide exceeded 30% vol.

Higher alcohols produced meet all requirements to use them as components of motor fuels and as raw materials for high octane motor fuels production.

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METHOD FOR PRODUCING OF METHYL LACTAT

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Introduction

The steady growth of oil cost and the sharp problem of environmental contamination by petrochemical products force scientists looking for new chemicals which are biodegradable and could be produced on the base of renewable source. One of such product is methyl ester of lactic acid. The row stock for methyl lactate is L-lactic acid which is produced by means of biotechnological method from vegetable row materials. Progress in biotechnology, large resources and low and comparatively stable prices of vegetable raw materials make "green" chemicals, such as methyl lactate, competitive with petrochemicals.

Methyl lactate can be synthesized by means of etherification of lactic acid by methanol. It is impossible to achieve the technologically acceptable conversion because this reaction is reversible and water existing in lactic acid and resulting from reaction shifts the equilibrium back to initial reagents. Moreover water makes difficult the separation of target product because of formation of azeotropic mixture and hydrolysis of methyl lactate.

Experiments and results

In order to avoid problem mentioned above we used the oligomers of lactic acid as initial reagent. The oligomer can be easily produced by self-esterification of lactic acid. In tern target methyl lactate can be synthesized by means of alcoholysis of oligomer with methanol. In this case end products don't contain water hence methyl lactate can be easily separated.

The kinetics of alcoholysis of oligomer with methanol catalyzed by $Ti(OC_4H_9)_4$ was investigated in the following range of conditions: temperature 120-180 °C, catalyst concentration 0.5-1.5 %. The treatment of experimental data allowed us to propose scheme of reaction (Fig. 1) and kinetic model and to calculate parameters of last one which provided adequate description of process.

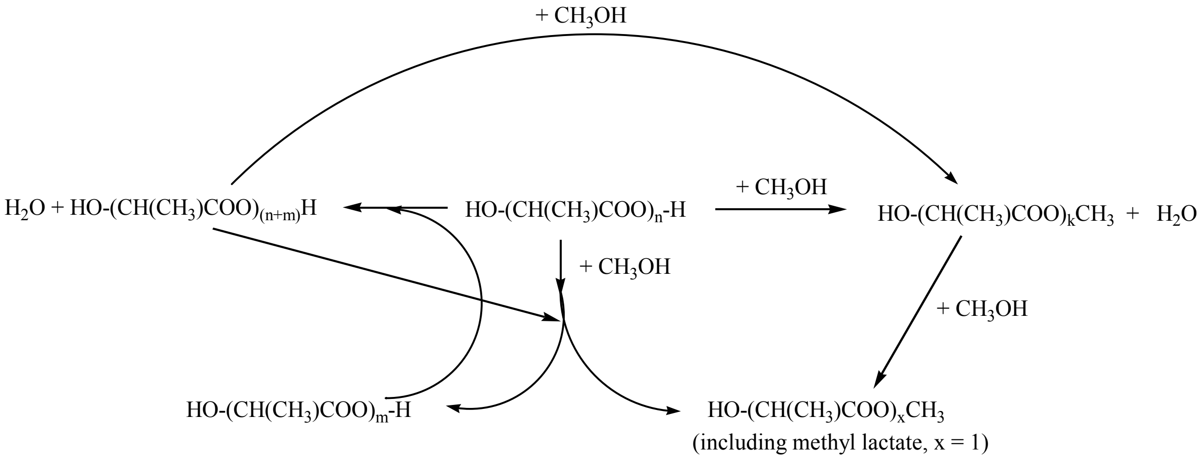

Fig. 1. Scheme of reaction.

Then the laboratory installation including continuous mixed flow reactor was set up and examined. The initial mixture consisting of methanol and oligomer was continuously fed into reactor. In the reactor the methanolysis of oligomer in presence of catalyst continuously ran. Reaction products comprised of methanol, methyl lactate and traces of water, lactic acid and methyl ester of lactic acid dimer were continuously flowed from outlet of reactor.

The experimental optimization of reaction conditions was carried out with variations of following parameters: temperature (170-225 °C), contact time, molar ratio of reagent, type of catalyst. It was found that the most effective catalysts were Liwes acids such as tin octoate and titan tetrabutoxide. The optimal process conditions were determined that provided capacity of reactor about 1 kg (methyl lactate)/(l×h).

Conclusions

The kinetics of methanolysis of oligomer of lactic acid was investigated. The scheme of reaction and mathematic model were proposed and kinetic parameters were calculated. The optimal conditions for continuous mixed flow reactor for methyl lactate producing were experimentally determined.

ON THE ANALYSIS OF PACKED BED STRUCTURE OF SPHERICAL PARTICLES IN CYLINDRICAL CONTAINERS

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Introduction and objective

Cylindrical packed beds are widely used in almost all chemical process industries. Catalytic fixed bed reactors with either single or two phase flow are one of most important examples. In such type of units catalytic particles can have sizes fairly different from fine powders, often reaching several millimeters. The model employed to simulate the reactor determines the degree of information required about packed bed structure. For the nowadays increasing use of the computational fluid dynamics technique -CFD- it is necessary to state the positions of all particles [1]. Therefore, the knowledge of packed bed structure is of paramount importance.

In a previous paper [2], we have developed an algorithm to simulate the structure of a cylindrical container filled with spherical particles of uniform size. The approach employed is called soft spheres algorithm. It allows some degree of interpenetration between particles. The force balance accounts for gravity and a contact force (to take into account the interpenetration) and neglect the friction force between particles. The result obtained from the algorithm is the position of each sphere in the container. From this information, all the packed bed structure properties can be calculated. The results obtained with the simulation were contrasted with the experimental data for overall void fractions. The comparison was very satisfactory [2].

The objective of this contribution is to present additional results obtained through simulation. Particularly, the radial and axial void fraction profiles and contact points between particles and between particles and the wall were analyzed. Taking into account the algorithm characteristics, a wide range of values of aspect ratio (i.e. tube to particle diameter ratio) has been studied. In this way, some special features at low aspect ratios can be assessed.

Results and discussion

Taking into account that the results obtained from the algorithm are the position of each sphere in the container, to calculate the void fraction at each radial or axial position the procedure presented by Mariani et al. [3] was employed. On the other hand, knowing the position of the centre of each sphere, the contact point can be calculated in a computational way.

The results were compared with experimental values from bibliography and own experimental results. A satisfactory agreement was obtained for any value of the aspect ratio, which means an additional support to the capability of the algorithm proposed. As an example, in Fig. 1, a comparison of experimental (Giese et al. [4]) and simulated results of the radial void fraction distribution is presented.

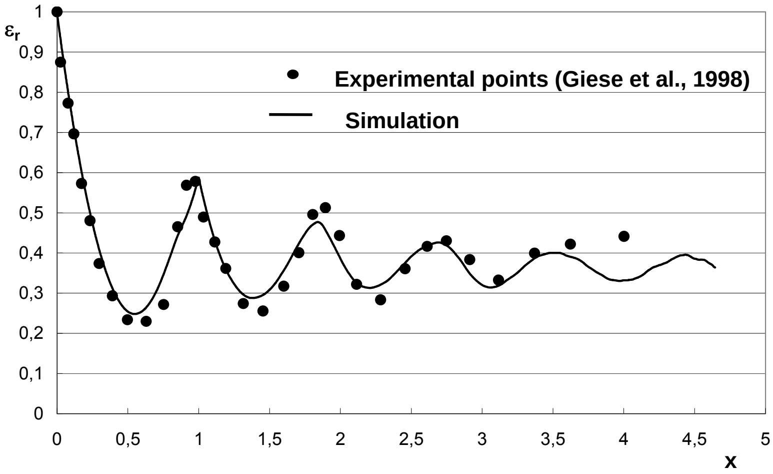

Figure 1: Comparison of experimental and simulated results of the radial void fraction distribution.

On the other hand, the results obtained allow to check that the fractions of the spheres contacting the wall diminishes as the aspect ratio increases. Besides, the average number of particles contacting each other (average contact number) varies significatively depending on whether the particles contact the wall or not. A simple expression to predict the average contact number as a function of the fraction of particles contacting the wall is proposed.

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PRODUCTION OF METHYLETHYLKETONE BY OXIDATION OF *n*-BUTENES WITH DIOXYGEN IN THE PRESENCE OF HOMOGENEOUS CATALYST (Pd + HETEROPOLY ACID)

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Methylethylketone (MEK) is used as solvent for dyes, enamels, polyurethane and other resins as well as for deparaffination of lubricating oils with the aim of security of their frost-resistance. MEK is a raw material for production of fine chemicals too.

In yearly 1970s we suggested a method of direct catalytic oxidation of *n*-butenes with dioxygen to MEK via reaction (1) [1].

$$n\text{-}C_4H_8 + O_2 \xrightarrow{\text{Pd + HPA-x}} CH_3COC_2H_5 \qquad (1)$$

Aqueous solutions containing Pd(II) complex and Keggin-type Mo-V-phosphoric heteropoly acids $H_{3+x}PV_xMo_{12-x}O_{40}$ (ГПК-x, $2 \le x \le 6$) were used as catalysts for this process.

To secure explosion-safety and maximal selectivity (> 97%), process (1) was carried in two stages. Interaction of *n*-C_4H_8 with the catalyst solution via reaction (2) took place at 60°C in a reactor 1 to yield MEK and reduced form of HPA-x (H_mHPA-x). Regeneration of HPA-x by dioxygen was realized via reaction (3) at 130–140°C in a reactor 2. When this scheme is used, the liquid catalyst continuously moves in a closed loop. In the course of reactions (2) and (3), vanadium atoms undergo redox transformations: $V(V) \rightleftharpoons V(IV)$.

$$n\text{-}C_4H_8 + \text{HPA-x} + H_2O \xrightarrow{Pd^{II}} CH_3COC_2H_5 + H_m\text{HPA-x} \qquad (2)$$

$$H_m\text{HPA-x} + {}^1/_2\, O_2 \longrightarrow \text{HPA-x} + H_2O \qquad (3)$$

MEK prepared in the reactor 1 was separated from the reduced catalyst by distillation in a layer evaporator. Degree of the catalyst reduction, $m_{red} = [V^{IV}] / [H_m\text{HPA-x}]$, was maximal at the output from reactor 1, and minimal at the output from reactor 2. Inasmuch as productivity of the catalyst in process (1) is determined by its *oxidative capacity*, OC = $C_{\text{HPA-x}}\cdot(m_{red(2)} - m_{red(3)})$, solutions of HPA-x with high vanadium content (x) must be used as catalysts.

Study of kinetics of reaction (2) allowed us to conclude that its mechanism is described by two stages (4) and (5). At stage (4), Pd^{II} complex oxidizes *n*-C_4H_8 into MEK. At stage (5), HPA-x does Pd^0 into Pd^{II} [2]:

$$n\text{-}C_4H_8 + Pd^{II} + H_2O \xrightarrow{\text{fast}} CH_3COC_2H_5 + Pd^0 + 2\,H^+ \qquad (4)$$

$$\text{HPA-x} + 2\,\text{H}^+ + \text{Pd}^0 \longrightarrow \text{H}_m\text{HPA-x} + \text{Pd}^{II} \qquad (5)$$

Reaction (3) is many-stage too. Its completeness corresponding to minimal $m_{\text{red(3)}}$ value increases with rise of temperature and O_2 pressure [3]. Therefore, catalyst regeneration is to be favorably performed at maximum possible temperature. However, catalysts based on Keggin-type HPA-x proved to be poorly thermally stable. At T > 140°C, they began to yield vanadium-containing deposits.

In the course of optimization of the catalyst composition and conditions of the process, we have elaborated new catalysts in which high-vanadium Mo-V-phosphoric HPA solutions having non-Keggin-type composition $H_aP_zMo_yV_{x'}O_b$ (HPA-x'_{zP} where $x' \geq 6$, $z = 2–4$, $y = 12–20$, $a = 2b - 6y - 5(x'+z)$) are used [4]. Solutions of modified HPA-x' can endure temperatures up to 170°C for a long time without yielding deposits. The catalysts based on HPA-x' solutions have 3.5-fold greater productivity than the ones based on HPA-x solutions.

Pilot tests for MEK-process with use of the (Pd + HPA-x') catalyst have confirmed that the modified HPA-x' solutions are really stable up to 170°C. At present time we look for possibilities of additional stabilization of Pd in the reduced catalyst solution.

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CLEANING OF CRACK SURFACES OF METAL ALLOY PARTICLES

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The operation of aviation gas turbine engines is accompanied by formation of cracks on the turbine blades caused by high temperatures, high aerodynamic and mechanical loads, etc. The blades are very expensive. Therefore, the development of repair-recovery technologies aimed at extending the blade service life is one of the topical problems in the turbine construction.

At present, the DAYTON method is widely used to recover cracked metallic parts, which permits one to considerably prolong service life of the above parts, to save materials and to reduce labour inputs. The DAYTON recovery is performed via two steps:

- Cleaning of the crack surface from metal oxides;
- High-temperature soldering of cracks using special heat-resistant solders.

The key step of the DAYTON technology (developed and patented by the UDRI-University of Dayton, Research Institute in 1980) is the process of qualitative removal of metal oxides from the crack mouth surface (FCP-Fluorocarbon Cleaning Process) [1, 2].

Thus, the cleaning of cracks from metal oxides is a necessary condition for repair of details with cracks using the high-temperature vacuum soldering method.

The researchers of the Institute of Catalysis and the Institute of Hydrodynamics (SB RAS) performed a series of works aimed at developing a new cleaning method of micro cracks of metallic materials using a nickel-based alloy as an example [3]. A setup was developed and manufactured to experimentally substantiate the developed method (Fig. 1). Basic units of the setup are: reactor supplied with a contact heater with controlled capacity (which is controlled by a thermocouple with digital temperature indication); reservoir for solution with heat supply; steam-generator supplied with a heating element and temperature and fluid level sensors; water-cooled condenser.

In the experiments, the state of the cracks surface of the samples-simulators was controlled by an INCA Energy (X-ray energy dispersion) spectrometer, installed on the LEO-420 focused beam electron microscope. The chosen gas- and hydrodynamics parameters of the process as well as varying temperature (60 to 120 °C) and compositions of etching solutions permit removal of metal oxides from narrow gaps (70-120 mkm) during 0.3 – 0.5 h.

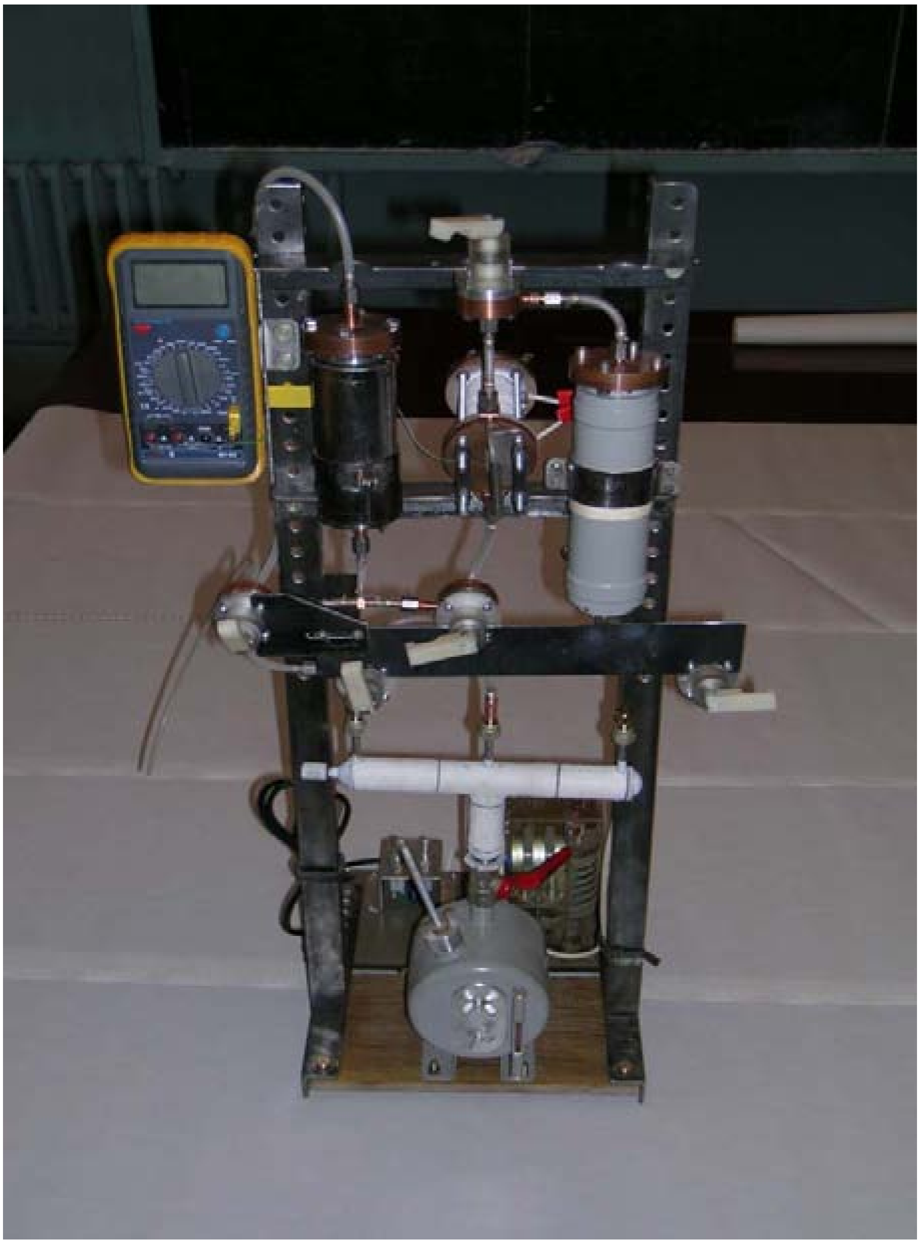

Fig. 1. A setup for cleaning cracks of the metal alloy parts

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CATALYTIC OXIDATION OF ORGANIC SUBSTRATES WITH HYDROGEN PEROXIDE IN TWO-PHASE SYSTEMS

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In our earlier works [1], we synthesized and characterized the catalysts based on the tetra(oxodiperoxotungsto)phosphate ($\{PO_4[WO(O_2)_2]_4\}^{3-}$ with quaternary ammonium cations, such as $[(n\text{-}Bu)_4N]^+$, $[C_5H_5N(n\text{-}C_{16}H_{33})]^+$, and $[MeN(n\text{-}C_8H_{17})_3]^+$. Such catalytic systems provide efficient synthesis of a number of important aliphatic and aromatic epoxides as well as mono- and dicarboxylic acids by direct oxidation of different organic substrates with hydrogen peroxide in two-phase systems [2].

Since tungstate peroxocomplexes have a significant place in the organic substrate oxidations, the present study was aimed at *in situ* synthesis of oxoperoxotungstates containing organic ligands – tertiary phosphine oxides and testing of their catalytic activity in the organic substrate oxidation reactions (cyclooctene, benzyl alcohol).

Tertiary phosphine oxide ligands (tris[2-(2-pyridinyl)etnyl]phosphine oxide, 1-diphenyl-1-[2-(1-ethylimidazol)-1-hydroxymethyl]phosphine oxide, 1-diphenyl-1-[2-(1-vinylimidazol)-1-hydroxymethyl]phosphine oxide) synthesized by the method described elsewhere [3]. Oxidation of benzyl alcohol was performed in a two-phase systems (organic phase - aqueous phase) at 80 °C upon varied [W] / [L], [Sub] / [Cat] and [Ox] / [Sub] ratios. Epoxidation of cyclooctene was performed at 60 °C in a two-phase system.

Thus, the experiments showed that the bifunctional homogeneous metal complex catalysts based on the peroxopolyoxotungstatophosphates combined with organic ligands such as tertiary phosphine oxides can be recommended for the selective oxidation of organic substrates with hydrogen peroxide in two-phase systems.

The oxidation reactions of benzyl alcohol and cyclooctene were used to illustrate the prospects of tungstatophosphoric acid and tris[2-(2-pyridinyl)etnyl]phosphine oxide or 1-diphenyl-1-[2-(1-ethylimidazol)-1-hydroxymethyl]phosphine oxide as precursors of peroxopolyoxotungstate catalysts. It was established that the presence of groups with an unsaturated C=C bond in the phosphine oxide molecule adversely affect both the conversion degree and selectivity of the oxidation reactions.

PP-III-35

This study was financially supported by the Siberian Branch of the Russian Academy of Sciences (Project No 32).

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THE ORGANIC COMPOUNDS OXIDATION PROCESSES AT THE PRESENCE OF HOMOGENEOUS CATALYSTS

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The unsaturated organic compounds oxidation into their corresponding epoxides or carboxylic acids plays a central role in fine chemicals manufacture. Traditionally, such transformations involve multi-step synthesis or have been performed with inorganic oxidant (ozone, potassium permanganate, alkaline-earth metal chlorides, promoted by chlorine-containing substances, etc.) or organic hydroperoxides [1, 2]. The selectivity of these reactions to target product is not high because of the formation of a large amount of by-products. In the oxidation processes of organic compounds it is important to replace of stoichoimetric oxidation by catalytic oxygen transfer processes in combination with oxygen donor like for example hydrogen peroxide because it is very attractive from a synthetic and industrial viewpoint since this reagent is relatively inexpensive, and environmentally clean. Metal complexes are mainly used as catalysts in these reactions. Utilization of catalytic properties of the metal complexes is of particular importance in the performance of liquid-phase reactions in two-phase systems.

It is common knowledge that different organic substrates (olefins, alcohols, aromatic hydrocarbons) may be oxidized at presence of tungsten peroxocomplexes, $PW_xO_y^{z-}$, which form in the systems: $H_2O_2 – H_3PO_4 – Na_2WO_4$ and $H_3PW_{12}O_{40} – H_2O_2$ [3]. *In situ* synthesis of the catalyst is accompanied by formation of a mixture of peroxopolyoxometallates (PPOM) such as $PO_4[WO(O_2)_2]_4\}^{3-}$, $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$, $\{HPO_4[WO(O_2)_2]_2\}^{2-}$ [2]. Note that tetrakis(oxodiperoxotungsto)phosphate $\{PO_4[WO(O_2)_2]_4\}^{3-}$ exhibits the highest catalytic activity. In this work we used a number of catalysts based on the above PPOM anion and phase transfer catalysts being quarternary ammonium salts (QAS). Such catalytic systems permit one to develop new efficient approaches to synthesis of a series of practically valuable aliphatic and aromatic epoxides as well as mono-, di- and polycarboxylic acids via direct oxidation of various organic substrates with hydrogen peroxide.

The advantages of this method are that the process occurs in one step, in mild conditions, is efficient and ecologically safe, and requires inexpensive reagents.

Thus, the reactions of oxidation of organic materials by hydrogen peroxide in the two-phase conditions (*organic phase – aqueous phase*) predominantly proceeds in the organic phase. Peroxopolyoxometallate complex containing an organic cation dissolves well in the organic phase and acts as an active agent of oxygen transportation to substrate. Regeneration of the complex proceeds on the phase boundary upon its interaction with hydrogen peroxide. To increase the phase interface, one should intensively mix a two-phase system in the «catalytic duck» reactor.

As follows from our study, epoxidation reactions of olefins (1-octene, cyclooctene, cyclohexene) and unsaturated fatty acids (oleic and ricinoleic acids) to corresponding epoxides carry out at temperature 40-65 °C, atmospheric pressure. For example, the yields of 1,2-epoxycyloalcanes in cycloolefine epoxidation processes by hydrogen peroxide are 70-90% at 92-94% of selectivity, and the yields of *cis*-9,10-epoxyoctadecanoic and *cis*-9,10-epoxy-12-hydroxyoctadecanoic acids in oxidations of oleic and ricinoleic acids are 86% and 78%, respectively.

Processes of oxidation cleavage of these substrates also proceed with high yields and selectivities.

This study was financially supported by the Siberian Branch of the Russian Academy of Sciences (Project No 32) and the RAS Integration Project No 5.6.3.

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MESOPOROUS CERIA-PRASEODIMIA CATALYSTS FOR OXIDATION OF HYDROCARBONS

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Introduction: Ceria-based materials find a wide range of applications in the field of catalysis and fuel cells [1, 2]. In many of these applications, ceria is used as an oxygen storage material or as an oxygen ion conductor. Therefore, particular attention has been attracted by doped ceria. Doping with other rare-earth elements such as praseodymium creates oxygen vacancies which enable the migration of oxygen ions through the lattice and thus provide the materials with high oxygen ion conductivity [3]. This property can be more evidenced by development and use of nanostructured ceria doped with rare-earth elements. The purpose of this study is to understand the role played by the substitution of cerium with praseodymium cations in CeO_2 synthesized by hydrothermal treatment method in presence of surfactant. The effects of properties and behavior of Pr/CeO_2 materials, with various compositions, in catalytic oxidation of CH_4 were evidenced.

Experimetal: Ce_{1-x} Pr_xO_2 oxides (were x are 0.1, 0.5 or 0.9) were prepared by hydrothermal treatment from cerium and praseodymium nitrates as metal precursors, cetyltrimethylammonium bromide (CTAB) as surfactant, urea as hydrolyzing agent and tetramethylammonium hydroxide (TMAOH solutions 25 wt. % in water) as precipitate agent. The molar ratio of urea: metal was 4.5: 1. The aqueous solution of inorganic precursors was introduced under stirring to a mixture of 2.8g CTMABr and 60 ml H_2O, after 2h stirring. Subsequently, urea was added by dropwise and reaction proceeded at 80 °C for 4h, under stirring. The pH was adjusted at 9 using a tetramethylammonium hydroxide (TMAOH) and the obtained gel was aged for 3 days in Teflon link steel autoclave at 100 °C. The wet precipitates were filtered, washed (with deionized water- samples W or ethanol- samples E), dried at 100 °C and calcinated in N_2 flow and followed by air at 550 °C. The obtained materials were characterized by X-ray diffraction, SEM and TEM microscopy, N_2 adsorption-desorption, IR, UV-Vis and X-ray Photoelectron spectroscopy. The oxidation of CH_4 was performed under atmospheric pressure with a quartz-made tubular reactor. The effluents from the reactor, containing reaction products were analyzed by gas chromatography.

Results and Discussion: The X-ray diffraction peaks of $Ce_{1-x}Pr_xO_2$ samples correspond to the face-centered cubic fluorite structure type CeO_2 and PrO_2. A very homogeneous materials with spherical morphology and an insignificantly variation of lattice parameter were evidenced by XRD and SEM microscopy of the $WCe_{1-x}Pr_xO_2$ samples with various Pr content. This may be due to the uniformity of Pr^{4+}: Pr^{3+} ratio and oxygen vacancy in these materials. The lattice parameter systematically increases with the Pr content for $ECe_{1-x}Pr_xO_2$ samples and formation of two phases was evidenced by SEM microscopy at high Pr percent. The oxidation states of cerium and praseodymium ions have been determined by XP and UV-Vis spectroscopy. While cerium is mainly in the +4 oxidation state, about one-half of the praseodymium ions were found to be in the +3 state. The large amount of Pr^{3+}cations seems to be a particularity of the doped ceria samples.

A high variation of the surface stoichiometry and Pr^{4+}: Pr^{3+} ratio was evidenced for the W and E type samples. The catalytic performance of oxides depends strongly on the precipitate washing. The catalytic activity is probably attributable to the migration of Pr ions and their distribution at interface or into the ceria network. The activity of all $WCe_{1-x}Pr_xO_2$ samples in oxidation of CH_4 is very high (Fig. 1). In contrast, $ECe_{1-x}Pr_xO_2$ samples exhibit lower activity. The activity of $ECe_{1-x}Pr_xO_2$ increases with Pr content.

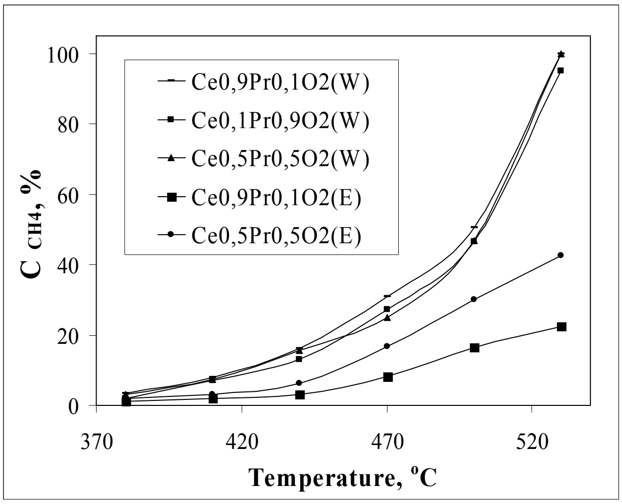

Fig. 1. The variation of CH_4 conversion with temperature.

Acknowledgements: The financial support by the Romanian Ministry of Education and Research -CEEX-AMCSIT 267 is highly appreciated.

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NON-ARRHENIUS MECHANISMS OF VERY FAST SOLID PHASE CHEMICAL TRANSFORMATIONS IN «UNIVERSE-REACTOR» NEAR ABSOLUTE ZERO OF TEMPERATURES

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The presented here work are connected with an absolutely new field of applications of fracture problem in solid phase chemistry. Main Non-Arrhenius goal of the works is interacting (feedback coupling) between of fracture and activation of solid matrix in chemical processes in solids, in particular, in a such global reactor as chemical transformations in Universe.

Autowaves of fracture as a reason of fast chemical evolution of matter in Universe.

The work proposes new approaches for explanation of a many-centuries mystery concerning of nature of super-fast chemical solid state evolution of matter in the «Universe-Reactor» under temperatures near to absolute zero and also chemical mechanisms of forming of the solid crust on the cold planets of the Solar system.

The concept is based on discovered two decades ago non-usual autowave self-propagation phenomena of anomalous fast transformations in the cryo-chemical reactions [1,2]. These travelling waves had velocities equal to ones in most fast high temperature processes of combustion nevertheless the transformations were realised under temperatures 4-77 K (in liquid helium and nitrogen). The chemical solid state waves initiated by local brittle fracture propagated layer by layer over the frozen sample of reagents. The chemical reaction starts on the surface resulting from local brittle fracture of the solid matrix. Temperature gradients arising during the reaction lead to further dispersion of the reacting sample. This feedback mechanism leads to propagation of autowaves of chemical conversion. Such an autowave regime is observed for several classes of reactions (hydrocarbon chlorinating, olefin hydrobrominating, polymerization and copolymerization). The classical Arhenius concept could not explain the phenomenon. These observations lead to a completely new autowave concept of chemical activity in solid state.

The developed theory of the phenomenon rests on the assumption that a mechanical energy accumulated in solid matrix can be transformed into a chemical energy even at extremely low temperatures, therefore leading to rates of chemical transformation many orders of magnitude larger than predicted by classical Arrhenius factors. This energy transformation is a result of self-sustained brittle disruption (fracture in form of dispersed solid substance) of solid matrix and this phenomenon may be named «autowave self-sustained tribo-chemical mechanism».

The first simple theoretical model of autowave processes in solid-phase cryochemical reactions was proposed in [1,2]. The model considered was constructed on the physical scheme that brittle fracture is induced by thermal strain from reaction heat generation. The theory is being developed by the work [3] which are investigating different bifurcation phenomena concerning of critical conditions with parameters of heat-transfer, sample sizes, and also with thresholds of «cold» ignition of autowave transformation in frozen reagents by local disruption etc.

We suppose the autowave hypothesis may give an ideological base of fast cryochemical evolution of the cosmic substances. In particular, one can imagine the formation, from the frozen mixture of elements, of compounds such as ammonia and methane that are found in appreciable amounts in crusts of the cold planets of the Solar system.

APPLICATION: autowaves of fracture of metastable phase states in solids as a new approach for explanation of mechanisms of geotectonics phenomena and earthquakes.

By using above presented mechanism of solid phase chemical transformations we formed a nonlinear theoretical model for describing of mechanisms of initiating and dynamics of moving in time and space of geotectonic phenomena and earthquakes. A base of the model is the «gasless detonation» in fracture of solids, supersonic wave theory created in [4,5] for explanation of catastrophically fast decays of metastable phase states in solid matter. The untraditional fracture notions was developed for different solid transformations in physics of semiconductors, in physics of explosives sensibility to friction and shock. Possibility of application of the theory to geophysical processes is based on a hypothesis that geotectonic phenomena and earthquakes are a result of catastrophic phase transitions in rocks of Earth Crust. Classical theory of polymorphism describes a lot of metastable phases in earth rocks but never investigated dynamics of the transitions between them. A bifurcation approach to modeling of the geological phenomena is proposed in the present work.

The phenomenon is modeled by coupling the reaction diffusion equation, describing chemical or phase transformations, and the wave equation, describing elastic perturbations. The feedback coupling considered in this work involves (i) a dependence of the sound velocity on the phase (chemical) field, and (ii) the destruction (fracture) of initial phase equilibrium when the strain exceeds a critical value: such critical strain destroys the matrix because of difference of initial and finishing products densities and induces phase transformation. An exhaustive analytic and numerical study of travelling waves of fracture reveals the existence of supersonic modes of transformations. The very important for geotectonics problem of ignition (starting) of earthquakes catastrophic waves by local disturbance in earth rock is investigated. With the present model, the critical strain necessary to ignite gasless detonation by local perturbations is determined.

There are discussed some works of geophysicists [6,7] in which a phase transformation concept was used for explanation of earthquakes phenomenon. There is discussed the question about possibility of laboratory experimental modeling of earthquake with example of super-fast decay of metastable silicate glasses – chemical analogues of earth rock matter (explosives of «Prince Ruppert Drops» [8] and «Tempered Glasses» [9]).

The work performed at the financial support of RFBR № 07-03-00259.

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PP-III-39

CATALYTIC REACTORS WITH STRUCTURED BEDS OF FIBER-GLASS CATALYSTS

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Novel catalysts comprising noble metals (Pt and Pd), supported on fiber-glass woven support [1] has attained a lot of attention recently both from theoretical and applied points of view. The research investigations [2] showed that such catalysts demonstrate unique catalytic properties and may be used for performance of a wide range of catalytic reactions.

Moreover, specific heat/mass transfer properties [3], original geometry, high flexibility and high mechanical strength of such catalysts give the way to develop really new catalytic processes and novel reactor designs.

Two basic reactor designs for fiber-glass catalyst were proposed: a) with radial packing of the catalytic fabric [4] (Fig. 1) and b) with spiral roulette cartridges [5] (Fig. 2).

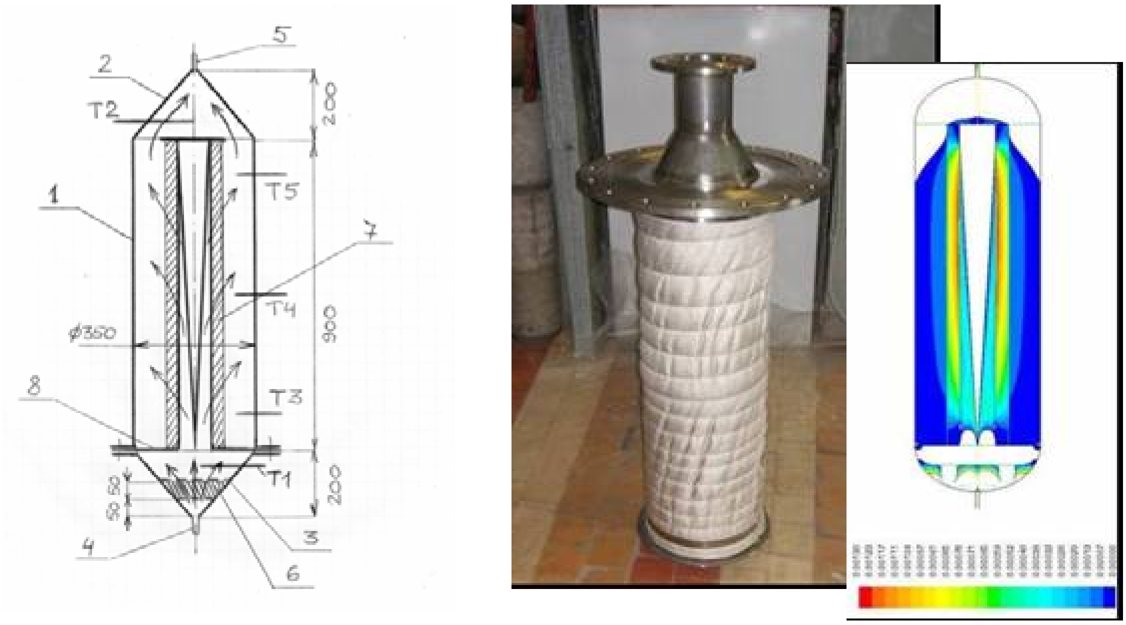

Fig. 1. Catalytic reactor with radial bed of the fiber-glass catalyst fabric

The proposed reactors design were applied at the semi-commercial and pilot scale in various catalytic processes:

- purification of automotive exhausts;
- incineration of VOCs in waste gases;
- utilization of chlorinated VOCs;

- selective hydrogenation of acetylenes in olefin/diolefin media;
- SO_2 oxidation.

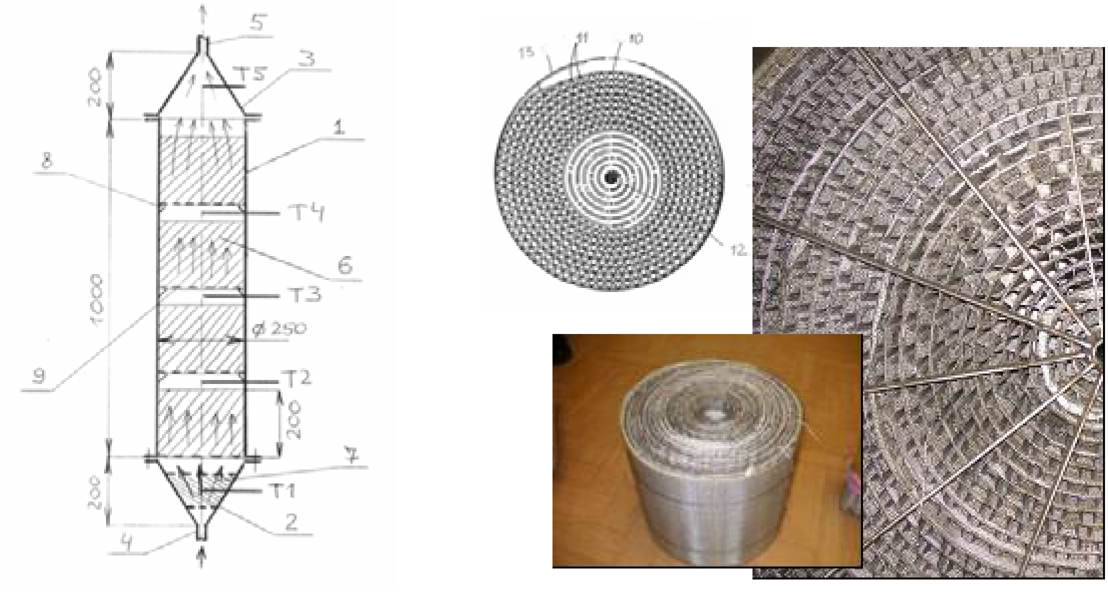

Fig. 2. Catalytic reactor with spiral cartridges of the fiber-glass catalyst fabric

The efficiency and issues of practical application of the proposed designs are discussed in the presentation.

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PP-III-40

THE OXIDATIVE DEHYDROGENATION OF BUTANE OVER Fe-ZSM-5 ZEOLITES

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The iron containing ZSM-5 zeolites have shown remarkable activity and selectivity in the oxidative dehydrogenation of propane with N_2O as well as hydroxylation of benzene and epoxidation of propene. This is related to the oxygen species formed via N_2O activation over the Fe-ZSM-5 zeolites. In this work, a series of iron containing zeolites with varying Si/Al ratios (11.5 to 140) and low iron content (~0.9 wt. % Fe) were synthesised by solid-state ion exchange of commercially available zeolites. The catalysts were tested for the dehydrogenation of butane with N_2O and their performances were compared to reference Fe/SiO_2 samples. The catalysts were characterised by XRD, SEM-EDX, Ar-Adsorption, NH_3-TPD, H_2-TPR, DRIFT, UV/vis and XPS and, on the basis of the structure-activity results, a model of the iron species responsible of the activity of both dehydrogenation and total oxidation is proposed.

Experimental

Fe-ZSM-5 catalysts were prepared via solid - state ion exchange using NH_4-MFI and $FeCl_2 \cdot 4H_2O$ (Merk AG, Germany) according to the procedure given in [1]. The preparation of Fe/SiO_2 samples has been described elsewhere [2]. Chemical composition of the samples was determined by inductively coupled plasma emission spectroscopy (ICP). After iron exchange, samples were characterised by XRD, SEM-EDX, Ar-Adsorption, NH_3-TPD, H_2-TPR DRIFT, UV/vis and XPS. The decomposition of N_2O and dehydrogenation of butane with N_2O, O_2 and N_2O/O_2 mixture were carried out in a fix bed reactor (i.d=20 mm; L=600 mm). Prior to experiments the catalysts were pre-treated in flowing He at 773 K for 2 h. After the pre-treatment, the He flow was replaced by the reaction mixture and evolved product gases were continuously monitored by gas chromatography. The oxidative dehydrogenation of butane with O_2, N_2O and N_2O/O_2 mixture with different C_4H_{10}: Oxidant ratios (1:1; 1:2) were performed at 723 K for WHSV of 24000 ml. $h^{-1} \cdot g_{cat}^{-1}$.

Results and discussion

Figure 1 shows in the influence of Si/Al ratio of the parent zeolites with similar iron content (~ 0.9 wt. % Fe) in the dehydrogenation of butane at 723 K. With increase in the Si/Al ratio, an increase in the propane conversion and almost no change in the selectivity towards butene are observed. In addition, a slightly decrease in the selectivity towards propene with increase of Si/Al ratio is observed (not shown here).These are likely to be related to the change of zeolites acidity with varying Si/Al and therefore the number of iron cations introduced into zeolites. In the low Si/Al ratios (Si/Al < 40), the percent of products such as CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6 formed via the hydrocraking of butane are enhanced. But, the higher Si/Al ratios lead to an increase in oxidative dehydrogenation of butane to butene and butadiene.

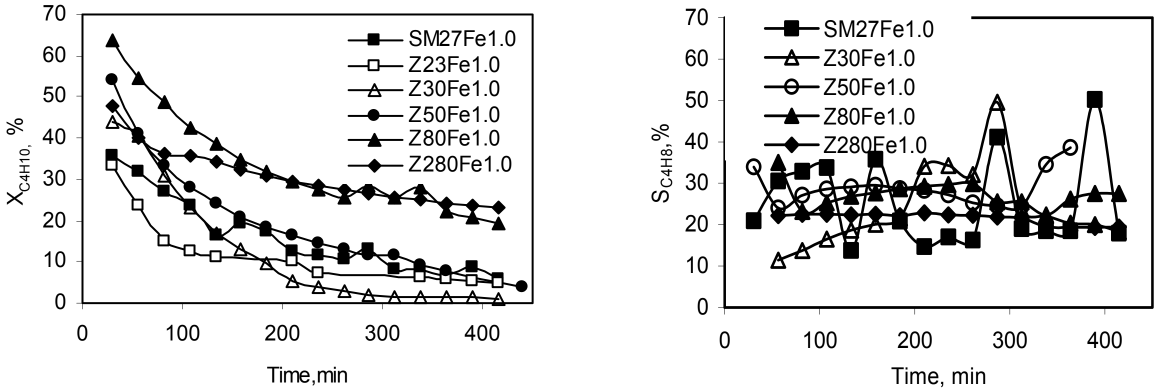

Fig.1. Butane conversion and butane selectivity as a function of time in the presence of N_2O in the feed (W_{cat}= 0.5 g, T= 723 K, C_4H_{10}:N_2O=1:1, F_{total}=200ml/min). ZxFey: x= SiO_2/Al_2O_3 and y= wt. % Fe.

The presence of O_2 as well as N_2O in the feed over Z280Fe1.0 not only prevents the formation of butane and butadiene, but also leads to a significantly decrease in the conversion of butane, from 50 % to 3.0 %. The butane mainly converts to CO_x via total oxidation

The nature of the iron species responsible for the N_2O decomposition (not shown here) and dehydrogenation of butane appears clearly different as could be observed with of H_2-TPR, UV/vis, XPS, DRIFT, and NH_3-TPD. It can be concluded that although N_2O decomposition and the total oxidation of butane are favoured over isolated iron-oxo/hydroxo-cations formed over Fe-ZSM-5 with low Si/Al, the uncharged nonosized multinuclear iron oxoclusters formed in 80 and 140 of Si/Al can mostly catalyze the dehydrogenation of butane.

Additionally, in this work the kinetics of global and elementary steps for oxidative dehydrogenation of butane can be obtained under the unsteady-state and steady-state experiments.

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PP-III-41

MODELLING AND DESIGN OF THE REACTORS FOR THE PROCESS OF THERMOCATALYTIC HYDROGENATION OF LIQUID PRODUCTS OF PYROLYSIS FOR OBTAINING BENZENE

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At present, sources of raw material for obtaining of benzene are the aromatic hydrocarbons C_7-C_9 and hydrorefined fraction of pyrocondensate, benzene-tolnene-xylene(BTX). Hydrodealkylation and hydrocracking of non-aromatic hydrocarbons of BTX fraction is carried out by thermal and catalytic methods under pressure of hydrogen, 2.5-6.3 MPa and at high temperature, 620-730°C. Shortages of the thermal process are greater formation of polycyclic aromatic hydrocarbons, lesser yield of ethane and propane and high temperature. Shortages of the catalytic process are high pressure, complication of regulation of temperature and large expenditure of the catalyst.

In our Institute it has been developed the thermocatalytic process which combines the advantages of thermal and catalytic processes [1]. Thermocatalytic version of the process foresees the realization of hydrogenation of BTX fraction in two consecutive adiabatic reactors. In the first reactor with injection mixing, the degree of hydrocracking achieves 90%. In the second reactor with the polyfunctional catalyst – B-17/3, the reaction of hydrocracking of non-aromatic hydrocarbons finishes completely. At the description of mechanism of the process we have considered the aromatic hydrocarbons, C_8; naphthene hydrocarbons, C_6-C_8; paraffin hydrocarbons, C_6-C_8 and hydrocarbons, C_1-C_4 in the aggregated form. Taking into account that hydrodynamics of the injection reactor corresponds to model of ideal stirred, the kinetic model of the thermal reactor may be written as:

$$\begin{aligned}
P_1 &= P_1^0 + V(R_2 - R_1)/v \\
P_2 &= P_2^0 + V(R_1 - 2R_5 - R_6)/v \\
P_3 &= P_3^0 + V(-R_2)/v \\
P_4 &= P_4^0 + V(R_6 - R_3)/v \\
P_5 &= P_5^0 + V(R_3 - R_4)/v \\
P_6 &= P_6^0 + V(R_5)/v \\
T &= T^0 + V\left(-\sum_{i=1}^{6} R_i \Delta H_i / C_p \rho R T - \alpha(T - T_X)\right)/v
\end{aligned} \tag{1}$$

where R_i is a rate of reaction i; ΔH_i is a heat of reaction i; C_P is an average heat capacity of the reaction environment; ρ is a density of the reaction environment; V is a volume of the rector; v is a volumetric flow rate; T_X is the local wall temperature; α is a heat transfer coefficient; P_1^0, P_2^0, P_3^0, P_4^0, P_5^0 and P_6^0 are the initial partial pressure of: toluene, benzene, aromatic hydrocarbons C_8, naphthene hydrocarbons C_6-C_8, paraffin hydrocarbons C_6-C_8 and condensation hydrocarbons accordingly.

Equations of a rate for *i*-th reactions:

$$R_1 = k_1 P_1^{1.5} P_7^{0.5} \qquad R_2 = k_2 P_3^{1.5} P_7^{0.5}$$

$$R_3 = k_3 P_4 P_7 - k_7 P_5 \qquad R_4 = k_4 P_5 P_7$$

$$R_5 = k_5 P_2^2 - k_8 P_6 P_7 \qquad R_6 = k_5 P_2 P_7^3 - k_9 P_4$$

where P_7 is partial pressure of hydrogen.

For taking into account of influence of pressure, temperature and ratio of hydrogen to raw material on the rate constants we have used the modified equation of Arrhenius which is given by

$$k_i = K_{0i} \theta^{\alpha_i} \exp\left(-\left(E_i + \Delta V_i (P-1)\right)/RT\right)$$

where θ is ratio of hydrogen to raw material.

By using model (1) it has been calculated the construction parameters of the injection rectors with productivity on raw material 31 ton/h.

For calculating of the catalytic reactor it has been used two-dimensional one-phase quasi-homogeneons model of the reactor with fixed bed catalyst.

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PP-III-42

COMPLEX TECHNOLOGY OF TREATMENT OF CHROMIUM CONTAINING WASTE WATER

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Hexavalent chromium is present in the effluents produced during the electroplating, leather tanning cement, mining dyeing and fertilizer and photography industries and causes environmental and public health problems.

Hexavalent chromium has been reported to be toxic to animals and human and usually of anthropogenic origin and rarely occurs naturally [1,2]. Cr (VI) is a skin and mucous membrane irritant and some of these hexavalent compounds produce an allergic contact dermatitis characterized by eczema [3,4]; it is also recognized as a pulmonary carcinogen [1.2]. Its concentrations in industrial wastewaters range from 0.5 to 270.0 $mg.\ell^{-1}$ [5]. The tolerance limit for Cr (VI) for discharge into inland surface water is 0.1 $mg.\ell^{-1}$and potable water is 0.05 $mg.\ell^{-1}$ [6]. In order to comply with this limit, it is essential that industries treat their effluents to reduce the Cr (VI) to acceptable levels.

The basic purpose of the given work is development of complex technology of treatment of chromium containing waste water with use of different reagents, reductions, precipitations, and approbation on model waste water. Objects of research had been chose model solutions of chromic acid, and dichromate salts. The choice of model solutions is based by that the given salts of chromium use in tanning, textile and other chemical industries. As reducer the solution of sodium sulphite that is caused by that the given reagent is received as a waste at treatments of off-gases of production of sulfuric acid has been chosen.

This study investigated a new treatment process for the removal of Cr (VI) from aqueous solutions by applying as homogeneous catalysts under the basis of content of chromium from tannery chemical, metallurgical, machine-building industries wastes.

Suggested technology of chromium containing waste water treatment submitted in two ways, that is functional chart with use of sulfuric acid and use of additives of salts of metals.

Waste water treatment by using additives of salts of metals presented in figure 1.The second way differs that reduction and precipitation of compounds of chromium carry out in neutral medium 5 %- sodium sulphite at the presence of the additive of 10 % solution of salt $Cu(NO_3)_2$ or $Fe(NO_3)_3$, used as homogeneous catalyst. Process of treatment carry out in one stage, thus the degree of reduction and treatment of a solution of compounds of chromium achieves 51-100 % at temperatures 20-80°C. It allows to exclude some reagents (H_2SO_4, NaOH) and to simplify separation of slimes from a purified outlet. Sequence of realization of technological operations:

1. The waste liquors containing compounds of chromium (VI) from the tanning, metallurgical enterprises bring to a reactor of mixture at the temperature of 80°C beforehand having equalized them in the receiving tank equalizer;
2. In a capacitor reactor at t = 80°C there is a reduction of hexavalent chromium by sodium sulphite at the presence of the additive of iron nitrate ;
3. The processed solution enters in a receiving tank - settling tank where there is its cooling and within two hours there is a settling sediment Cr (III);
4. Cooled down solution pass through пресс the filter (the drum-type vacuum filter) where there is a separation of a sediment from a liquid which subsequently dump in city collector or a reservoir;
5. The formed sediment is exposed to incinerate at the temperature of 400°C, and then is used as a pigment by production of varnishes and paints, in silicate production.

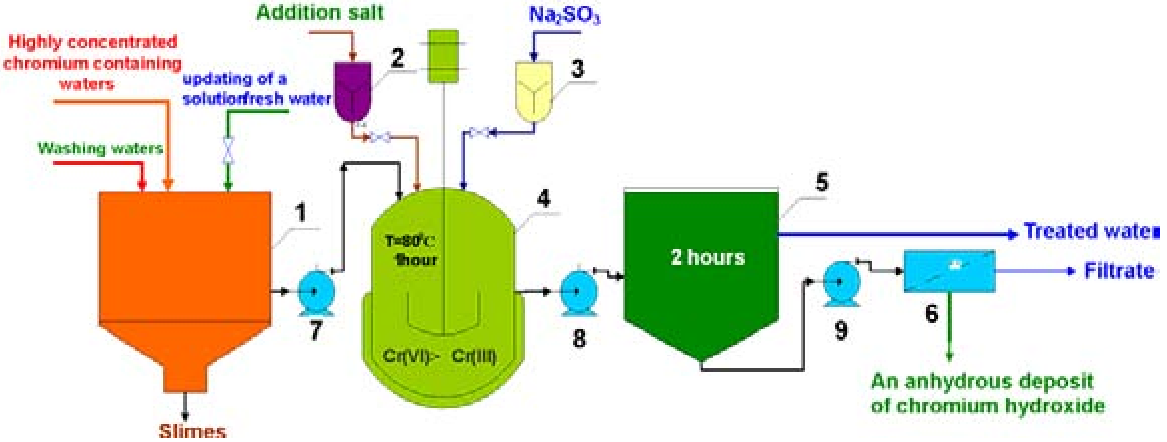

Fig. 1. A functional chart treatment of chromium containing waste water using additives of salts of metals
Apparatus: 1 - Receiving tank equalizer 2, 3 - Containers for solutions of iron nitrate (III) and sodium sulphite 4 - reactor 5 - settling tank 6-filter 7, 8, 9 - Pumps

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PP-III-43

PHOTO ELECTROCHEMISTRY APPLIED IN THE SEPARATION OF METALLIC IONS BY MEMBRANE PROCESS

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The transport phenomena through ion exchange membrane may be improved by the application of different forces inside or outside the systems. The electrical current, produced by synthetic photo electrode, is applied to enhance the separation of metallic ions. The cation exchange membrane placed between the two compartments permitted the separation and concentration of the ions M^{2+} (= Cu^{2+}, Zn^{2+} and Ni^{2+}). The movements of M^{2+} from the aqueous solution to the membrane and inside the membrane are followed by the flux determinations and the potential measurements. In this study, the three cations are studied alone or as binary and ternary systems. It was observed that the illuminated CdS electrode leads to an increasing of the transport flux at least 10 times more than that calculated in the obscurity. Moreover, in all the cases the potential of the first specie electrode M/M^{2+} in the feed compartment increases until a maximal value reached at ~ 100 min. above which it undergoes a diminution. The membrane is more selective to Zn^{2+}; this selectivity decreases in the binary and ternary systems. On the other hand, the photo electrochemical properties of the hexagonal CdS showed strong light absorption of wave lengths shorter than 520 nm. The shape of the intensity potential curve under illumination and the negative flat band potential (-1.02 VSCE) provide unambiguous evidence of n-type conductivity. The conduction band located at -1.25 VSCE leads to a thermodynamically M^{2+} reduction under visible light and accentuates the diffusion process.

MODELING AND OPTIMIZATION OF NOVEL PHOTOCATALYTIC SYSTEMS BASED ON NANOSTRUCTURED TITANIA

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Modeling and optimization of novel photocatalytic systems based on nanostructured titania has been proposed and investigated. Particularly, photocatalytical coatings consisting of titania-based nanocontainers incorporated in the hybrid SiO_x:ZrO_x film were modeling and optimized. The embedded nanocontainers demonstrate an ability of efficient light-driven release of the loaded materials and at this basis novel multifunctional «smart» light-controllable coatings with extra high bactericidal activity are developed.

The incorporation of nanodispersed titania particles into the hybrid SiO_x:ZrO_x-based films permits to immobilize the different catalysts and obtain photacatalytically-active coatings at low temperatures. The resultant thin-film photocatalysts reveal high activity towards photodestruction of organics both in aqueous solutions and in air conditions. The enhanced hydrophilicity inherent to the titania-loaded hybrid sol-gel films makes them a promising material for air purification and for self-cleaning coatings. These films also show high affinity to microorganisms and demonstrate enhanced photoinduced pathophysiological activity towards both gram-negative and gram-positive bacteria. Of principle meaning is also the fact that the hybrid SiO_x:ZrO_x-based films used as the photocatalyst carrier are highly adhesive and, being deposited onto the metal surface, behave as the anticorrosion coatings. The proposed approach permits one to change radically the whole scheme of assembling the photocatalytically-active coatings since the titania particles to be embedded into the hybrid sol-gel film can be synthesized, annealed and then modified (if needed) separately. Moreover, the dispersions of different photocatalysts can be embedded in the SiO_x:ZrO_x matrix yielding photocatalytically-active coatings with mosaic surface that opens strong possibilities of controlling the adsorption of chemical and bacterial contaminants.

By applying polyelectrolyte shell over the particles of mesoporous titania via layer-by-layer assembly of oppositely charged polyelectrolytes it is possible to fabricate nano-scaled reservoirs which being immobilized by hybrid sol-gel film demonstrate an ability of light-driven release of the loaded materials. On this basis novel photocontrollable coatings which could be opened under UV or IR laser irradiation have been modeling and optimized.

PP-III-45

MODELING OF CATALYTIC α-OLEFINS OLIGOMERIZATION IN THE FLOW-TYPE REACTOR

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The possibility of modeling the α-olefin oligomerization reaction in a column flow-type reactor with a mechanical mixing device representing a multi-tier mixer with plane vanes has been discussed. The dependence of the mean residence time of the reaction mass in the apparatus on the space velocity of the flow has been experimentally found. It has been shown that the description of the oligomerization process in the said reactor by several logically acceptable kinetic models including those of: ideal reactor displacement, cascade of ideal mixing reactors, diffusional model, ideal displacement and ideal mixing reactors in succession, and visa verse, does not reveal any substantial difference in the final degree of α-olefin conversion to oligomers between the models under consideration. The reason of this may be attributed to the fact that in these computations the observed mean residence time, being a corrective factor while modeling is taken. For example, while using the ideal displacement reactor kinetic model on the kinetic parameters of decene-1 oligomerization at different temperatures a rather adequate approximation of the experimental and calculated values of the total olefin conversion to oligomers has been obtained. Given a sufficient experimental data base is available, the dependence of the yield, oligomer mean molecular mass and viscosity on the process conditions may by described by regressive equations and can be combined into a unified computer system permitting to control the oligomerization process in a flow-type reactor to produce oligomers with desired molecular-mass and viscosity characteristics. The reactor under discussion proves to be versatile for α-olefin oligomerization in the presence of pseudo-homogeneaus and homogeneaus catalyst. One of the definite advantages of the reactor consists in the combination of intensive reaction mass mixing being especially important while using pseudo-homogeneaus catalysts, providing for the required mean residence time to attain maximum possible monomer conversion.

MATHEMATICAL MODELLING OF A CO-CURRENT REACTOR

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This paper deals with mathematical modeling of a cooled catalytic fixed-bed reactor where single exothermic reaction occurs. An important class of reactors is that for which the wall temperature is not constant but varies along reactor length. Such is the case when the cooling tubes and reactor tubes form an integral part of a composite heat exchanger. In this study co-current flow of coolant and reaction mixture is considered. It is assumed instantaneous heat transfer between the solid catalyst and the reacting gas mixture, constant heat-physical properties and negligible diffusivity inside catalyst pellets. The heat and mass transfer resistance through the packing and gas mixture inside the bed are described by the effective coefficients of conductivity and diffusivity. Reaction rate varies with temperature by Arrhenius law. With these assumptions a two-dimensional pseudo homogeneous model of heat and mass transfer was used. The partial differential equations (PDE) involve three decision variables (coolant temperature, gas mixture temperature and concentration), which vary on time and along two space coordinates.

Due to high non-linearity and major number of system parameters of these equations the problem can only be solved in this form by numerical techniques. In order to obtain a preview of possible dynamics and initial guesses for computations it is necessary to simplify the problem and give equations which can be solved analytically. For that the set of PDE was converted to ordinary differential equations (ODE) by discretization of the spatial derivatives with finite differences. Then the resultant ODE system (the dynamical system of the 3rd order) was used for finding steady states and periodic solutions, determining their local stability and bifurcation points. By applying the methods of bifurcation theory [1] the analytical expressions for bifurcation diagram and non-unique boundary were obtained. It was found that the system can possess from 1 to 3 different equilibrium states. One equilibrium state represents a meta-stable and the remaining two states correspond to high- or low-temperature regime, depending on initial conditions. The stability of steady states was investigated on the basis of linear approximation of simplified model by applying the 1st Lyapunov method and Routh-Hurwitz stability criterion [1]. The parametric equations of stability boundaries in the plane «inlet gas temperature»(ϑ_0) – «reaction heat»(q) were obtained. These boundaries divide the parametric plane ϑ_0,q into 6 regions with different type of stability and number of steady states. It was shown that for realistic parameter values cooled reactor can exhibit as unique regime (stable or auto oscillating) as multiple regimes with low- or high temperature steady states, which can be stable or unstable depending on region.

To examine the qualitative prediction by the bifurcation theory, the predicted regimes were numerically computed using two-dimensional model. An explicit finite difference approximation was applied [2]. The results of comparison show, although some negligible discrepancies between predicted approximately-analytically regimes and those obtained numerically are happened, in total strongly nonlinear simulation supports the existence of auto-oscillating, stable, unique and multiple regimes as established by linear theory. Thus it can be concluded that simplified model describes all qualitative features of the two-dimensional model. So obtained analytic results may be used for prediction the dynamics in the reactor, quick estimation of magnitude of influence of various design and operating parameters on the reactor behavior and for choice of parameters of required regimes for numerical computations.

As well known the non-isothermal packed tubular reactor, where exothermic reaction occurs is very sensitive to change in wall temperature. So it was interesting to examine on both models the effect of inlet coolant temperature and coolant flow rate on the reactor stability and dynamics. It was obtained that temperature in the reactor increases with decrease in coolant flow rate. Value of inlet coolant temperature impacts on temperature distribution within reactor, its maximal temperature, character of the regime and may cause thermal instability in the sense than reaction may either extinguished or continue at a higher temperature level.

Finally the effect of imposing periodical variations on inlet gas mixture temperature was examined, and amplitude-frequency characteristic of the given system was obtained.

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KINETIC MODELING AND SIMULATION OF TRICKLE BED REACTOR IN GAS OIL HDS

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Abstract:

A trickle bed reactor model has been developed for hydrodesulfurization of dibenzothiophene as sulfur component exists in gas oil feed. This model incorporates the contributions of partial wetting and stagnant liquid hold-up effects for a complex consecutive/parallel reaction scheme under consideration represented by Longmuir-Hinshelwood type kinetics. As the reaction is highly exothermic, the heat effects have also been incorporated in the model. Hougen-Watson rate equations for the hydrogenolysis of DBT into BPH and H_2S, for hydrogenation of DBT into THDBT and HHDBT, for hydrogenation of BPH into CHB, and for the subsequent hydrogenation of CHB into BCH were developed. The reactor performance for partial wetting of catalyst particles and in the presence of stagnant liquid pockets has been compared and the significance of different parameters discussed. Experimental data for catalyst, reactor and operating conditions were obtained from an industrial plant. The model predictions were compared with experimental data and were found to agree very well. The model proposed here also allowed prediction of maximum temperature rise in the catalyst bed and which was also found to agree well with the steady state experimental data.

Keywords:

Hydrodesulfurization, kinetic modeling, trickle bed reactor, Dibenzothiophene, stagnant liquid pockets

Model Development and Integration Method:

For the purpose of developing a trickle bed reactor model, the approach of Tan and Smith (1980) was used to evaluate the approximate solution of catalytic effectiveness factor under conditions of partial wetting of catalyst particles. For the developing of dimensionless mass and heat transfer equations, two different types of active sites were considered: σ sites for hydrogenolysis and τ sites for hydrogenation. Accordingly, mass and heat transfer equations have been developed and the approach of partial wetting of catalyst particles has been incorporated in the model. The integration in the axial direction was performed using a fourth order Runge-Kutta routine with constant step size. The initial guesses are then updated, using a Newton-Raphson method, until the required accuracy is obtained.

Results and discussion:

The considered reactor is composed of three discrete sections and the desulfurization operation is being done in each section. According to the experimental data given from an industrial plant, and the resulted obtained from simulation, the temperature and sulfur content of gas oil feed at different sections is as follows:

	Inlet	Bed 1	Bed 2	Bed 3
Experimental Sulfur content (wt.%)	13%	9%	5%	~ 0%
Simulated sulfur content (wt.%)	13%	9.2%	5.35%	0.5%

Bed 1 Temperature (°C)	**Experimental**	Inlet	354
		Outlet	369
	Simulated	Inlet	354
		Outlet	368
Bed 2 Temperature (°C)	**Experimental**	Inlet	354
		Outlet	370
	Simulated	Inlet	354
		Outlet	369.41
Bed 3 Temperature (°C)	**Experimental**	Inlet	359
		Outlet	369
	Simulated	Inlet	359
		Outlet	368

According to above tables, a good agreement between experimental data and simulation results is observed. Thereupon, we can conclude that the accuracy of the presented model is very good and it is applicable in simulation activities.

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SIMULATION OF A THREE-STAGE TRICKLE BED HYDROTREATING REACTOR USING GAS OIL OVER $CoMo/Al_2O_3$ CATALYST: EFFECT OF RADIAL TEMPERATURE DISTRIBUTION ON DESULFURIZATION

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Abstract:

Presence of sulfur in crude oil and petroleum fractions imposes plenty of harmful effects to environment and process equipment. So, elimination of this compound from petroleum cuts has been considered extensively. In this study, the process of HDS of dibenzothiophene as on of the most stable sulfur compounds has been discussed and nonisothermal heterogeneous modeling and simulation of the three-stage trickle bed reactor has been done. The catalyst used in this operation is $CoMo/Al_2O_3$. The kinetic model used in the simulation was based on the Langmuir-Hingshelwood method of rate determination. Petroleum feed used in this simulation was gas oil and the operation has been done at inlet temperature of 354°C and pressure of 70barg. In developing the recommended model, we have used the viewpoint of the presence of stagnant liquid pockets between catalyst particles and the heat effects have been incorporated in the model due to highly exothermic HDS reaction (approximately 21628 kcal/kg mol). The simulation shows the sulfur conversion of 99% in final product and very good agreement between simulation results and experimental data has been demonstrated. Also, two-dimensional modeling of 1st bed of reactor has been done and the results have been shown. Accordingly, conversion in regions near to bed wall is more. The presented model has the ability of determining the position and numerical amount of hot spots inside the reactor.

Keywords:

Hydrodesulfurization, kinetic modeling, trickle bed reactor, Dibenzothiophene.

Results:

Comparison of simulation results with experimental data has shown that using the approach of liquid stagnant pockets between catalyst particles, promotes the accuracy of the results. Sulfur concentration in final product of the reactor is about 0.04wt.% that shows conversion of about 99%. Also, observed temperature difference between the presented approach and experimental data shows little and negligible error and this is because of consideration of liquid stagnant pockets phenomenon that plays an important role in hydrodynamics of trickle bed reactors.

The presented computer code, prepares the ability of predicting the applications of trickle bed reactors exactly and therefore, an important tool for design and optimization of HDS reactors has been prepared.

PP-III-49

FIBROUS PALLADIUM-SUPPORTED CATALYSTS FOR REACTION OF HYDROGEN OXIDATION

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New methods of synthesis of fibrous ion-exchangers have been developed in our institute for ceveral decades. These ion-exchangers find a use in many fields of application, including catalysis. One of the advantages of these materials is possibility of their use in systems with low hydraulic resistance, in slot reactors for instance. Low fiber diameter (ten times lower then granule diameter) determines higher rate of mass-exchange processes and, as a result, higher rate of whole process.

Current work deals with preparation of palladium supported catalysts on the basis of fibrous ion-exchangers. Effect of ion-exchanger composition on the degree of reduction of palladium, dispersion and catalytic activity of supported metal in the reaction of hydrogen oxidation was investigated.

As supports for palladium-containing catalysts various fibrous ion-exchangers were chosen: sulphocationite FIBAN K-1 in H- and Ba-forms, carboxylic cation-exchanger FIBAN K-4, anion-exchangers FIBAN A-1, FIBAN AK-22-1, FIBAN A-5 and FIBAN A-6 and polyampholyte FIBAN AK-22-B. Monofunctional ion-exchangers (strong acidic sulphocationite FIBAN K-1 and strong basic anionite FIBAN A-1) were synthesised on the basis of polypropylene (PP) with grafted styrenedivinylbenzene copolymer, FIBAN K-4 – on the basis of PP with grafted polyacrylic acid, anionites FIBAN A-1, FIBAN AK-22-1, FIBAN A-5 and FIBAN A-6 and polyampholyte FIBAN AK-22-B – on the basis of polyacrylonitrilic fibers.

Palladium-containing catalysts were prepared by means of ion-exchange under static conditions and at room temperature. Ion-exchange was conducted by treatment of sulphocationites and carboxylic cation-exchangers with aqueous solutions of $[Pd(NH_3)_4]Cl_2$ and by treatment of anionites with muriatic aqueous solutions of $PdCl_2$. Supported palladium was reduced by treatment of ion-exchanged sumples with hydrazine (aqueous solution) or molecular hydrogen. Degree of reduction Pd^{2+} to Pd^o in catalysts (α_{Pd}) was determined according to difference of quantity of ion-exchange palladium in sample before and after reduction measured by means of atomic emission spectroscopy. Metal particles size in reduced samples was measured by means of electron microscopy.

Activity measurements of synthesized catalysts were conducted in a specially designed glass flow type reactor with adjustable height of catalyst layer [1]. The thermocouple could be moved inside the catalytic bed. Volume of the catalyst loading was the same for all experiments – 10 cm^3, volume weight of catalyst – 0,1 g/cm^3, feed rate of the reaction mixture (3 vol. % of H_2 in air) – 125 cm^3/min. Efficiency of reduced palladium catalysts in H_2 oxidation reaction was characterized by the specific activity of Pd^o ($A_{Pd(o)}$) at 70°C.

Table. Physicochemical properties of ion-exchangers and palladium-supported catalysts on their basis. (Palladium loading in samples – 0,3 wt %. The temperature of palladium reduction with 5 wt. % hydrazine solution – 40°C).

№	Ion-exchanger	Functional groups	Exchange capacity, meq/g	W, $g_{H2O}/g_{ion\text{-}exchanger}$	α_{Pd}, %	$A_{Pd(o)}$, cm^3/$g_{Pd(o)}$/s
1	FIBAN K-1	$–SO_3^-H^+$	3,0	1,1	98	3,07
2	FIBAN K-1	$(–SO_3^-)_2Ba^{2+}$	3,0	0,55	96	12,54
3	FIBAN K-4	–COOH	4,5	0,65	97	3,58
4	FIBAN AK-22-B	≡N, =NH –COOH	2,75 2,0	0,65	70	3,0
5	FIBAN AK-22-1	≡N, =NH –COOH	4,5 1,0	0,7	58	15,6
6	FIBAN A-5	$–N(CH_3)_2$, =NH –COOH	3,82 0,65	1,81	49	18,4
7	FIBAN A-6	$(C_3H_5O)(CH_3)_2N^+Cl^-$ $–N(CH_3)_2$	1,96 1,27	1,66	48	28,96
8	FIBAN A-1	$–N^+(CH_3)_3Cl^-$	2,7	0,8	45	21,1

Reduction of $PdCl_4^{2-}$ ions, immobilized on the anionite, is found to proceed more difficult then reduction of $Pd(NH_3)_4^{2+}$ on the cationite, and smaller degree of reduction Pd^{2+} to Pd^o in catalysts on the basis of anionites was observed. Catalysts on the basis of H-forms of cationites FIBAN K-1 and FIBAN K-4 and polyampholyte FIBAN AK-22-B have shown low activity in the reaction of H_2 oxidation. The most active sample of catalyst was prepared on the basis of anionite FIBAN A-6 with high content of strong basic amino-groups. According to electron microscopic studies, reduced palladium present in low-activity catalysts in the form of particles with diameters in the range 3-130 nm, while for samples on the basis of FIBAN A-6 mean particle diameter is 1-4 nm.

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Section 4.

Catalytic technologies in fuel and energy production
– production of hydrogen
– production of environmental friendly fuels
– environmentally friendly engineering

AUTOTHERMAL SORPTION-ENHANCED STEAM REFORMING OF HYDROCABONS WITH SUPERADIABATIC COMBUSTION SORBENT REGENERATION

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Active development of hydrogen-based energy technologies is in a great extent limited today by availability of efficient and low-cost hydrogen production. The most promising technological way in this direction is application of sorption-enhanced catalytic methane steam reforming. This approach, first formulated even in 19-th century [1], has received a lot of attention in modern practice since 1980-s and now is developing extremely fast by numerous research groups worldwide [2-5].

The sorption-enhanced catalytic methane steam reforming concept except usual methane and carbon monoxide steam conversion catalytic reactions, widely applied in conventional technologies

$$CH_4 + H_2O <-> CO + 3\ H_2 \tag{1}$$

$$CO + H_2O <-> CO_2 + H_2 \tag{2}$$

also includes the adsorption of product CO_2 by solid sorbent, e.g. calcium oxide:

$$CaO + CO_2 -> CaCO_3 \tag{3}$$

leading to favorable equilibrium conditions for reactions (1), (2) and to achievement of high yield of high-purity hydrogen in one conversion stage. After saturation of sorption capacity of the sorbent it is necessary to provide its regeneration according to reaction

$$CaCO_3 -> CaO + CO_2 \tag{4}$$

Though the research efforts in this area are very intensive and active, the achieved level of process efficiency is still far from ideal. While performance of basic reaction cycle (reactions 1-3) is well studied and more or less optimized, the source of most complications is sorbent regeneration reaction stage (4). The major attention in current developments is concentrated on application of mixed catalyst-sorbent fixed beds with so called «isothermal» sorbent regeneration, meaning external bed heating during regeneration stage. Such heating approach is characterized with high level of inefficient energy losses. Moreover, efficient and uniform heating of the bed in this case is possible only in reactors with relatively small diameter and this factor limits the scale of approach application or requires unreasonable complication of reformer design. Much more promising, but much less studied, regeneration method is adiabatic or autothermal regeneration, meaning heating of the catalyst-sorbent bed by exothermic reaction performed directly inside the bed [7]. In this case CO_2-sorbent regeneration is performed according to reaction (4) with supply of heat, necessary for regeneration, by oxidation of available combustible substances (say, the same feedstock methane) in the air flow directly in the adiabatic sorbent-catalyst bed:

$$CH_4 + 2O_2 \Rightarrow CO_2 + 2H_2O \tag{5}$$

Both process stages may be performed in a periodical «traveling heat wave» regime and in this case it becomes possible to create at each process stage the axial profiles of catalyst temperature, optimal for performance of next stage. Especially efficient operation mode may be realized by application of counter-current (or reverse flow) operation, when methane/steam and air/fuel mixtures are fed into processor bed in opposite directions.

Notably, the co-current heat wave of combustion reaction (5) at the regeneration stage is superadiabatic, i.e. the maximum temperature in such wave significantly exceeds the adiabatic one and, therefore, the high temperatures required for efficient sorbent regeneration may be obtained with air-methane mixtures with very low methane content.

Such approach will provide fast and efficient sorbent regeneration with minimum heat losses to environment. Application of low-cost and available within the process combustible fuels (such as recycled unused hydrogen from fuel cell or methane from initial natural gas) will result in advantageous economic efficiency of the proposed technology in comparison with existing processes. Application of cheap and simple equipment (adiabatic reactors with fixed beds of sorbent-catalyst, absence of external furnaces and heat supply piping etc.) will make the proposed hydrocarbon fuel processor inexpensive and simple in operation.

The presentation discusses process modelling and pilot tests results, confirming the capability and high efficiency of proposed technological concept.

The research was performed under financial support from Russian Foundation of Fundamental Research, grants No.06-08-00258, 06-08-08089.

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KINETICS & ECOLOGICAL ASPECTS OF THE SYNTHESIS OF ACRYLIC ESTERS ON PTC METHOD

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These investigations have allowed to develop the synthesis of unsaturated ethers (as allyl furfuryl, propargyl furfuryl ethers) and esters (as an esters of acrylic and methacrylic acids), which have wide application in industry for the synthesis of unique polymeric materials [1].

Procedures based on PTC in the substitutions usually excel over traditional methods owing to their simplicity, high yields and quality of final products. This method is especially valuable for reaction with compounds sensitive to water [2].

The offered method for acrylic ester synthesis in comparison with the traditional methods has more advantages: high speed of process, soft condition of reaction allowing to lower of a power expenses, the complete exception of application of hazardous and dangerous organic solvents, by virtue of – it is sharp reduction of air pollution, much smaller volumes of waste water. It should be note that the in offered synthesis of acrylates the alkylating agent – allyl bromide use completely. All of this is devoted to technological problems of the synthesis of ethers in the aspect of protection of an environment.

This reaction was carry out in aqueous phase, there acrylic acid is stable [3]. But, it`s known that reaction systems that lack an aqueous phase are very attractive to chemists. Therefore, we have tried to carry out reaction with smaller amount of water (10N), thus having solved also ecological task. We hope that the proposal synthesis of acrylic esters will give the chance for a choice of optimum variants environmentaly friendly technology by comparison with existing processes.

We carry out also the definition of kinetic characteristics of the synthesis of more interesting monomer – allyl acrylate. The reaction mixture was heated up to necessary temperature, which keep up constant during 1 hour. The tests were selected on the analysis every 10 minutes (fig.). The reaction temperature was varied at the limits of 25-65 °C. Activation energy (E) and K_o graphically determined from Arrhenius coordinates:

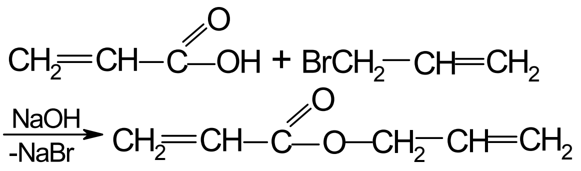
$E = 55625$ kjoule/kmol (13,28 kkal/mol), $k_o = 1{,}922\times107\ m^{3{,}078} / (kmol^{1{,}026}\ min)$.

PP-IV-2

It had been established that the kinetic of reaction acrylic acids with allyl bromide in PTC conditions can described by the equation:

$$-\frac{dC_a}{d\phi} = kC_a^{1,975}C_B^{0,051},$$

Where: $K = 1{,}922 \cdot 10^7 e^{-\frac{55625}{8{,}314 \cdot T}}$ C_A – concentration of acrylic acid, C_B – concentration of allyl bromide



$$CH_2{=}CH{-}C({=}O){-}OH + BrCH_2{-}CH{=}CH_2 \xrightarrow[-NaBr]{NaOH} CH_2{=}CH{-}C({=}O){-}O{-}CH_2{-}CH{=}CH_2$$

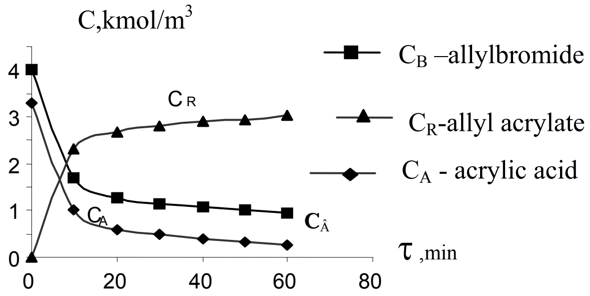


Fig. The kinetic curves of the charge initial substances and accumulation of a product of reaction at the synthesis of allyl acrilate at t=65 °C.

Received kinetic equation allows us to determine optimum parameters of synthesis acrylic esters for account the fixed-bed catalytic reactor.

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ALUMINUM ACTIVATED BY LIQUID ALLOYS AS SOURSE OF PURE HYDROGEN

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Aluminum has an excellent resistance to corrosion. The high corrosion resistance is attributed to the formation of a protective oxide film which under normal circumstantances, if damaged, repairs itself in shot time. Aluminum can only react with water after the passivating aluminum oxide film. Massive corrosion reaction of Al activated by liquid In-Ga alloy which takes place in regular tap water can be utilized to produce hydrogen by aluminum-assisted water split reaction:

$Al + 2H_2O = Al(OOH) + 1.5H_2$ 1.24 l/gThe purpose of this work was to study chemical interaction of the In-Ga eutectic with Al and Al-base alloys using a number of physicochemical characterization techniques with the aim of gaining information about the mechanism of this interaction and the processes responsible for the subsequent disintegration of the material and its dissolution in water with the formation of pure hydrogen.

Intermetallic phase of aluminum alloys ($TiAl_3$ or $CuAl_2$) did not react with water after activation and retained aluminum. The likely reason is that indium is nonreactive with water, while gallium is oxidized by water and is probably then incorporated into the aluminum hydroxide lattice.

Subsequent grain-boundary and volume diffusion of liquid In–Ga into aluminum or its alloys gives rise to the embrittlement of the material and drastically increases its reactivity with water. We carried out tensile strength tests on aluminum plates. The plastic strain of activated aluminum was substantially lower. In that case, the fracture surface was cracked and textured in a direction normal to the loading axis. We also examined the tensile strength of aluminum as a function of activation temperature.

The observed reaction between a liquid In–Ga alloy and aluminum, accompanied by changes in the surface morphology of aluminum, is associated with surface, grain-boundary, and volume diffusion. The relatively fast rate of reaction propagation is primarily due to surface and grain-boundary diffusion. The likely reason is that indium is nonreactive with water, while gallium is oxidized by water and is probably then incorporated into the aluminum hydroxide lattice.

INTERACTION OF ACTIVATED ALUMINIUM WITH WATER: A MECHANISM STUDY

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Hydrogen is considered currently as the most promising energy carrier. The main advantage of hydrogen with respect to conventional hydrocarbon energy carriers consists in the possibility to convert the chemical energy of hydrogen oxidation directly into electric power without any harmful emissions.

The use of hydrogen as the energy carrier imposes some problems caused by high risk of explosion and low volume density. On-site application of the reaction of aluminium oxidation by water to release hydrogen allows principal relief of the problems related to hydrogen transportation and potential application as the energy carrier. In recent years, intensification of R&D on hydrogen production processes based on the reaction of activated aluminium with water is observed both in Russia and abroad.

The present work is aimed at the analysis of the possibility to use activated aluminium, produced by special technology, for the development of hydrogen-generating sources and for realization of new environmentally sound non-waste processes for energy carriers and energy generation and transportation.

Diffusion of aluminium in the In-Ga eutectic melt was studied by ellipsometry method. The measurements were performed in a special Teflon cell.

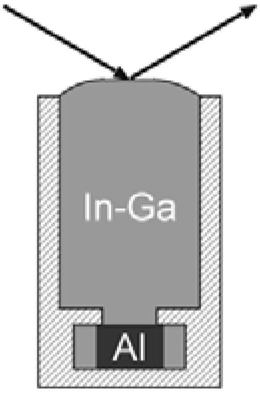

Fig. 1. Schematic diagram of the measuring cell.

Optical characteristics (dependence of the refractive index on the wave length, $N(\lambda)=n(\lambda)-i{\cdot}k$) of the In-Ga melt and growing oxide film were determined by means of a null-ellipsometer «Spectroskan-150». Spectral dependencies of the ellipsometric angles $\Psi(\lambda)$ and

Δ(λ) were measured in a 400-700 nm wave length range. Spectral resolution of the instrument was 2 nm, scanning pitch – 20 nm, incidence angle – 60°. Four-zone averaging measurements were applied.

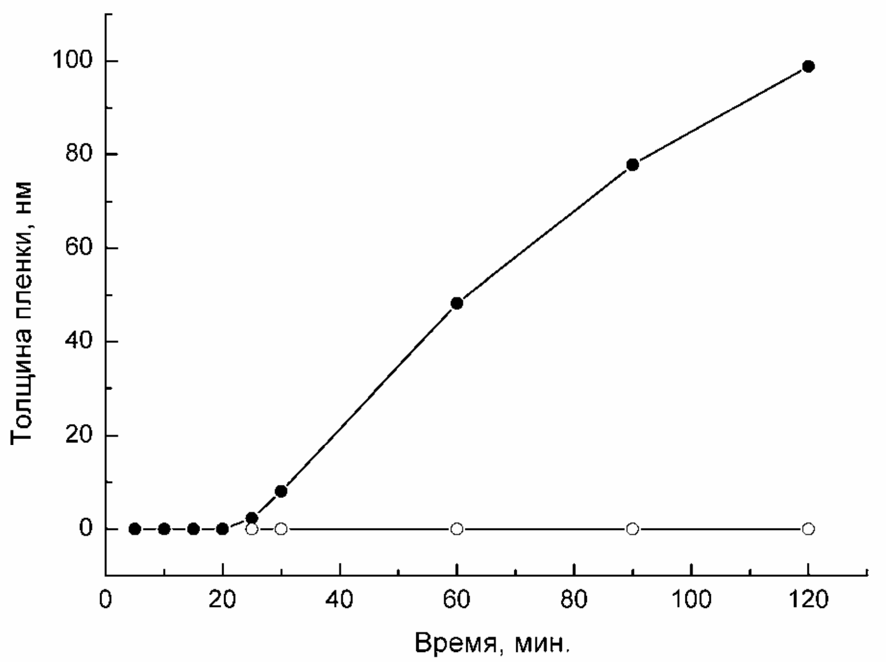

Fig. 2. The dependence of the oxide film thickness on the time of In-Ga melt keeping without Al (white points) and with Al (black points).

As the presented dependencies show, the oxide film forms quite rapidly. The mechanism of aluminium dissolution is most likely determined by the transfer of the dissolved Al in the Al-In-Ga system to the melt-water interface followed by the formation of aluminium hydroxide and hydrogen.

PP-IV-5

ENVIRONMENTALLY FRIENDLY PROCESS FOR PESTICIDES REMOVAL FROM WASTE WATER WITH THE FOLLOWING OXIDATION

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Nowadays the problem of removal of hydrocarbons from wastewater stream is becoming more actual. The concentrations of hydrocarbons, particularly of pesticides in wastewater are increased rapidly due an agricultural development. Some pesticides have been identified as human carcinogens.

Pesticides cannot be removed by conventional gravity separation technology. One of the best method for wastewater treatment from organic pollutants, in particularly pesticides, is an application of inorganic and organic adsorbents [1]. Current treatment processes usually involve also biological degradation or chemical oxidation of the waste organics.

It is known, that adsorbtion of hydrocarbons having p-electronic bonds – aromatic and unsaturated (alkenes), decreases at transition from naphthalene to one-nuclear benzene and alkenes. At last, the adsorbtion of cyclanes (which molecules have no p-electronic bonds) becomes first very small and, secondly, it changes a mark passing adsorbtive-azeotrope point.

In this paper the results of researches on application of natural Armenian zeolites as sorbents of pesticides (malathion, fenitrotion, cipermetrin) are presented.

The adsorptive activities of zeolites at removal of organic substances from tetrachloromethyl solution (CCl_4) were investigated previously [2]. It has appeared that phenol removal is better on H-mordenite.

During this study it was found that the best adsorption of pesticides was achieved on zeolites which have H-sites in continuous-flow stirred-tank reactor (CSTR). The hydrogen bond is the reason of association in water solutions. Such bond is shown during the sorption on adsorbents, containing on a surface hydroxilic groups. The molecules of benzene and toluene can not penetrate in a cavity of zeolites such as 5Å (a cavity makes approximately 4-5Å), but freely will penetrate in a cavity of zeolites such as ZSM (a cavity makes approximately 7.5Å and more). Adsorption of the pesticide molecules of water practically depends on the sizes of the pore and consequently is proportional to a specific surface hydroxyl group.

Oxidation destroys toxics in industrial wastewater by breaking down molecular structures into simpler components organic molecule. The process is based on the discovery that organic compounds will oxidize in water at relatively low temperatures as long as oxygen is present and the proper operating pressure is maintained. The research indicates that pesticides will be oxidized under these conditions.

Here we have solved to conduct processing the adsorbed pesticides on natural zeolites by oxygen, with intention herein after pesticides removal in water ambience straight. The oxidation occurs at the same reactor on the zeolite surface.

Removal of pesticides on zeolites. All experiments were performed at the room temperature. Solutions were constantly stirred for one hour. The removal of pesticides is carried out as follows. The precisely weighed portions of sorbents are brought in to the certain volumes of pesticides in water, which initial concentration vary. The mix is carefully shaken up during 8h. Further test is settled. The quantity of the besieged substance on zeolites is determined by the precipitated organic fraction in the filtered solution by the methods of UV Spectroscopy and Highly Effective Liquid Chromatography (HELCh). The amounts of sorpted pollutants were calculated from the differences between the amount of pollutants added and that remaining in the final equilibrium solution.

Oxidation of pesticides. The zeolite place in flask and add tetrachlormethyl solution of the pesticides under intensive agitation, so, to provide even moistening of adsorbent. The solvent drive away and reactionary mixture subject to drainage. After it's done the full drainage of residual. When cooling till – 75 °C blow out the oxygen with mixture of small amount of ozone. The temperature of the process rises, until – 60 °C. Hereon organic solvent select the products of the oxidation.

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PP-IV-6

THE 5%Ni-2%Au/Al_3CrO_6 SYSTEMS AS A CATALYSTS FOR SYNGAS AND HYDROGEN PRODUCTION

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Introduction

The synthesis gas and hydrogen are produced in CH_4 reforming processes. The partial oxidation of methane - POM, ($CH_4 + ½ O_2 \rightarrow CO + 2H_2$) is suitable reaction to receive syngas with molar ratio H_2:CO = 2, which can be used as a key feedstock for many processes like Fischer-Tropsch synthesis. The hydrogen is a product of oxy-steam reforming of methane-OSR, ($CH_4 + H_2O \rightarrow CO + 3H_2$). The commercial catalysts for CH_4 reforming are usually supported Ni catalysts, which exhibit good catalytic activity. Unfortunately, low stability and low resistance to carbon deposition is observed for nickel based catalysts. The support modification and the use of bimetallic active phase could improve catalytic performance of catalyst in partial oxidation of methane and steam reforming of methane.

The effect of gold addition and the binary oxide support on production of syngas and hydrogen was studied in this work. The influence of reactants composition (CH_4:O_2:H_2O) on hydrogen production was researched. The physicochemical properties of Al_3CrO_6 support and 5%Ni/Al_3CrO_6 and 5%Ni-2%Au/Al_3CrO_6 catalyst were investigated.

Experimental

The binary Al_3CrO_6 support was co-precipitated using appropriate mixture of solution ($Cr(NO_3)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$) and after water removal it was dried and calcined at 400°C/4h/air. The supported catalysts 5%Ni/Al_3CrO_6 and 5%Ni-2%Au/Al_3CrO_6 were prepared by wet impregnation method of precursors: $Ni(NO_3)_2 \cdot 6H_2O$ and $HAuCl_4$. Catalysts were dried and calcined at 400°C/4h/air. POM and OSR activity tests were carried out in a flow quartz reactor in the temperature range 25-950°C with GC analysis. The physicochemical properties were studied by BET, TPR, XRD and ToF-SIMS techniques.

Results and Discussion

The specific surface area was 93m^2/g for Al_3CrO_6 support, 70 m^2/g for 5%Ni/Al_3CrO_6 and 55 m^2/g for 5%Ni-2%Au/Al_3CrO_6 after their calcination in air at 400°C. TPR results for support exhibited the presence of two kind of reducible chromium oxide species in Al_3CrO_6 network which are reduced at 250 and 320°C. The use of Al_3CrO_6 caused the increase of activity in POM reaction in comparison to alumina alone, probably as a result of the increase of oxygen mobility in support network.

The Ni – support and Ni-Au interactions play very important role in the catalytic activity of these catalysts. According to TPR results, two nickel phases were observed: first - well dispersed and easy reducible NiO and second – NiO oxide strongly bonded with support. The high temperature reduction effect was observed for nickel-gold catalyst after its oxidation at 900°Cand it was atributed to reduction hardly reducible Ni-support structure. The spinel structure like $NiCr_2O_4$ was observed also by erlier XRD analysis.

The CH_4 conversion degree for supported Ni and Ni-Au catalysts was abut 100% above 700°C for POM and OSR reactions (Fig.1.). The promoting role of gold was observed during 24 h POM – run reaction in the limitation of carbon deposition on bimetallic catalysts (Table 1). The obtained results suggested the analogical effect for reaction of oxy-steam reforming, where stability of nickel-gold catalysts was higher than nickel catalyst. The increase of steam H_2O addition (0,65; 0,84; 1,2%) to 5% mixture of CH_4 and O_2 increased the production of hydrogen (Fig. 2.).

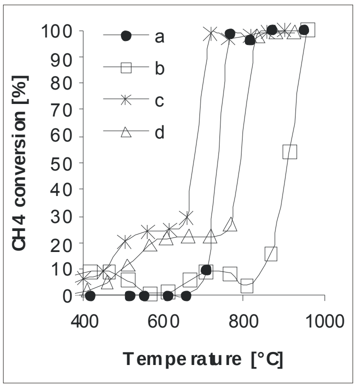

Fig. 1. The CH_4 conversion for $5\%Ni/Al_3CrO_6$ in POM and OSR:a,c and for $5\%Ni\text{-}2\%Au/Al_3CrO_6$ in POM and OSR:b,d.

Catalyst	CH_4 conversion [%] at 900°C	Carbon deposition [%] after 24h POM
5%Ni/Al₃CrO₆	100	12
5%Ni-2%Au/Al₃CrO₆	100	1

Table 1. The CH_4 conversion and carbon deposition in POM reaction.

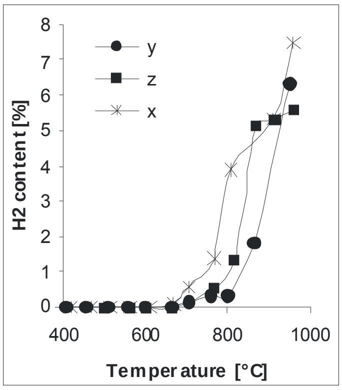

Fig. 2. The H_2 content at 900°C in OSR for H_2O steam: 1,2%-x, 0,84%- y 0,65%-z.

Conclusions

The $5\%Ni/Al_3CrO_6$, $5\%Ni\text{-}2\%Au/Al_3CrO_6$ catalysts are promising for partial oxidation and oxy-steam reforming of methane. The support modification of conventional alumina support improved the activity of catalysts, while the gold addition increased their stability and carbon resistance in both reactions.

PP-IV-7

MESOPOROUS ANODES BASED ON YSZ DOPED WITH TiO_2 OR CeO_2 FOR DIRECT OXIDATION OF HYDROCARBONS IN ELECTROCATALYTIC MEMBRANE REACTOR

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Introduction

Fuel cells with solid oxide (SOFCs) show the most promise for being able to directly utilize hydrocarbon fuels [1]. Developments of intermediate-temperature solid oxide fuel cells require optimization of anode compositions and microstructure. Incorporation of titania or ceria was proved to enhance the performance of conventional anode cermets, consisting of metallic Ni and yttria stabilized zirconia (YSZ). The present study is centered on the synthesis of mesoporous Ni and 8 mol% yttria-stabilized zirconia doped with titania or ceria and utilization of these materials in direct oxidation of hydrocarbons in electrocatalytic membrane reactor. The application of membrane reactors to the hydrocarbon oxidation has attracted considerable attention in the recent years [2,3].

Experimental

Mesoporous $x\%TiO_2$ (CeO_2) - ZrO_2 – $8\%Y_2O_3$ powders with x = 5, 10, 15, 20 and 30 molar content were synthesized by hydrothermal treatment using cetyltrimetyl-ammonium bromide as surfactant, zirconium oxychloride - $ZrOCl_2$, $Y(NO_3)_3$, titanium propoxide as inorganic precursors and urea as the hydrolyzing agent. The molar ratio used was the following: oxide/surfactant/urea = 1: 0, 36: 7. The mixture was loaded into Teflon link steel autoclave and heated 3 days at 100 °C. All the products obtained were filtered, washed and dried at 100 °C and calcinated in a flow of N_2 followed by a flow of air at 550 °C. Ni was supported by impregnation from aqueous Ni $(NO_3)_2$ solution. The obtained materials were characterized by X-ray diffraction, SEM and TEM microscopy, IR, UV-Vis, X-ray Photoelectron and electrochemical impedance (EI) spectroscopy, N_2 adsorption-desorption. Two electrode and three electrode cell configurations were used in conjunction with EIS, in the range of 100 KHz to 10m Hz, to determine the ionic resistivity and its dependence on the TiO_2 and CeO_2 concentration. The electrochemical reactor was constructed from YSZ disc of

25 mm diameter and 2 mm thickness [2]. The Ag paste was applied as cathode metal onto a side of the disc then a mixture of Au paste and catalyst powders were applied as anode-catalyst with onto the other side of the YSZ disc. The reactor was placed in an electric furnace to control the temperature. Catalytic properties were tested in direct oxidation of propane in membrane reactor between 200 and 600 °C.

Results and Discussion

The XRD patterns of all the calcined samples correspond to the fluorite phase of the oxidic systems. Small-angle X-ray diffraction patterns and nitrogen adsorption-desorption isotherms indicate a mesoporous structure of the calcinated powders. The surface stoichiometries reveal a good agreement with the nominal ones from the sample's bulk. All the results show that the improvement of morphology, microstructure and composition of the materials for the SOFC components play an important role for achieving a high cell performance. The value of determined resistivity decreases with increasing content of TiO_2 and CeO_2. The analysis of EI spectra suggests that the higher electrochemical activity may be due to an extension of the reaction zone into the porous zone of mixed conduction caused by the introduction of TiO_2 and CeO_2, leading to the decrease in the specific resistivity. The highest C_3H_8 conversion was obtained, at 600 °C, over Ni/CeO_2-ZrO_2–Y_2O_3 catalyst followed by Ni/TiO_2-ZrO_2–Y_2O_3. Decreasing in Ni loading in the catalysts resulted in a substantial decrease in the activity.

Conclusions

All the results show that the improvement of morphology, microstructure and composition of the materials for the SOFC components play an important role for achieving a cell performance.

Acknowledgements

The financial support by the Romanian Ministry of Education and Research - CEEX-AMCSIT 267 is highly appreciated.

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PP-IV-8

ADVANCED OXIDATION PROCESS FOR THE WATER CONDENSATES RECYCLING IN SHUTTLE ORBITER

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Introduction

During manned missions in space, the accumulated waste waters must be reclaimed on-board spacecraft, otherwise significant higher quantities of hydrogen and oxygen, normally used in the fuel-cells for electrical energy, would be needed to produce high purity water (as a valuable by-product) thereby maintaining the water balance [1].

The humidity condensates from breathing can be collected with condensing heat exchangers. Chemical analysis of this recovered water enlightened, as key pollutants, short chain alcohols, carboxylic acids and other hydrophilic low molecular weight organics which originate as airborne contaminants consequent to human metabolism and material out-gassing.

The used of advanced oxidation processes (AOP) by e.g. electrochemical oxidation have several advantages: low concentration contaminants require the consumption of a comparatively small electric energy, despite the AOPs are not selective and water regeneration is allowed without hardly any use of consumables [2].

Experimental apparatus concept and prototype

Three sequential processes must be combined: electrocatalysis in anodic oxidation, photocatalytic oxidation and electrodialysis. This concept enables several advantages as the generation of excess oxygen at the anode in the electrochemical cell may provide a valuable reactant for the production of OH° radicals in the photocatalytic reactor, whereas the electrodialysis cell, beyond reducing the ions dissolved in water and therefore the overall TOC values, generates a brine solution which can be used as an highly conductive solution in the cathode compartment of the electrochemical cell. The core of the experimental apparatus is the electrochemical cell (Fig. 1), which exploits the high reactivity of the OH° radicals generated at the anode. A complete abatement to carbon dioxide and water can be achieved [3]. In the anodic compartment a simultaneous reaction with oxygen evolution due to water electrolysis can take place as far as the electrode material is kept at sufficiently high overpotentials. This produced oxygen permits through a reaction series to produce other OH° radicals, which continue the oxidation process in the following photocatalytic reactor. The electrolyte solution is fed to the cathode, whereas the condensate water is fed to the anodes. The electrokinetic tests were carried out under a constant direct current with current density of about 5 mA/cm^2. At this point the treated water is rich of oxygen and can be either fed back to the reservoirs or undergo the photocatalytic treatment to reach lower TOC values. The photocatalytic reactor can be operated either as a trickle bed reactor or as a thin film one. In this reactor, the working length of the UV lamp can be regulated. Continuous analysis of the treated solutions was accomplished through suitable probes meanwhile measuring the pH value to get an idea of the acid concentration by oxidation reaction.

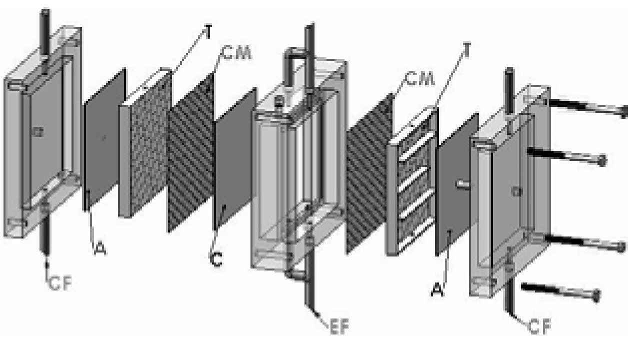

Fig.1. cell exploded scheme. CF: condensate feed; A: anode; T: turbulence promoter; CM: cationic membrane, C: cathode; EF: electrolytic feed.

Results and Discussion

Several runs were performed to determine the TOC concentration, nitrate and nitrite, ammonia and pH and conductivity evolution during the regenerative treatments. The TOC decrease after 1 hr of treatment from 190 ppm to 46 ppm when a pH equal to 3 is reached due to formation of organic acids, which have to be considered as rather refractory to further electrooxidation and thus require photocatalysis.

Several tests have been performed with cationic (CM) and anionic membrane (AM) for a comparison. When the CM is used, ammonia is generated from nitrogen organic contaminants in the acidic environment; it is then converted into ammonium ions, which reach the cathodic compartment via electro-migration ionic, where the local basic lead once again to ammonia formation and removal as gas. Conversely, AMs forced only nitrate and nitrite ions to move towards the cathode side, where they are concentrated. However, the benefit of CMs is somehow reduced by the lower electrical conductivity of the treated solution.

Since NASA potable water TOC specification is below 500 ppb, a second photocatalytic step would be required and possibly favored by the fact that space UV emissions are strong.

Acknowledgements

The financial support of Alenia Space and Regione Piemonte is gratefully acknowledged.

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PP-IV-9

PROCESSING OF POLYMERIC CORD OF USED AUTOMOBILE TYRES BY LOW-TEMPERATURE CATALYTIC PYROLYSIS

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Introduction. Constant increase of cars production favors to accumulation of used automobile tyres, which is the serious ecological problem [1].

During the automobile tyres processing by mechanic crushing the large amount of polymeric cord is accumulated. Mixture of polymeric cord and resin crumb do not destruct for a long time in nature. During the warehousing and burial of this waste the environment is polluted by decomposition products. However, the mixture of polymeric cord and resin crumb is a valuable organic source material, which can be used for the production of liquid and gaseous fuels. Catalytic pyrolysis causes the special interest, as the waste treatment proceeds in closed cycle, which makes the processing to be environmental friendly [2, 3].

Experimental. Method of low-temperature catalytic pyrolysis of polymeric cord of used automobile tyres allows increasing the rate of polymer destruction and thus decreasing the process temperature. The use of the catalysts favors the increase of raw material conversion as well as selectivity of the process.

In this work the catalytic influence of iron sub-group metal chlorides on the process of gaseous products formation during the pyrolysis of polymeric cord was studied. Investigations were conducted at the temperature range of 400 – 600 °C. Catalyst concentration was varied from 1 to 12% (wt.). Obtained data was compared to the analogous non-catalytic process. Major gaseous products of thermal decomposition of mixture of polymeric and resin fractions are hydrogen, cardon mono- and dioxide, methane, ethane, ethylene and propane. Concentrations of all the major components of gaseous pyrolysis products were determined by gas chromatography. Kinetics of specific heat of combustion of gaseous pyrolysis products was also investigated.

Results and discussion. The activity of iron sub-group metal chlorides in the process of low-temperature catalytic pyrolysis with obtaining of combustible gases increases according to the following order: $FeCl_2 > CoCl_2 > NiCl_2$. It is necessary to mention that during the increase of catalytic system activity the loss of calorific value of obtained pyrolysis gas takes place. It is due to the excessive destructing influence of the catalyst, which results to the formation of large amount of low-molecular weight gas – hydrogen. The use of iron subgroup metal chlorides allows increasing the volume of gaseous products in 1.25 – 1.5 folds and the rate of hydrocarbons formation in 1.5 – 2 folds in comparison to non-catalytic process.

Conclusion. The best result was observed while using $CoCl_2$, in the presence of which the rate of hydrocarbons formation increased twice. The volume of prodused gas was also increased up to 25 % in comparison to the non-catalytic process. The conditions of low-temperature catalytic pyrolysis: 450 – 550 °C, cobalt chloride concentration – 1 – 5%.

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PP-IV-10

EFFECT OF SULPHUR ON THE CATALYTIC PARTIAL OXIDATION OF METHANE OVER RHODIUM BASED CATALYSTS

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Introduction

The presence of sulphur containing compounds, naturally occurring in natural gas or added as odorants, can adversely affect the performance of noble metals based catalysts for the partial oxidation of methane to syngas. Until now, studies on the effect of S compounds on the catalytic partial oxidation of hydrocarbons over Rh based catalysts remain scarce and only recently few papers have been published highlighting its detrimental effect, even at very low concentrations [1, 2]. It is therefore of significant importance to investigate the mechanism by which sulphur affects the catalytic performance of catalytic partial oxidation (CPO) and how to increase the tolerance of the catalyst to sulphur poisoning. In this work the effect of SO_2 addition on the CPO of methane was investigated on Rh (1wt.%) catalysts prepared by IW impregnation method on to two different high temperature commercial γ-alumina supports, stabilized either with 10% SiO_2 or 3% La_2O_3 (Sasol).

Experimental

Catalysts were mainly characterized by BET, H_2-TPR and FT-IR spectroscopy. FTIR experiments were performed on powders pressed into self-supporting disk and placed in the IR cell, where temperatures of up to 800 °C can be achieved under reaction mixture. TPD-MS experiments (up to 1000 °C) were also carried out to measure the extent of sulphation after standard treatment with 100 ppm SO_2 in air at 300 °C for 2 h. Catalytic tests on powders were carried out in order to compare the intrinsic activity of samples: a fixed bed flow reactor was run pseudo-isothermally with a very diluted feed mixture $CH_4/O_2/N_2 = 1/0.6/98.4$, at GHSV = 8×10^4 h^{-1} and externally heated from 300 °C to 800 °C at 10 °C/min. To examine the poisoning effects of sulphur, 20/100 ppm SO_2 were added under reaction at 500 °C for 1 hr following transient response; thereafter the light-off was repeated in order to determine the extent of catalyst deactivation and recovery from poisoning. CPO experiments were also performed under autothermal conditions at high temperatures and short contact times in order to reproduce conditions of practical interest, using 600 cpsi monoliths in the shape of disks (L=11 mm, D=17mm). Reactor temperatures were measured by means of thermocouples in the centre of each monolith and in the exit gas. In these experiments the undiluted inlet

CH_4/air mixture (with eventual SO_2 addition), was normally fed at GHSV = 8 × 10^4 h^{-1}. Continuous analysers were employed to measure concentrations of H_2, CO, CO_2 and CH_4 and an on line GC was used for other minor species.

Results

TPD-MS experiments illustrated that the Rh/SiO_2-Al_2O_3 catalyst stores half as much less sulphur than the corresponding Rh/La-Al_2O_3 sample and that most of the stored sulphur is released at a lower temperature as silica type supports do not readily form stable sulphates and are more S tolerant. The initial activity and syngas selectivity was similar for both catalysts. Comparing selectivities for CO, CO_2 and H_2 as a function of temperature it emerges that the first catalytic event is combustion of methane. When almost all the oxygen is consumed hydrogen starts to be formed by both direct partial oxidation and indirect steam reforming of combustion products. The presence of sulphur was found to severely inhibit the steam reforming reaction which is in agreement with latest findings on Rh-Ce coated monoliths [2]. The results of the current study also demonstrate that the support plays a crucial role in the partial oxidation reaction. In the presence of a sulphating support such as La-Al_2O_3 the partial oxidation reaction was much less inhibited than a less sulphating support such as SiO_2-Al_2O_3 (Fig. 1). The sulphating support acts as a sulphur getter and keeps the sulphur away from the active metal sites and this minimises the build-up of S near the active Rh sites where reactions at the metal-support interface take place [3]. Under these experimental conditions Rh on La-Al_2O_3 appeared to be rather immune to sulphur poisoning and the sulphation of the support is implicated as the main cause of deactivation during hydrogen generation. The results were also confirmed by FT-IR spectroscopy.

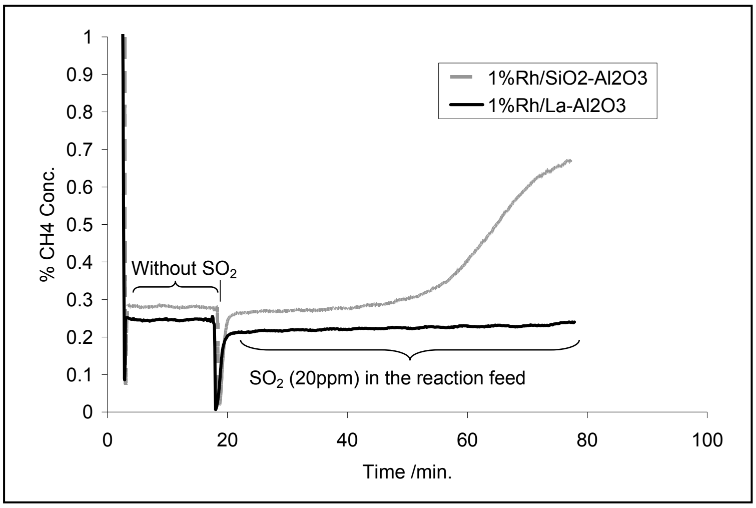

Figure 1: Effect of addition of 20 ppm SO_2 to reaction mixture at 500 °C on CH_4 outlet concentration.

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PP-IV-11

OXIDATIVE CONVERSION OF METHANE AND METHANOL ON STRUCTURED CATALYSTS M/Al_2O_3/CORDIERITE (M=Ni, Cu, Zn)

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Among strategic problems of XXI century at transition from fundamental science to industrial technologies the processes of steam and CO_2 conversion as well as partial oxidation of methane to carbon monoxide and hydrogen take leading positions [1]. In context of hydrogen fuel production reactions of methanol reforming are also in focus [2]. In this work the results of CO_2 conversion of methane and partial oxidation of methanol over structured catalysts – Ni/Al_2O_3- and Cu-ZnO/Al_2O_3- composites, applied on ceramic monoliths of honeycomb structure from synthetic cordierite $2Al_2O_3 \cdot 2MgO \cdot 5SiO_2$ (c), are presented. The structured alumo-nickel catalysts are shown to surpass essentially the conventional granulated ones with respect to productivity (CH_4 5.5, CO_2 7.0 % vol., 6000 h^{-1}):

Catalyst	Temperature of 80 % CH_4 Conversion, °C	Productivity × 10^6	
		Mol $s^{-1}g^{-1}$(cat.)	Mol $s^{-1}g^{-1}$(NiO)
GIAP-18, d=1-2 мм	485	12.96	1.62
8.2%NiO+11.2%Al_2O_3/c	480	38.3	4.8
3.8 % NiO/11.2%Al_2O_3/c	492	30.0	7.8
1.0 % NiO/2.0 % Al_2O_3/c	533	27.6	27.6

The increase in stability of their work is achieved by regulation of the acid-base properties of a surface via introduction of alkali metal (Na, K) oxides. Such an approach causes retardation of carbonization of the surface [3].

In partial oxidation of methanol under stoichiometric conditions (C_{CH3OH}/C_{O2} = 4/2) on Cu-ZnO/Al_2O_3/cordierite catalysts the yield of hydrogen is close to 90 %. A synergetic effect consisting in decrease in selectivity of CO formation on Cu-ZnO-based catalyst, as compared with corresponding samples containing individual components Cu and ZnO, is found:

Cu(ZnO) Percentage, % wt.	CH_3OH Conversion, % /T, °C	Selectivity, %		Yield, %
		H_2	CO	H_2
8 % Cu	79/505	23	26	18
8.5 % Cu, 7.5 % ZnO	→100/505	88	5	88
6 % ZnO	→100/495	89	13	89

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LOW-TEMPERATURE REFORMIG OF ETHANOL ON NICKEL CATALYST

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Hydrogen is a perspective fuel for different kinds of power plants including the devices of low power (1-50 Wt) such as portable fuel cells and charging units to energize notebooks, cell phones, etc. However, the accumulation and storage of molecular hydrogen a nowadays problem connected with safety during use of hydrogen accumulator and a small capacitance to hydrogen. A generation of hydrogen from hydrocarbons, e.g. alcohol (methanol or ethanol) in the process of water steam catalytic conversion is one of the possible ways to overcome these difficulties. In this case ethanol has some obvious advantages over methanol: low price, low toxicity, easy transposition and use and a possibility to produce it from renewable sources (bioethanol). In the present work the process of low-temperature pyrolysis of ethanol on nickel catalyst developed earlier for the production of nanostructures such as nanotubes and nanofibers has been investigated. The peculiarities of pyrolysis of alcohol vapors on the catalyst NiO/SiO in a continuous reactor have been qualitatively studied with the use of IR spectroscopy method. It has been shown that at the temperature above 400 °C the alcohol molecules first decay into acetaldehyde and hydrogen, then to more simple compounds such as methane and carbon monooxide. Further disproportionation of CO resulted in the precipitation of nanofiber carbon on catalytic substrate. It has been established later that within the temperature range 250–350 °C only the first reaction is realized, which makes the process suitable for production of hydrogen from ethanol. The investigations of ethanol reforming were carried out in continuous cylindrical microreactor 70 mm in length with inner diameter 4 mm. The temperature of the process varied within the range 20–400 °C. The rate of the gas carrier (argon) varied within the range 20–100 cm/min. A rectificate with water content 4 mass.% was used as an initial mixture. The analysis was performed by gas chromatographic method in two phases: molecular sieve A5 (detection of gases, 2 m in length) and polysorb (detection of ethanol, water and vinegar aldehyde, 2 m in length). The rectificate was fed by two ways: by gas carrier from bubbler and by peristaltic pump. It has been shown that during the process of ethanol reforming without prior activation of catalyst the catalytic pyrolysis with extraction of hydrogen took place. In this case other possible conversion products such as methane, carbon oxide, etc were not formed. At the temperature of the process 300–350 °C ethanol was practically fully converted. In the case of prior activation of catalyst even at 200 °C aldehyde, carbon oxide and methane were formed. At 350 °C the yield of hydrogen reached its peak.

PP-IV-13

CATALYTIC FLUE GAS CONDITIONING IN ELECTROSTATIC PRECIPITATORS OF COAL-FIRED POWERPLANTS

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Coal-fired power generation capacity in the Russian Federation is approximately 29 GWe, accounting for about 19% of the total electricity generation in the area. Though some decrease of coal consumption in Russia was observed in the 1990's, it is projected that coal's share of fuel usage in the country will be increased due to the fast rise of natural gas prices. Still, with a large amount of the coal used in Russian power plants having an ash content that exceeds 40 wt%, particulate matter (PM) retention in the flue gas is still a rather urgent problem. Almost a half of such power plants are equipped with electrostatic precipitators (ESPs) for control of PM emissions from. The collection efficiency of the ESP partially depends on the electrical resistivity of the fly ash. Ash that is too resistive is difficult to charge and collect, and once collected, is difficult to remove from the ESP collection electrodes. High resistivity ash can also cause «back corona», in which corona is generated on the collection electrodes, further degrading precipitator performance. Estimates indicate that at typical flue gas temperatures of 140-150 °C, the combustion products of about 40% of the coals fired in Russian and ex-USSR power plants possess unfavorable electrophysical properties.

Therefore, there is great value in increasing the efficiency of ESPs by lowering the resistivity of fly ash. This may be accomplished via an ESP upgrade technique known as flue gas conditioning. Injecting small concentrations (2-10 ppm) of SO_3 is a proven way to condition the flue gas for improved ESP performance. The surface absorbed SO_3 (or H_2SO_4) is very electrically conductive and effectively lowers the resistivity of the bulk fly ash. Controlled catalytic oxidation of SO_2 may be a cost-effective upgrade to condition the flue gas for improved ESP performance.

The new generation of highly-efficient catalysts for SO_2 oxidation on the base of fiber-glass supports, using platinum and vanadia as active components, was developed. 19 samples were synthesized for primary selection (Fig. 1).

Fig. 1. Fiber-glass catalysts samples for oxidation of sulfur dioxide.

The tests of the catalytic efficiency of these catalysts has shown that the highest activity is observed for the catalysts with platinum mostly present in ionic form. The fiber-glass catalysts were found to be preliminary characterized with significantly wider temperature window of efficient operation than conventional vanadia catalyst, therefore, fiber-glass catalysts are much more promising for development of new process with minimized SO_2 emissions and much lower capital and operating costs than the similar process on the base of vanadia catalysts, which are applied currently for flue gas conditioning.

On the base of performed comparative technological and technical-economical analysis performed of different variants of the process arrangement for conditioning of flue gases of coal-fired boilers, it was shown that optimal technological decision is the process of sulfur dioxide oxidation in synthetic SO_2-containing stream in a separate reactor with following introduction SO_3-containing flow into the main coal boiler gas duct. Undoubted benefits of this process are: complete independence of the process from flow rate, composition and temperature of the flue gases; possibility to control SO_3 concentration in the flue gases in the wide range; complete absence of dust in the gas flow; possibility to process gases with high SO_2 concentration, providing low gas flow rate and low catalyst loading; absence of limitations for the pressure drop of the catalyst bed.

The research is performed under the financial support from U.S. Environmental Protection Agency via the International Scientific-Technological Center (ISTC grant #3662).

PP-IV-14

RIBBON POROUS NICKEL BASED CATALYSTS FOR PARTIAL OXIDATION OF METHANE TO SYNTHESIS GAS

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At present, the process of catalytic partial oxidation of natural gas is considered to hold much promise for generation of synthesis gas. Partial methane oxidation is an exothermal reaction, thus in order to prevent local overheating of catalysts and to develop mechanically strong catalysts, it is wise to use the metal based catalysts.

In the present work we studied peculiar features of formation of nickel catalysts supported on the ribbon porous nickel with a magnesium oxide precoat and their catalytic properties in the reaction of partial methane oxidation to synthesis gas.

To prepare nickel supported catalysts, ribbon porous nickel (Ni_{rb}) (thickness, 0.1 mm) prepared by rolling ($S_{sp} \sim 0.15$ m^2/g, $V_\Sigma \sim$ cm^3/g, $r_{preval} \sim 5$-100 μm) was used as a support. MgO carrier (5 wt.%) was supported by impregnation with solution $Mg(NO_3)_2$ and subsequent drying and calcination at 550°C in a flow of N_2 or H_2. Nickel (3-5 wt.%) was supported by impregnation with solution $Ni(NO_3)_2$ and subsequent drying and calcination at 450°C in N_2.

The as-prepared catalysts were characterized by the following methods: XRD, low-temperature adsorption of nitrogen and TEM HR in combination with EDX analysis. Catalytic activity in the partial oxidation of natural gas was determined by a flow method (P = 1 atm, T = 800°C, natural gas = 22 vol.%, air =78 vol.%, GHSV = 18750 h^{-1}). Prior to testing the catalysts were reduced at 800°C in H_2 during 1 hour.

It was established that during MgO formation, Ni^{2+}-cations from the support oxide film tend to incorporate into MgO precoat. Nickel is detected by EDX spectra of MgO as spectral lines of weak intensity corresponding to a nickel concentration of ~ 2 at.%.

In the supported nickel catalysts, dispersal nickel particles (3-5 nm) are epitaxially bonded with support MgO, which is evidenced by the Moire picture.

As test reaction lasted 100 hours, both the conversion and composition of the reaction products did not practically change (see Fig.).

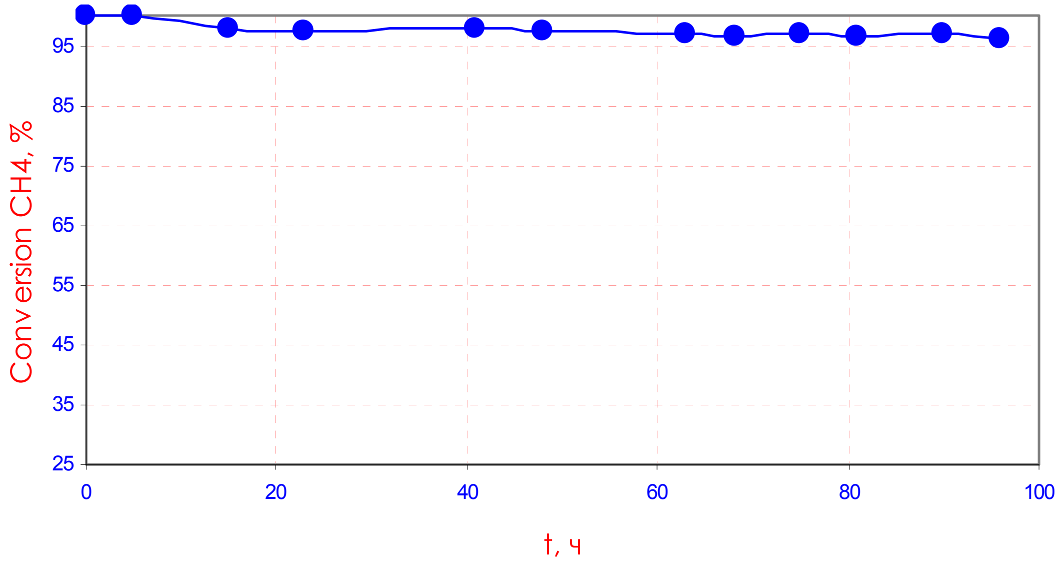

Fig. Effect of the test period on the degree of conversion of methane in the reaction of partial methane oxidation. Catalyst - 5.0% Ni/Nirb + 5.0 % MgO.

Testing of the axial cylindrical monolith, made of the nickel catalyst supported on the ribbon porous nickel and formed by alternate flat and corrugated bands (h = 54 mm, d = 36 mm), showed that in the partial oxidation of natural gas (autothermal mode, 25 vol.% of natural gas in air, τ = 0.04-0.09 sec), the conversion of methane was not lower than 90 %, the yield of synthesis gas was 41-48 %.

Thus, the nickel catalysts supported on the ribbon porous nickel with MgO precoat are active and stable in the partial oxidation of natural gas.

PP-IV-15

ETHANOL CONVERSION TO HYDROGEN CONTAINING GAS OVER COPPER SUPPORTED ON NANOCRYSTALLINE CERIA

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Current trends in modern fuels development are mainly focused on their ecology friendliness. Many countries tighten their legislation in terms of decreasing industrial and transportation exhaust gases emissions. Among the other chemicals hydrogen is the most probable candidate to be the fuel of the new millennium. Its oxidative conversion in recently developed fuel cells lead only to water, which is absolutely safe from ecological viewpoint. The efficiency of fuel cells use is higher than the combustion engine, and operation temperature of fuel cells prohibits the formation of NO_X compounds. However, the chemical methods of hydrogen production always include oxidation of carbon containing compounds, for example water reforming of methane or coal, which produce a lot of CO_2, CO and other unfriendly exhaust gases. The next problem is hydrogen storage, because convenient methods implicate not safe high pressure gas tanks with low hydrogen capacity. The one of possible solution is on board hydrogen generation from methanol or ammonia, but these compounds are toxic and not available everywhere.

Another way is to use ethanol as the source of hydrogen. Ethanol can be produced from biomass and therefore preserve additional CO_2 emissions closing a natural CO_2 cycle. Also, the easiest availability of water ethanol mixtures is an important advantage. There are several types of ethanol conversion: oxidative, steam-oxidative, and steam. All of them lead to CO_2 and H_2 as the main product, but differs in water/oxygen ratio in reactants and also in reaction temperature range. This work deals with steam reforming of ethanol (1), which can produce up to 6 molecules of hydrogen from one ethanol molecule.

$$CH_3CH_2OH + 3\,H_2O \rightarrow 2\,CO_2 + 6\,H_2 \quad (1)$$

However a number of side reactions exist leading to formation of other compounds:

$$CH_3CH_2OH + H_2O \rightarrow 2\,CO + 4\,H_2 \quad (2)$$
$$2\,CH_3CH_2OH + H_2O \rightarrow (CH_3)_2C{=}O + CO_2 + 4\,H_2 \quad (3)$$
$$CH_3CH_2OH \rightarrow C_2H_4 + H_2O \quad (4)$$

The most important are CO production (2), ethanol to acetone conversion (3), ethanol dehydratation (4), and some others leading to formation of acetaldehyde, methane, and other carbon containing compounds. Reaction (1) need high temperatures > 500 °C and the catalysts are ceria supported transition metals. The properties of supported ceria catalysts are very sensitive to the ceria structure, particle sizes, and surface area.

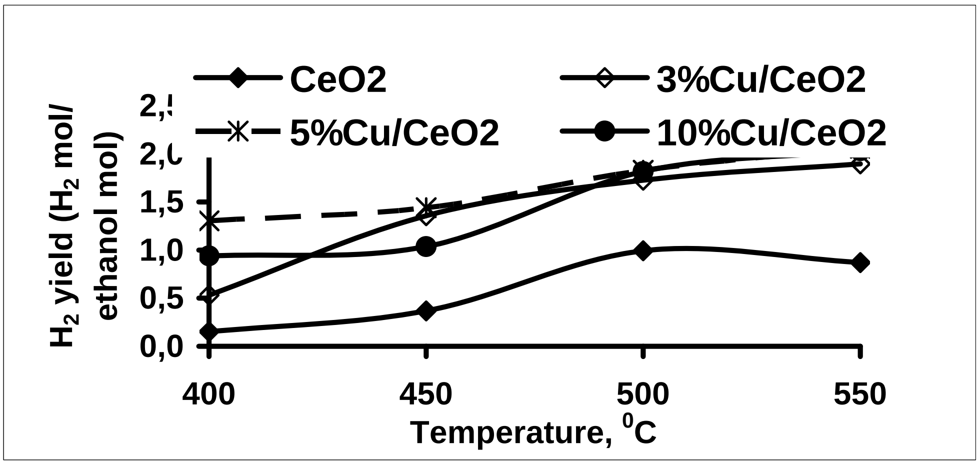

Fig. 1. H_2 yield over Cu/CeO_2 catalyst in steam reforming of ethanol (GHSV = 3000 h^{-1}).

Currently, we have developed the method based on ceria precipitation from water/alcohol mixtures producing near uniform ceria samples with high surface area and particle sizes between 4-8 nm. After incipient wetness impregnation of ceria with corresponding amount of copper nitrate, followed by calcination at 400 °C in air flow, a set of Cu/CeO_2 catalyst with different copper loading was prepared. Their activities in the reaction (1) are presented on fig.1 and table 1. The best activities were achieved on in the range of 1-10% of copper loading with selectivity near 2 moles of hydrogen per one mole of ethanol. Obtained results shows that copper supported on nanocrystalline CeO_2 are promising catalysts for steam ethanol reforming but the further development is needed to improve their selectivity to H_2.

Table 1. The products of ethanol conversion over Cu/CeO_2 at 500 °C (GHSV = 3000 h^{-1}).

Cu loading, % wt	C_2H_5OH conversion, %	H_2 yield[1], %	Product composition, % mol				
			H_2	CO	CO_2	CH_4	C-other[2]
none	70,0	16,6	46,0	0,3	20,3	10,6	22,8
0,5	28,7	11,9	58,0	0,2	22,2	6,4	13,2
1	90,1	29,1	51,5	0,2	23,0	8,4	16,9
3	93,5	28,8	51,0	1,3	22,5	6,9	18,3
5	84,6	30,5	54,0	0,2	23,1	7,3	15,4
10	63,4	30,3	59,0	0,8	22,6	8,1	9,5
20	54,0	16,0	52,0	0,3	22,2	4,9	20,6
30	57,2	18,7	52,0	0,3	22,8	7,9	17,0

[1] The mole ratio of hydrogen formed and theoretical hydrogen yield
[2] including ethane, ethylene, acetaldehyde, acetone

PP-IV-16

A HIGH-EFFICIENT MICROREACTOR WITH Zn/TiO$_2$ CATALYST FOR METHANOL STEAM REFORMING

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Copper containing catalysts is widely used for steam reforming of methanol (SMR) processes because of their low operation temperature (160-250 °C). But these catalysts can lose activity during a rather short operation time depending of the synthesis conditions. Therefore, the improvement of synthesis procedures and development of more stable catalysts of SMR are of prime importance in the design of fuel reformers. Zn/TiO$_2$ catalysts are known to exhibit high catalytic activity in the SMR process, but at temperatures exceeding 350 °C. Thus, at 400-450 °C Zn/TiO$_2$ catalysts exhibited a higher activity than copper catalysts and underwent considerably slower deactivation.

The present work was aimed at elucidating the effect of a type of microchannel plates and methods of Zn/TiO$_2$ catalyst deposition on the kinetics of SMR in a microreactor as well the catalyst deactivation during operation time.

Zn/TiO$_2$ catalyst was synthesized by impregnation of highly dispersed TiO$_2$ –anatase by aqueous solution of Zn(NO$_3$)$_2$ with subsequent drying and calcination at 450 °C. The experiments were performed in a rhombic (34x34x10 mm) stainless steel microreactor with free space volume of 3.6 cm^3, containing microchannel plates (20x30 mm). An input reagent flow was directed to the free trapezoidal microreactor zone to provide a uniform distribution of a gas flow through all channels. The microreactor was heated by an external heat source. Microchannel plates MCP1 and MCP2 were prepared by cold pressing from foamed nickel and copper respectively. The rectangular channels (cross-section 0.15x5 mm, length 20 mm) were formed on each microchannel plate. Microchannel plate MCP3 was prepared from a corrugated brass foil. Triangular channels (height 0.5 mm, width 1.0 mm) were formed by stacking alternate corrugated and flat plates in the microreactor.

Study of Zn/TiO$_2$ catalyst supported on the microchannel plates showed that the catalyst exhibited sufficient activity in the SMR processes and outperformed the known copper catalysts in some cases. The maximal catalyst activity was observed on the foamed copper microchannel plate MCP2. Thus, a microreactor with a total volume of 12 cm^3 at 450 °C and the 80% methanol conversion produced 78.6 l/h of hydrogen. The hydrogen production in the microreactor with the microchannel plates of foamed nickel and corrugated brass foil (MCP1 and MCP3) was 1.6 and 2.4 times respectively lower than that with foamed copper plates (MCP2). Specific hydrogen production (relative to the catalyst mass) for MCP1 and MCP3 was 1.6 and 1.2 times respectively lower than that for MCP2 due to lower catalyst mass in MCP3. Thus, from the practical standpoint, foamed copper is the best material for microchannel plates used in the above microreactor (then comes foamed nickel).

In the high-temperature region (400-450 °C), the SMR process probably goes through hydrolysis of methylformate (the activation energy of the reaction is 132 kJ/mole) and does not depend on the microchannel plate material where a catalyst is deposited. The reaction order α =0.5 does not also depend on the type of microchannel plates. For comparison, the activation energy of the SMR process on the copper catalyst is lower than100 kJ/mole.

Long-term tests showed that stability of Zn/TiO_2 catalyst supported on the different microchannel plates in the SMR process depends on the material of the microchannel plate used. The highest operation stability of the catalyst was observed for the foamed copper microchannel plates. Thus, during a 160-hour continuous operation of a microreactor supplied with the foamed copper microchannel plates, the initial methanol conversion of 80% decreased by 8%. During 500-hour tests, the methanol conversion decreased by 32%. The main reason of the catalyst deactivation is sintering of zinc microparticles which are responsible for the catalyst activity, at that the rate of the catalyst deactivation directly depends on heat conductivity of a material of the microchannel plates. It was shown that activity of the deactivated catalyst can be restored by annealing it in air. An increase in the concentration of water and addition of oxygen in the inlet mixture improves the catalyst activity and reduces its deactivation.

PP-IV-17

DIRECT DECOMPOSITION OF NITROUS OXIDE OVER A K-DOPED Co_3O_4 CATALYST IN THE PRESENCE OF OXYGEN

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1. Introduction

Nitrous oxide (N_2O) has a high global warming potential, 310 times larger than that of CO_2 and contributes to the destruction of the ozone layer in the stratosphere [1]. With increasing concerns about protecting our environment, the catalytic removal of nitrous oxide from exhaust becomes very attractive. We reported that the alkali-promoted Co_3O_4 catalysts have high activities even in the presence of oxygen [2,3]. In the present work, reaction rate and activation energy for N_2O decomposition in the presence of oxygen over a K-doped Co_3O_4 catalyst was examined.

2. Experimental

The catalyst (K/Co = 0.02) was prepared by impregnation of $CoCO_3$ (Nacalai) with a solution of potassium nitrate and subsequent thermal decomposition in air at 400 °C for 4 h. Catalyst tests were carried out in a fixed-bed flow reactor. The catalyst was tabletted, pulverized into 10–22 mesh, and set in the reactor together with 15–20 mesh sea sand. The catalyst bed was heated to 500 °C in a helium gas flow and held at that temperature for 30 min and cooled to 300 °C. Then, the reaction gas composed of 0.25–2 % N_2O, 1–3 % O_2 and He balance was introduced to the catalyst bed at $W/F = 0.019$ g s ml^{-1} (total gas flow = 400 ml min^{-1}). The effluent gases from the reactor were analyzed every 5 min with an on-line micro-gas-chromatograph and data after keeping the reaction temperature for 10 min are given in this paper.

3. Results and discussion

Figure 1 shows the dependence of N_2 formation rate upon partial pressure of N_2O. The N_2 formation rate monotonously increased with increasing the N_2O partial pressure. The reaction order with respect to N_2O concerning the formation of N_2 was calculated to be 0.99–1.07 at 150–250 °C. Arrhenius plots for the measured rate constants are shown in Fig. 2: The activation energy for the reaction was calculated to be 48–54 kJ mol^{-1}, which was much smaller than the values reported for the other catalysts (120 kJ mol^{-1} for ZnO [4]; 190 kJ mol^{-1} for Fe-ZSM-5 [5].) The low activation energy required for direct decomposition of N_2O over the K-doped Co_3O_4 catalyst seems to be one of the reasons for high activity of the catalyst.

As shown in Fig. 3, the N_2 formation rate decreased with increasing oxygen partial pressure. However, the reaction order with respect O_2 was in a range from -0.108 to -0.156, indicating that the inhibitory effect of O_2 in the feed is not strong at the initial stage of the reaction.

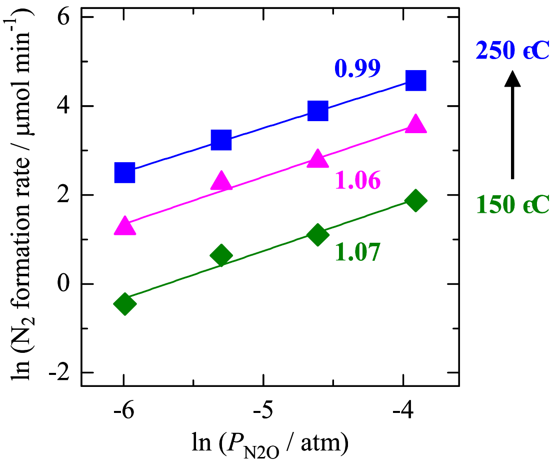

Fig. 1. Dependence of N_2 formation rate on the partial pressure of N_2O at 150–250 °C. Catalyst: K-doped Co_3O_4/sea sand = 1/3 React. conditions: N_2O, 0.25–2 %; O_2, 2 %; He balance; W/F = 0.019 g s mL^{-1}.

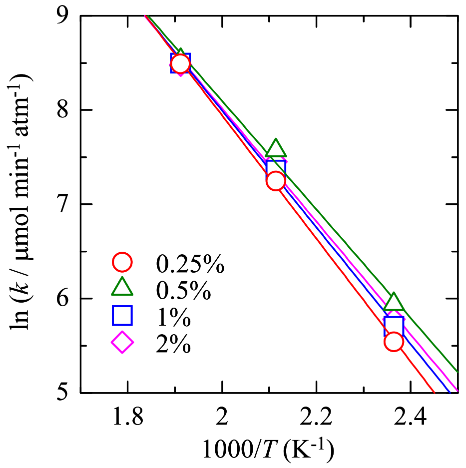

Fig. 2. Arrhenius plots for formation of N_2 by decomposition of N_2O over K-doped Co_3O_4.

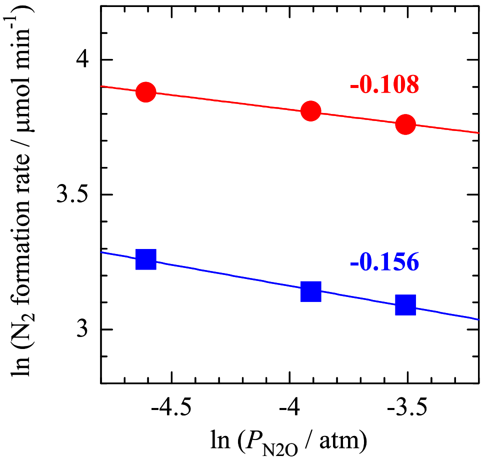

Fig. 3. Dependence of N_2 formation rate on the partial pressure of N_2O at 250–300 °C. Catalyst: K-doped Co_3O_4/sea sand = 1/3 React. conditions: N_2O, 0.5 %; O_2, 1–3 %; He balance; W/F = 0.019 g s mL^{-1}.

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PP-IV-18

NICKEL CATALYSTS BASED ON POROUS NICKEL FOR METHANE STEAM REFORMING TO SYNTHESIS GAS

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The past few decades have seen an intensive development of a new trend of power engineering – fuel cells which provide electrochemical oxidation of hydrogen with oxygen. One of the most preferred methods of hydrogen generation is that steam reforming of methane or other hydrocarbon fuels. Fuel cells exhibit the maximal operation efficiency if the endothermic reaction of methane steam reforming is simultaneously performed with the exothermic reaction of oxidation of exhaust anode gas containing unreacted hydrogen. One way to solve the problem is the development of reactors-heat exchangers conjugated with respect to heat flows of the above reactions. The main structural unit of reactors-heat exchangers is a metallic wall, one side of which is covered by a catalyst of steam methane reforming, the other, by a catalyst of anode gas oxidation [1]. This raises the problem of development of heat-conducting catalysts of steam methane reforming and hydrogen oxidation.

This work was aimed at developing heat-conducting catalysts of steam methane reforming to synthesis gas. We prepared a number of nickel catalysts supported on the plate-like porous metallic nickel with a magnesium oxide precoat and studied their physico-chemical properties and catalytic properties in the above mentioned reaction.

The nickel porous plates (pNi) (thickness 0.5-1 mm) prepared by rolling (S_{sp} ~0.1 m^2/g, V_{Σ} ~ 0.1 cm^3/g, $r_{prevailing}$ 5-30 μm) were used as catalyst support. MgO precoat (5 wt.%) was deposited on nickel plates by impregnation with aqueous solution of $Mg(NO_3)_2$ and subsequent drying and calcination at 550 °C in a flow of N_2 (support I) or H_2 (support II); nickel (5-9 wt.%) was deposited by impregnation with aqueous solution of $Ni(NO_3)_2$ and subsequent drying and calcination at 450 °C in N_2. The prepared catalysts were characterized by XRD, the nitrogen adsorption at low temperatures, mercury porosimetry and electron microscopy along with X-ray spectrum microanalysis. Catalytic activity in the methane steam reforming reaction was determined by the flow-circulating method (750 °C, $H_2O/CH_4=2$, p=1 atm, GHSV 16860 h^{-1}). The samples were reduced at 750 °C in flow of H_2.

According to XRD data, the phase of nickel is presented in metal support, whereas support I also contains phases of NiO and MgO with lattice parameter 4.206 Å, support II contains phases of NiO and MgO with lattice parameter 4.218 Å. It was found that during the formation of MgO the introduction of Ni^{2+}-cations from oxide layer to support MgO takes place. In supports I and II, nickel is detected by EDX spectra of MgO as spectral lines of weak intensity corresponding to a nickel concentration of ~ 2 at.%. In reaction conditions or reduction conditions these Ni^{2+}-cations form dispersal nickel crystals.

The reduced supported catalysts exhibit phases of nickel and solid solution NiO in MgO which disappeared in reaction condition. In the supported nickel catalysts, dispersal nickel particles are epitaxially bonded with support MgO, which is evidenced by the Moire picture.

The conversion value for support MgO I is 52 % and for MgO II - 65 %. The additional deposition of nickel results in the increasing of conversion value. Note that the prepared nickel catalysts on supports I and II are characterized by comparable conversion values.

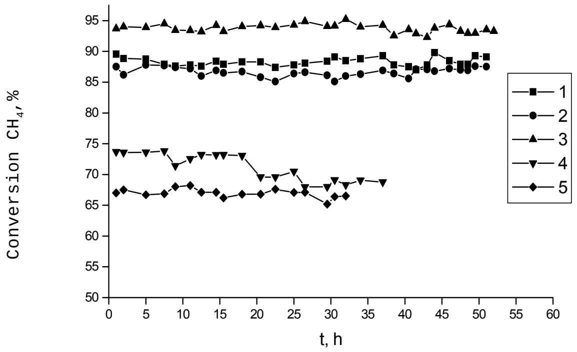

Fig. Influence of reaction time on methane conversion in steam reforming reaction: 1 – 5.0 % Ni/pNi + 5.0 % MgO (I) (plate, V=0.7 cm^3, m=3.29 g); 2 – 5,7 % Ni/pNi + 5.0 % MgO (II) (plate, V=0.7 cm^3, m=3.28 g); 3 – 7,2% Ni/pNi + 5,0% MgOII (plate, m=3.07g, V=0.7 cm^3); 4 – NIAP-18 (fraction 0,25–0,5 mm, m=0,80g); 5 – NIAP-18 (1/2 of grain, m=1,46 g, V=0,7 cm^3).

The catalyst activity was stable during 50 hour tests (Fig.). From TEM it was shown that there are not any carbon deposits in the tested catalyst samples. We suppose that formed from solid solution NiO-MgO or from surface combination dispersal nickel crystals are interacted with support and so they have increased stability to carbon deposition. The fact of interaction between nickel and support is confirmed by TEM HR data which do not show oxide layer in dispersal nickel particles (~20 Å) after additional calcinations (Ar, 550 °C, 2 h).

Thus, the nickel catalysts supported on the plate-like porous nickel with the MgO precoat are characterized by high and stable activity in the reaction of methane steam reforming and resistance to carbonization.

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SELECTION OF FAVOURABLE FEED COMPOSITION OF LIGHT NAPHTHA ISOMERIZATION

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Several national and international organisations are making efforts to decrease harmful effect of expanding traffic [1-3]. In the production of environmentally friendly and human biologically favourable blending components of engine gasoline's isoparaffin fractions having low carbon number (C_5-C_7) are indispensable. They have low sulfur content and they are free from aromatics and olefins; besides, they have high octane number of low sensitivity and comprises of clean burning compounds [1-3]. Hence, the demand for isoparaffin fractions is increasing constantly [3]. The isomerization of light naphtha has the potential to satisfy these quality and quantity requirements. Therefore, isoparaffins and naphthenes are the most favourable gasoline blending components among the groups of hydrocarbon compounds. Availability of naphthenes is strongly limited in gasolines. Their amount depends on the origin of crude oils and can not be increased. In fact, naphthenes – present in gasoline fractions of low octane number – can not be separated economically from other hydrocarbons because of their close boiling points. Therefore, isomerization of light n-paraffin fractions (C_5-C_7) is needed, so the objective of the research work was to investigate catalysts that are applicable for the isomerization of selected light naphtha fractions having different cycloparaffin concentrations. The influence of different feeds on the product composition was also investigated [3-6].

The investigated $Pt/SO_4^{2-}/MO_x$ catalyst, and new generation Pt/H-MOR have different n-hexane isomerizing activity depending on process temperature. n-Hexane fractions of various cycloparaffin content (0.0-15.0 % – Its amount depends on the origin and type of crude oils and separation system.) were used as feeds. Hydrocarbon composition, water and total sulphur content of the feeds and products were determined by standard test methods. The investigation of isomerization over the two different catalysts was carried out at different process conditions. Octane numbers of the products are high, compared to those of the feeds. The increase of octane number was very significant, approximately 25-40 units (liquid product-feed). This is the result of the underneath mentioned effects:

1. Proportionally less isoparaffin hydrocarbons are formed from n-hexane present in the cycloparaffin containing feed.
2. Octane numbers of the mixtures of cyclohexane and methyl cyclopentane are higher than those of isoparaffin mixtures at the investigated reaction temperature.

The yield of the mixture of iso- and cycloparaffins (ip+cp) obtained after separating n-paraffins with 100% efficiency was relatively high (60-75%). The cyclohexane isomerizes to methyl cyclopentane having high octane number. The RON of the mixtures of iso- and cycloparaffins are nearly the same for all products $RON_{ip+cp-feed}$~40-52. Advantages of the low temperature processΔ(79.0-82.5) and are the followings:

- energy-economical operation;
- significant capacity increase can be reached due to the lower n-paraffin recirculation (applying the same amount of catalyst and LHSV), or in case of the same capacity the amount of catalyst is lower which results in cost saving;
- more isoparaffin hydrocarbons (~4-6%) can be produced from a fraction of given amount and composition (raw material saving);
- hydrogen saving conversion, since the rate of hydrocracking reactions is lower as the catalyst is active at medium temperature, thus less hydrogen is
  $C_mH_{2m+2} + C_{n-m}H_{2(n-m)+2} \rightarrow$consumed. Hydrocracking: $C_nH_{2n+2} + H_2$
- product mixture having at least 2-5 units higher octane number can be produced by simple pass over.

Desulphurization of the feedstock and removal of water is not an issue in the process, because the sulphur content of engine gasoline – thus that of the gasoline blending components, as well – has to be reduced below 50 (10) ppm in the European Union from 2005 and it has to be practically water-free, too. Finally the obtained practically benzene-free (<0.05%) products are excellent gasoline blending components.

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PP-IV-20

FORMALDEHYDE FORMATION DURING NON-OXIDATIVE DEHYDROGENATION OF METHANOL

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Formaldehyde is one of important chemicals with annual production of 27 million tonnes, which are used for the synthesis of polymers, resins, paints and explosives. Currently, the most widely used technology for formaldehyde production is the partial oxidation of methanol (1):

$$2\ CH_3OH + O_2 \rightarrow 2\ CH_2{=}O + 2\ H_2O \qquad (1)$$

The main drawback of this technology is water produced during synthesis leading to formalin production instead of pure formaldehyde. Production of pure formaldehyde from formalin needs a complicated distillation procedure which increases its overall cost. The side reactions leading to formic acid are also not favorable from process organization and equipment.

Non-oxidative methanol dehydrogenation (2) gives a mixture of formaldehyde and hydrogen which is easy separable. Moreover, this method also produces hydrogen – clean fuel

$$CH_3OH \rightarrow CH_2{=}O + H_2 \qquad (2)$$

of XXI century, which could be used for heating the rector for formaldehyde production preventing toxic exhausts.

The catalyst based on modified silica (K-1) was developed for this process and tested at various conditions for methanol dehydrogenation. The results are presented in Table 1.

Table 1. Experimental data for formaldehyde production on K-1 catalyst at different reaction conditions

WHSV, h^{-1}	T, C	Catalysts volume, cm^3	N_2, l/min	CH_3OH, ml/min	CH_3OH conversion, %	Yield, %			$CH_2{=}O$ selecti-vity, %
						CH_2O	CO	CH_4	
0,141	900	3	0,326	0,35	85,4	1,8	83,6	~	2,1
0,315	750		0,326	0,335	23,5	4,16	19,34	~	17,7
1,19	900	20	1,4	2,8 +5%H_2O	45,4	12,6	32,8	~	27,7
2,02	900		0,7	2,8	50,5	21,3	29,2	~	42,3
1,59	900		0,7	2,8	48,0	16,8	31,2	~	35,0
2,12	900		1,4	5,6	40,6	11,2	25,9	3,5	27,7

Thermodynamic calculation shows that the desired reaction (2) starts only from 500 °C, but the typical catalysts (sodium-containing solids) performance starts near 900 °C. The current opinion is that active centers of catalysts for non-oxidative methanol to formaldehyde conversion are sodium atoms evaporated from the surface of catalysts. Gaseous state of active particles and gas-phase catalysis leads to extremely high sensitivity of the reaction to large amount of parameters: WHSV, catalysts loading and sodium content, impurities, dilution gas, temperature profile of reactor and even its form.

Using continuous-flow fixed-bed reactor we have achieved conversion value 50% with formaldehyde selectivity near 42 % on catalyst K-1 at 900 °C. Further efforts for improving conversion parameters are in progress and mainly connected with the form of reactor and catalysts loading to prevent further dehydrogenation of formaldehyde with CO formation.

PP-IV-21

PRODUCTION OF HYDROGEN-RICH FUEL GAS BY SHORT CONTACT TIME OXIDATIVE CONVERSION OF METHANE

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Processing of the natural gas is actual at the present moment. Nanosized polymetallic and polyoxide catalysts are developed for catalytic partial oxidation (CPO) of the CH_4 of natural gas into synthesis-gas during last decade /1-3/. It was found the high productivity of mixed Ni-Fe, Ni-Ce, and Ni-Co catalysts /4,5/. Introduction of the second element with variable valence to Ni results in increase of particles dispersity, facilitates its reduction, decreases the temperature of CPO process and promotes the formation of bimetallic clusters. We developed Ni-Cu-Cr catalyst supported on Ce/Al_2O_3. The received data testify that reduced catalyst is capable to carry out the selective oxidation of CH_4 to H_2-containing gas, synthesis-gas at very short contact times and high productivity. The optimal regime for preparation of catalyst by using of XRD, BET, TPR, TPO, TEM and TPD of O_2 and H_2 was detected. It was found that the presence of $NiCu_{3,8}$ (d=2,08; 1.08; 1,27Å) alloy over carrier promotes the formation of H_2-rich fuel gas. During investigation of the influence of space velocity on the process of selective oxidation of 1,4% CH_4 was shown that H_2:CO ratio in product was 2:1. S_{H2} and S_{CO} is very high (99-100%), at τ=3,3-3,64s it is decreased to 97% because of the formation of insignificant quantity of CO_2. It was detected that K_{CH4} is reduced from 81 to 51%, S_{CO} closed 100% and S_{H2} reduced from 100 to 83% at increase of CH_4:O_2 ratio from 2 to 3,75. Maximum α_{CH4}=80,6%, 100% selectivity by CO, H_2 and optimum H_2/CO=2.0 are observed at CH_4:O_2=2. The reduced Ni-Cu-Cr catalyst, supported on promoted by Ce alumina is capable carry out selective oxidation of CH_4 at 1173K with α_{CH4}=100% to synthesis-gas (H_2:CO=2) at very short contact time (2,8-8,0 ms) with high selectivity by CO and H_2.

0,5%Pt-0,5%Ru/2%Ce/Al_2O_3, reduced in H_2 at 1173 K carries out the partial oxidation of CH_4 into synthesis-gas at short contact times (3,27 ms) with high conversion of CH_4 and selectivity by CO and H_2 (close to 100%) due to the presence of Pt and Ru nanoparticles. Increasing of contact time reduced slightly the conversion of CH_4 to 82% and selectivity by CO and H_2. The ratio H_2/CO was close to 2. In our investigation the promoting of Ru by Pt and supporting over stabilised 2%Ce/θ-Al_2O_3 raises the degree of CH_4 conversion up to 100% at short contact times. EM data indicate on formation of Pt^o, Ru^o, Ce_6O_{11}, and $CeAlO_3$ clusters /6/. It is proposed that improvement of reaction parameters over mixed Pt-Ru catalyst on 2%Ce/θ-Al_2O_3 is caused by division of activation functions of reactants: CH_4 – on Pt^o, O_2 – on Ru^o or Ce_6O_{11}.

The prospecting investigations of alkanes conversion to H_2-containing mixtures have allowed showing an opportunity for application of low percentage catalysts on carriers on a base of polyoxometallates and production of sufficiently high yields of H_2. Catalysts with 5%Ni-%5K over Siral-40 or ZSM-5+Al_2O_3 had optimum properties (yield of H_2 – 70-75% at 900°C).

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PP-IV-22

INFLUENCE OF COMPOSITION OF THE SECONDARY CARRIER ON THE BASE OF TRANSITION METALS SUPPORTED ON A BLOCK METAL SCELETON IN REACTION OF OXIDATION OF METHANE

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Now natural gas basically is used in the power and household purposes. A level of chemical processing of natural gas into industrial useful products is very low. Numerous researches on processing of natural gas represent scientific and practical interest as allow receiving valuable chemical compounds. Despite of huge opportunities in conversion of methane researchers and manufacturers show interest to the following processes: direct catalytic oxidation of methane into oxygen-containing products such as formaldehyde, methanol, acetic acid, formic acid, synthesis gas, catalytic dimerization of methane to ethylene.

Synthesis gas is initial raw material for production of many chemical and petrochemical products. It is used in metallurgy for reduction of metals. Natural gas is the main raw material for production of synthesis gas. Steam conversion of natural gas is carried out at high temperature (900 °C). It is power consuming process. Steam conversion of natural gas is the main method for obtaining of synthesis gas. It is more advisable production of synthesis gas by direct oxidation of methane by oxygen of air at 500-700 °C and atmospheric pressure.

We carried out investigation on influence of the composition of secondary carrier on partial oxidation of methane by oxygen of air on such carriers as Cr_2O_3, NiO_2, V_2O_5, Al_2O_3, W_2O_3. Copper and nickel oxides were used as active components of catalysts. Preparation method of catalyst includes the following sages: supporting of secondary carrier on a metal skeleton block, calcination of carrier, impregnation of a surface of secondary carrier by the salts of nickel and copper with subsequent drying and calcination of catalysts. The investigations were carried out at 500-700°C and space velocity $2000h^{-1}$. Reaction products were determined by chromatographically on fluoroplastic column filled by Polysorb-1 processed by apiezone.

It was detected the influence of the composition of secondary carrier on direction of catalytic reaction. Such formaldehyde, methanol, and water were formed on the alumina, vanadium and tungsten oxides. Catalytic surface is covered by carbon and activity of catalyst is sharply decreased after short time. Carbon acids were determined on the catalysts with secondary carrier on the base of titanium oxide at 600 °C with 100% selectivity. Carbon was not found on the surface of catalyst during long time exploitation due to influence of the composition of secondary carrier.

The work was supported by ISTC grant K-1266.

PP-IV-23

PLASMACATALYTIC GAS TREATMENT REACTOR BASED ON FOAM METALS

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Plasmacatalytic reactor based on foam metals is developed for oxidation of hydrocarbons. Technology is based on foam metals catalytic blocks and dielectric low-temperature plasma barrier or surface discharge with use of ceramic coated electrodes.

The paper reports on the construction and operating characteristics of plasmacatalytic reactor based on foam metals. Foam metals and alloys represent a new type of high-porosity permeable cellular structures having unsurpassed porosity, permeability and cohesion. Technology is based on dielectric low-temperature plasma barrier or surface discharge with use of dielectric ceramic layer coated electrodes in contact with foam metal. Cold plasma is stably generated in volume of foam metal with catalytic layers on surface of bridges with barrier and surface discharge mechanism at voltage as low as 2500 V. The plasmacatalytic reactor was powered from special compact frequency inverter at 20000 Hz through a high voltage transformer. The corresponding power density was about 2W per cubic centimeter of discharge volume. Highly effective plasmacatalytic reactor stable working under changing operating conditions and gas compositions. Special emphasis was given to a simple and reliable construction, which was easy to assemble and is based on a new materials. The reactor works with undried gas without additional cooling. Highly permeable structure of foam metal effectively dissipates heat and removes decomposition reactions in a gas stream. Thus the generator can serve as an effective source for chemically active radicals, excited atoms and molecules in plasma gas converting applications. Such plasma-assisted oxidation can be combined with conventional catalytic incineration. The combination of heterogeneous catalysis and low-temperature plasma technologies has allowed to creation compact high-efficiency plasmacatalytic device. Computer simulation of heat-exchange, electric field, flow regime, temperature and pressure is carried out with use of a finite elements method. Results of simulation have allowed to optimize a design and to improve efficiency of reactor.

Acknowledgement

The authors are grateful to Foundation for Assistance to Small Innovative Enterprises (FASIE) for financial support of this work (projects 4043p/4931).

PP-IV-24

ONE-STAGE CATALYTIC CONVERSION OF NATURAL GAS TO LIQUID PRODUCTS

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Natural and associated gas, along with coal, oil and plant debris, has become the major source for the production of organic compounds [1]. Currently, most natural gas is used as fuel; its share in energy consumption is 24% [2]. The potentional value of natural gas is far higher than a mere energy source. Natural gas can substitute for oil in the production of most organic compounds. Here, we report our studies of the catalytic properties of gallium-containing zeolites, intercalated with gallium directly hydrothermal synthesis, in the conversion of natural gas to aromatic hydrocarbons.

Galloaluminosilicates (Ga-AS) with silica ratios (M) from 30 to 80 were prepared by the isomorphic substitution of gallium (III) for silicon (IV) in the zeolite during hydrothermal synthesis, via partially substituting gallium for aluminum ions in the precursor aluminosilica gel. The gallium oxide concentration in the sample was 1.2 or 2.2 wt %. The zeolites synthesized were converted to the H-form by double decationization with a 25% NH_4Cl solution at 90 °C for 2 h; they were dried at 110 °C for 8 h and calcined in air at 550 °C for 6 h.

Natural gas had the following composition, wt %: methane, 81.60; ethane, 6.46; propane, 7.40; butane, 4.04; and pentanes, 0.47. Conversion was carried out on a flow-through setup equipped with a silica glass reactor (14 mm in inner diameter) under the atmospheric pressure at the reaction temperature equal to 500-650 °C and the flow rate (W) equal to 1000 h^{-1}.

Fig. 1 illustration the temperature effect on the product composition of natural gas conversion over the 2.2% Ga-AS (M = 60) catalyst at a gas flow rate of 1000 h^{-1}. The degree of natural gas conversion and aromatic hydrocarbon yield increased with rising temperature to 600 °C; the benzene, naphthalene, and alkylnaphthalene concentrations in the product increased, while the toluene concentration decreased. The highest selectivity of aromatic hydrocarbons formation (71.9%) was achieved on the 2.2% Ga-AS (M = 60) sample at 600 °C. The degree of natural gas conversion was 2.1% higher than for 1.2% Ga-AS (M = 30) sample under the same conditions.

From the data displayed in Fig. 2, one can see that the composition of the zeolite framework and the gallium concentration in the catalyst significantly affected the yield of liquid products. The galloaluminosilicate with M = 60 had the highest catalytic activity in natural gas conversion. The aromatic hydrocarbon yield at 600 °C and 1000 h^{-1} reached 18.7% with a conversion of 26.0%.

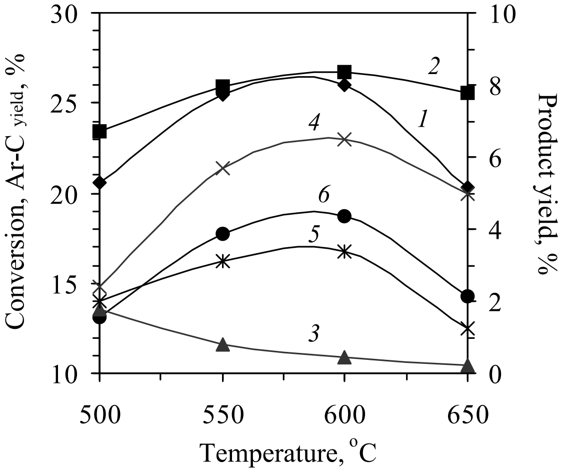

Fig. 1. (*1*) Conversion of natural gas on 2.2% Ga-AS (M = 60) and (*2-6*) yield of (*2*) benzene, (*3*) toluene, (*4*) naphthalene, (*5*) Ar-C_{11-12}, and (*6*) Ar-C_{6+} versus process temperature (W = 1000 h^{-1}).

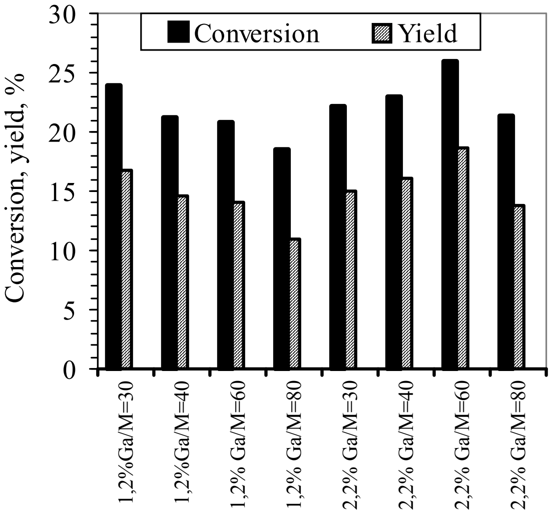

Fig. 2. Natural gas conversion and aromatic hydrocarbon yield over galloaluminosilicates with different silica ratios and different gallium oxide concentrations (T = 600 °C, W = 1000 h^{-1}).

This evolution of the catalytic properties of galloaluminosilicates during natural gas conversion is due to the fact that the aluminum concentration decreases with increasing silica ratio, thus increasing the ratio between the Lewis and Brønsted acid sites on the catalyst. In addition, gallium doping generates new strong aprotic acid sites in the zeolite, while the density of protic acid sites, which are associated with lattice aluminum, decreases.

Thus, galloaluminosilicates have a high catalytic activity in natural gas conversion to aromatic hydrocarbons. The most active catalysts have the silica ratio equal to 30 or 60 and contain 1.2 or 2.2 wt % gallium oxide, respectively. These catalytic systems make it possible to carry out the chemical conversion of gaseous hydrocarbons to liquid products in one stage; thus, the in addition make it possible to produce valuable organic compounds from alternative sources for use in petrochemical and chemical industries.

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THE STUDY OF METHANE DEHYDROAROMATIZATION OVER W/HZSM-5 AND Ni-W/HZSM-5 CATALYSTS

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Natural and associated gases as energy carriers assumed ever greater importance use of energy resources. In accordance with long-term forecasts of the development of the global energetic balance, the global energy supply in the next 10 years will be of resources of organic origin at the increase in the share of natural gas and decrease in the share of oil. In this connection the importance of effective technologies based on secondary processes of the processing of light hydrocarbon raw material will significantly increase.

Catalytic methane conversion into a valuable petrochemical raw material is of considerable interest as an interesting method for natural gas use.

The investigation of the effect of some transition metals on the catalytic properties of zeolite methane dehydroaromatization (DHA) has demonstrated that their activity decreases in the following order: Mo > W > Fe > V > Cr [1-4]. At high temperatures that are necessary for methane DHA process Mo sublimation takes place resulting in the change in the catalyst composition. For this reason in the process of methane conversion W characterized by much higher thermal stability should possess greater advantages over Mo.

The studied catalysts were prepared by mechanical mixing of HZSM-5 zeolite with SiO_2/Al_2O_3 of 40 and nanosized W and Ni powders produced by wire electroexplosion in argon medium. W nanopowder content in the catalyst was varied from 3.0 to 10.0 wt %. The catalyst (1 cm^3) was placed on the quartz grid in the quartz reactor ($d_{reactor}$ = 12 mm) of a flow installation. The sample was heated in the helium flow to 750 °C and kept at this temperature for 20 min. Then the catalyst was treated with methane 99.9% pure at the temperature 750 °C, gas hourly space velocity 1000 h^{-1} and a small excess pressure. The reaction products were sampled by a dosing valve every 40 min and analyzed by gas chromatography.

The activity of zeolite catalysts containing different amounts of W nanopowders was studied in the process of methane DHA. All the studied catalyst samples are characterized by a defined induction period, after which the catalyst activity reaches maximal values and then gradually decreases with reaction time. The 3.0% W/HZSM-5 has a smallest activity in process of methane conversion. The highest value of methane conversion is reached over zeolite containing 8.0% W. In further investigations 8.0 % W/HZSM-5 was used.

Figure demonstrates the results of the study of Ni addition influences to W/HZSM-5. The highest value of methane conversion of 12.4% is achieved on 0.1% Ni-8.0% W/HZSM-5 catalyst after 60 min of reaction. After that it was observed slow decrease of methane conversion.

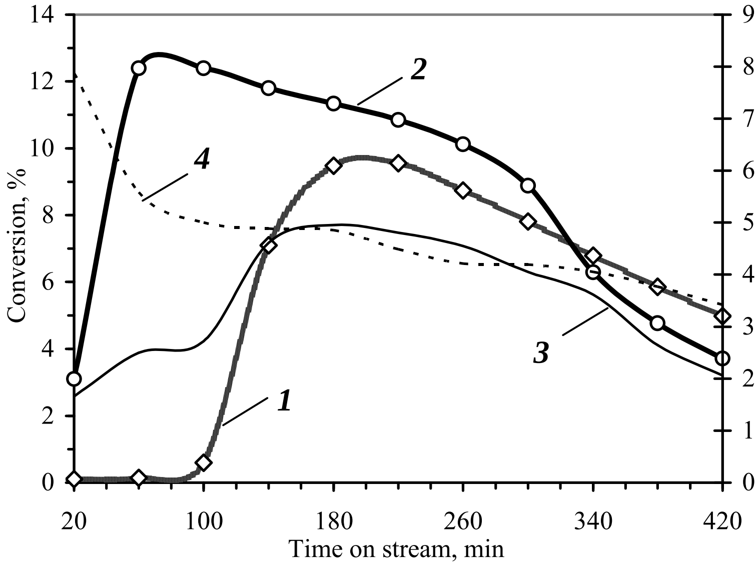

Figure. (*1, 2*) Methane conversion and the yield of (*3, 4*) C_{6+} arenes in the nonoxidative aromatization of methane over 8.0% W/ZSM-5 (*1, 3*) and 8.0% W-0.1% Ni/ZSM-5 (*2, 4*) catalysts at T = 750 °C and GHSV = 1000 h^{-1} as a function of time on stream.

It was found that addition 0.1% Ni to 8.0% W/HZSM-5 catalyst increases methane conversion and decreases of the induction period in the process of methane conversion.

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PP-IV-26

MCM-41-SUPPORTED PdNi CATALYSTS FOR DRY REFORMING OF METHANE

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The reforming of methane with carbon dioxide (dry reforming) offers an alternative way to produce hydrogen, efficient and low cost energy fuel. This reaction has received much interest from environmental point of view because of the possibility to reduce CO_2 and methane emissions as both gases are contributors to the greenhouse effect. Nickel-based catalysts have been proved to be the most suitable catalysts due to their high activity, low price and inherent availability. The addition of small amount of noble metal prevents their fast deactivation caused by coke deposition on the active nickel phase [1]. The aim of the work is to investigate the effect of the Ni/noble metal ratio on the surface and catalytic properties of PdNi/MCM-41 catalysts in the reaction of dry methane reforming.

MCM-41 obtained by hydrothermal synthesis was used as carrier for catalysts. Monometallic Ni/MCM-41 and bimetallic PdNi/MCM-41 with Ni/Si ratio of 0.2, 0.3 and 0.4 were obtained by impregnation technique. Pd content was about 0.6 wt%. The samples were characterized by N_2 isotherms, XRD, TPR, XPS and catalytic test.

The introduction of Pd into monometallic Ni catalyst leads to increase in the conversions of CH_4 and CO_2 (Table 1). The activity of the bimetallic PdNi catalysts depends of the nickel content. Maximum conversions of CH_4 and CO_2 are obtained for sample with ratio Ni/Si=0.3. The H_2/CO ratio is lower than 1, which is an indication of the occurrence of reverse water gas shift reaction. The addition of Pd into Ni/MCM-41 changes the catalytic behavior of the catalysts with time-on-stream. Bimetallic PdNi catalysts are more stable than monometallic Ni catalyst..

XRD analysis showed that the structure of MCM-41 was retained in all supported catalysts. The addition of Pd into Ni containing catalyst provokes a decrease of the NiO size and S_{BET} surface area compared to that of Pd-free Ni sample. PdNi catalyst with Ni/Si ratio of 0.3 possesses the smallest nanosized NiO particles (Table 1).

Table 1. Textural, XPS and catalytic activity characteristics of PdNi/MCM-41 ($T_{r.}$ = 773 K).

Catalysts	S_{BET} (m^2/g)	D_{XRD}, (nm)	BE (eV) Ni2$p_{3/2}$	XPS Ni/Si $_{at}$	CH_4 conv. (%)	CO_2 conv. (%)	H_2/CO
0.3Ni	580.7	25.7	852.3 (20)[a] 855.6 (80)[b]	0.077	16.2	24.5	0.69
0.2PdNi	523.6	13.9	852.3 (23) 855.6 (77)	0.156	22.5	30.5	0.70
0.3PdNi	514.7	12.3	852.3 (46) 855.6 (54)	0.193	35.3	51.1	0.73
0.4PdNi	556.6	20.5	852.3 (46) 855.6 (54)	0.337	29.6	40.6	0.83

[a] the percentages of Ni^0; [b] the percentages of Ni^{2+}

TPR and XPS results indicate the occurrence of some phase-support interaction. The addition of Pd to Ni-containing catalyst favors the reduction of NiO species (Table 1). The reduction degree of NiO increases with increasing the Ni content. 0.3PdNi catalyst shows the highest XPS atomic Ni/Si ratio, which is an indication for the highest dispersion of nickel particles. Favorable distribution of metallic nickel species in accessible sites of the MCM-41 lattice is probably created, which enhances the catalytic activity and stability of 0.3PdNi/MCM-41 catalyst.

The best catalytic performance of PdNi/MCM-41 catalyst with Ni/Si ratio of 0.3 can be attributed to the formation of finely dispersed and easy reducible nanosized Ni species, which are accessible active sites for dry reforming of methane.

Acknowledgements

The financial support of the projects between the National Council of Scientific Research, Spain, and TUBITAK and Bulgarian Academy of Sciences is gratefully acknowledged. The authors acknowledge financial support by project No X-1515/05 from National Science Fund at the Bulgarian Ministry of Education and Science.

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PP-IV-27

IMPROVING THE FLOW SHEET OF CHEMICAL REAGENTS INTRODUCTION IN OIL PRODUCTION SYSTEM

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Modern flow sheet of oil production consists of eleven main links and practically each of them necessarily is either an insertion or influence object of chemical reagent such as demulsifiers, corrosion inhibitors of metal, salt and paraffin accumulation, bactericides, improving oil recovery, injectivity, etc.

The existing scheme differs by its complexity, since nine from thirteen selected aims may be achieved by introduction of chemical reagents in oil well or its bottom zone. The oil well is the place of chemical reagents introduction for achieving all nine indicated purposes. Actually on certain oilfield at one or another development period the introduction of chemical reagents in oil well may solve no more than two or three practical problems.

However, the existing scheme is meant for introducing the reagents of one-aimed assignment that heaped the system. On the other hand, an introducing the one-aimed reagent is not always considered as effective one due to incompatibility of used reagents according their chemical composition.

The polyfunctional reagents`s using can solve the problem.

For the solution of the above mentioned purpose, we propose the more simplified scheme of introducing the polyfunctional aimed reagent in oil production system.

PARTIAL OXIDATION OF METHANE TO C_1-OXYGENATES OVER METALLIC OXIDES CATALYSTS

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Abstract

The catalytic partial oxidation of methane (POM) to C_1-oxygenates (CH_3OH and HCHO) with O_2 and N_2O gaz reactant has been investigated. The reaction was carried out at the atmospheric pressure at temperature range 700-780 °C, using Cu-Fe/Al_2O_3, Cu-Mo/Al_2O_3 oxide catalysts. The conversion and selectivity of reaction products strongly depends on reaction conditions. We have found that methane was transformed to methanol, COx, H_2, H_2O and to formaldehyde. It was found that increasing the temperature increased CH_2O selectivity and decreased CH_3OH selectivity.

The physico-chemical properties of the catalyst were detected before and after reaction using different techniques: N_2 adsorption, SEM, DRX and FTIR.

Keywords: Selective oxidation; Methane; Methanol; Formaldehyde.

PP-IV-29

THE PARTIAL OXIDATION OF CH_4 TO SYNGAS OVER RHODIUM AND NICKEL MODIFIED HEXAALUMINATES

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Introduction

Hydrogen production has been attracting great interest as a future clean fuel particularly for combustion engine and fuel cells. This is why; an efficient and compact hydrogen production process should be developed for such application purposes [1].

The partial oxidation of methane, leading to synthesis gas (H_2 and CO), has received big interests from the perspectives of enhancement of natural gas utilization.

Although precious metals, such as Rh, Pt and Pd, have been employed successfully for this reaction in terms of activity and selectivity, high price and limited availability of these metals makes their widespread industrial application impractical.

Thus, attention has been paid to ferrous transition metals (Ni, Co, Fe) for these goals. Particularly, nickel has been explored as a possible substitute for precious metals because of fast turnover rates, high activity and low cost [2].

However, previous investigations have provided evidence that nickel is more susceptible to coking at elevated temperatures than precious metals are.

And during high temperature reactions sintering and loss of nickel is difficult to avoid in industrial applications. Despite of the foregoing disadvantages, nickel is the metal of interest industrially due to economic reasons.

The use of materials which resist to sintering is though suitable for reactions such as the partial of methane.

Experimental

In the present study, catalysts based on hexaaluminate-type oxides, $\mathbf{BaM_xAl_{12-x}O_{19-\alpha}}$ (M=Rh, Ni; x=0.05-0.1-0.15) were prepared via the **citrate method,** calcined at **1000, 1200 and 1400°C.** The physico-chemical properties of the solids were investigated using X-ray diffraction (XRD), Temperature-programmed reduction (TPR) and BET measurements.

Results

In this work, a homogenous hexaaluminates phase containing uniformly active species in the lattice was obtained; no free nickel or rhodium oxide was observed. The deposits of the active species from the lattice could be formed on the oxide surface by H_2 reduction treatment at an elevated temperature and investigated for partial oxidation of CH_4. The catalysts showed high activity and selectivity and an excellent ability to suppress carbon deposition in the oxidation of methane to syngas for a long time (100h). The catalytic activity of the prepare solids depended weakly on the calcination temperature.

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PP-IV-30

PRODUCTION OF CO-FREE HYDROGEN THROUGH SELECTIVE CATALYTIC DECOMPOSITION OF PROPANE AND N-BUTANE

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Hydrogen is an important clean energy source for use in fuel cell. The most promising fuel cell is considered to be proton exchange membrane fuel cell (PEMFC) [1]. Hydrogen fuel for PEMFC must not contain CO admixtures, because CO is a poison for catalysts which are used in fuel cells.

The most perspective method of production of CO-free hydrogen at present-day is catalytic decomposition of hydrocarbons. The essence of this process is the following: gaseous hydrocarbons in the presence of catalysts which contain metals of the VIII group decompose to mainly H_2, CH_4 and carbon nanofibers. At that a negligible admixtures of hydrocarbons C_2-C_3 [2-3] can appear in products depending on the composition of hydrocarbon feedstock and conditions of process carrying out. It should be noticed that using of hydrocarbons heavier than CH_4 as a feedstock such as C_3H_8 and n-C_4H_{10} allows to carry out the process at much lower temperatures in comparison with CH_4 and also to receive higher H_2 yields per mass unit of a catalyst during its deactivation. Moreover C_3H_8 and n-C_4H_{10} catalytic decomposition under certain conditions allows increasing the selectivity of hydrogen and reducing the concentration of CH_4 in gaseous products almost to the zero-level. This circumstance has a great practical importance due to the fact that H_2 could be easier separated from C_2-C_4 hydrocarbons than CH_4 (e.g. by relatively inexpensive membrane separation).

Four types of high-loaded bimetallic catalysts was used: (70 wt.% Ni–20 wt.% Cu)/Al_2O_3, (63 wt.% Ni–24 wt.% Cu)/SiO_2, (50 wt.% Ni–40 wt.% Cu)/SiO_2 and (40 wt.% Ni–50 wt.% Cu)/SiO_2. Experiments were carried out in quartz flow reactor with a vibrofluidized bed under atmospheric pressure at 500–700°C. Undiluted C_3H_8 and n-C_4H_{10} were used. Hydrocarbon flow of 100 $L \cdot h^{-1}$ per 1 gram of catalyst was maintained by Mass-Flow controller.

Experimental investigations have shown that the (50 wt.% Ni–40 wt.% Cu)/SiO_2 catalyst exhibited the best activity and selectivity. At 600°C the catalyst provides production of mixture with more than 30 vol.% of hydrogen concentration (see Fig. 1).

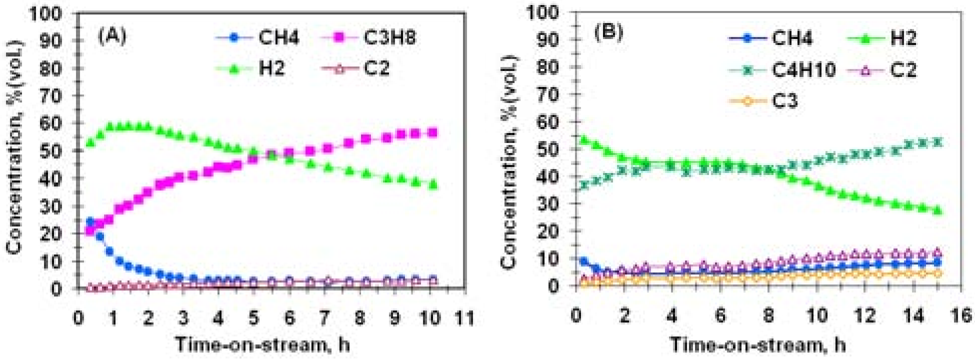

Fig. 1. Products distribution in the process of propane (A) and butane (B) decomposition on (50 wt.% Ni–40 wt.% Cu)/SiO_2 catalyst. T=600°C, G=100 L·h^{-1}·g^{-1}.

Thus the H_2:CH_4 ratio in the reaction products is more than 10:1 during more than 10 h proceeds. After removal of C_2-C_4 hydrocarbons from reaction products () the CO_x-free mixture of hydrogen and methane containing more than 90 vol.% of hydrogen can be obtained. This mixture is suitable for PEMFC as fuel. These results were used as basis for development of the new technology of conversion of liquefied hydrocarbons into hydrogen for PEMFC and nanofibrous carbons (see the schematic diagram in Fig. 2).

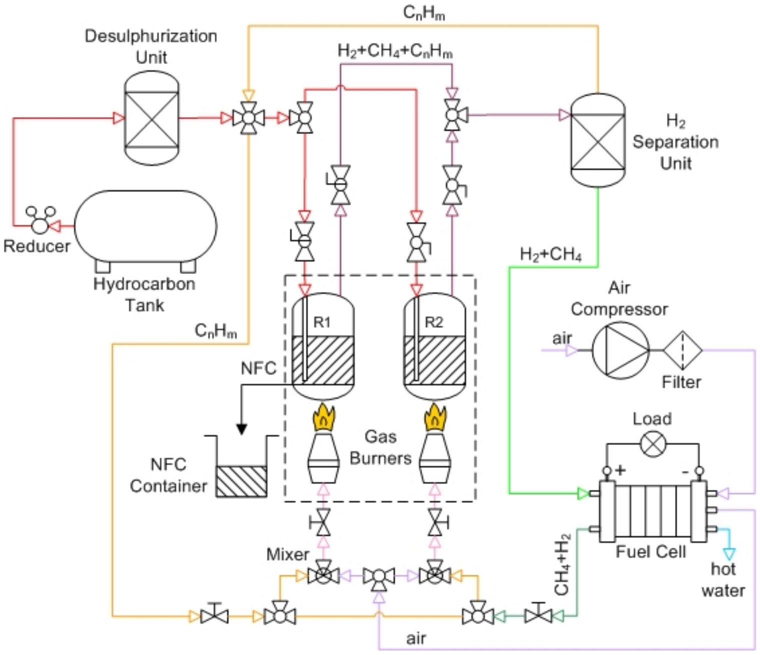

Fig. 2. The schematic diagram of C_nH_m decomposition system for the production of highly concentrated hydrogen for PEMFC and NFC.

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PP-IV-31

PHOTOCATALYTICAL ACTIVITY OF HEAT-RESISTANT TITANIUM DIOXIDE ALLOYED WITH ANION IMPURITIES

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It is known that photocatalytical systems on the basis of TiO_2 are capable, when exposed to UV radiation, of providing an environmentally friendly, reagentless decomposition of organic and bacterial contamination of air in flow-type reactors. For effluent purification, especially in regions with fairly intense daylight illumination, more promising are accumulation tanks with periodically regenerated photocatalyst [1-3].

The conventional photocatalyst applied worldwide is TiO_2 of P25 brand produced by Degussa. As is current practice, the electric conductivity and, consequently, photocatalytic activity (PCA), are increased by alloying TiO_2 with donor substitutional impurities. In P25, this impurity is OH^- whose content, proceeding from loss on ignition, corresponds to a concentration of about $7.8\cdot10^{20}$ cm^{-3}, which exceeds conventional concentrations by an order of magnitude. However, in P25 they are distributed unevenly since it contains 10-20% of rutile. It can be surmised that the rutile PCA is not maximally possible.

The work aims at creating effective and thermally stable photocatalysts on the basis of nano-size powders alloyed with TiO_2 anion impurities.

The samples were obtained by low-temperature hydrolysis of titanium salts in ammonia water containing weighed amounts of F^- or PO_4^{3-} anions. Thermal treatment was carried out at 60-1150 °C. The resulting samples were characterized relatively unalloyed ones (Cl) by BET, XPA and SEM microscopy. Their PCA was assessed by the level of degradation of brightly-red ferroine (FEK-56 PM) reduced in daylight.

The even distribution of alloying ions in the resulting anatase (XPA) in quantities of $1\div7\cdot10^{20}$ $at\cdot cm^{-3}$ sustains a developed surface (250-50 $m^2\cdot g^{-1}$) of the alloyed samples up to the calcination temperature of 700-900 °C.

The PCA of alloyed TiO_2 increases in the impurity series Cl^-, PO_4^{3-} and F^-, being complexly affected both by impurity content and treatment temperature. As shown by SEM, the decisive effect on the forming morphology is that of the nature of the anion. The F-surface of the samples is homomorphous and highly dispersive up to the temperature of rutilization. In the region of 400-500 °C the PCA diminishes probably due to restructuring of fluorinated anatase (according to XPA). The PCA of F^- and PO_4^{3-} modified TiO_2 did not change in the course of 50 hours of cyclic testing. The PCA of the TiO_2 samples synthesized is higher than that of Degussa-produced P25.

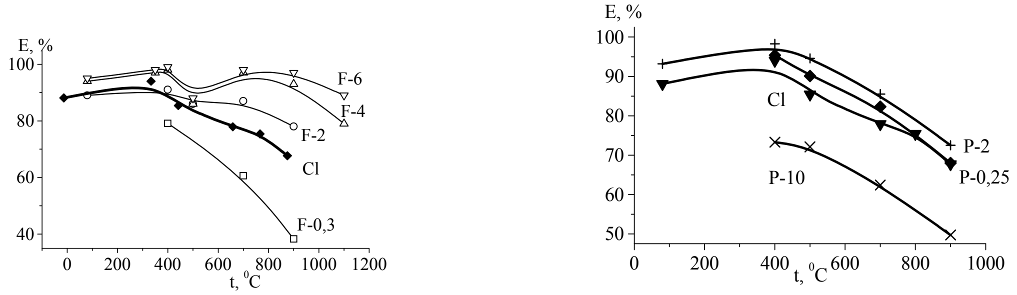

Fig. 1. Relationship between PCA (E, %) of F^- and PO_4^{3-}-alloyed TiO_2 powders and temperature (t, °C) and alloying ions concentration.

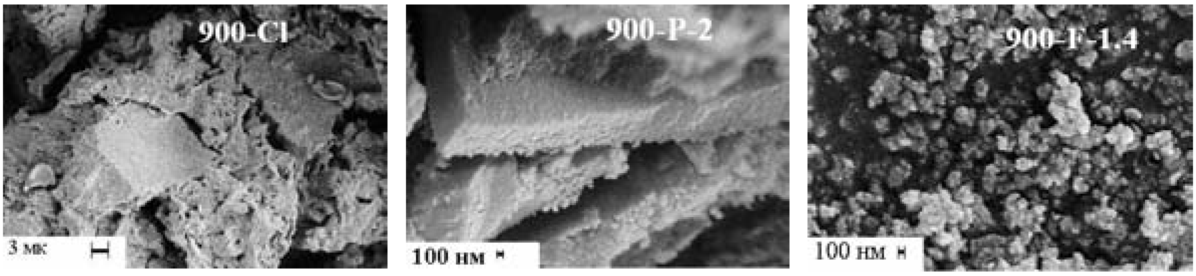

Fig. 2. Morphology of alloyed TiO_2 samples calcined at 900 °C.

The developed materials are intended for photocatalytical purification of effluents from cyanic compounds (gold-mining industry), organic and bacterial contamination (organic synthesis, cattle-farm and municipal sewage), as heat-resistant catalysts in organic synthesis and photocatalytic decomposition of water by using radioactive radiation.

The work has been performed with the financial support of the Russian Foundation for Fundamental Research (project № 06-08-00154-a).

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PP-IV-32

NEW ELECTRODE MATERIALS FOR ELECTROLYTIC HYDROGEN PRODUCTION

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One of the perspective and ecology-safety methods of hydrogen production is the water solution electrolysis having such advantages as using both available and inexhaustible raw material – water as well as output product high purity. At present in the industry to obtain hydrogen the water-alkaline electrolysis is utilized that involves steel cathodes and steel coated with nickel anodes, but electric energy consumption is still significant and requires the decrease. So electrolytic hydrogen production development consists in its cost price reduction, particularly by means of electrolyzer voltage diminution. As a way to solve such a problem is to design new electrodes having hydrogen evolution low overvoltage. Coatings by Fe-Co, Ni-W, Co-W alloys and $Fe_xO_y{\cdot}Co_mO_n$ mixed oxides can be used as effective and nonprecious electrode materials satisfying these requirements. Therefore the aim of the work is to explore the possibility and to ground the expediency of their application in electrolytic hydrogen production to low electrolyzer voltage and to rise the efficiency and the profitability of the process.

The electrolysis has been carried out in 1.5 M KOH solution. As work electrodes served sheets (square 1 cm^2) of nickel, iron, 0.8XH9T steel (in the sequel – steel) and coatings of Fe-Co with cobalt weight portion ω(Co)=20 % (in the sequel – Fe-Co20), Ni-W and Co-W with varied tungsten content ω(W) (in the sequel – the element weight portion is indicated by number). Fe-Co alloy has been electrodeposited from the sulphamate electrolyte in stationary mode, Ni-W and Co-W – from the citrate solution in pulse one. The voltage measurements have been done using B7-35 voltmeter; electrode’s potential values are given comparatively the hydrogen scale.

The electrolyzer voltage U analysis when current density being j=200 A/m^2 (figure) for different electrode pairs shows that for traditional materials it is the highest one among the examined pairs and amounts 2.14…2.16 V (1 and 2 variants). Light U decrease is observed for electrochemically synthesized Ni-W29/Ni, Fe-Co20/Ni and Fe-Co20/Steel coating pairs (3, 4 and 5 variants): 2.1 V, 1.99 V and 1.96 V respectively. Essential voltage decline takes place for the Fe-Co20/Fe-Co20 and Co-W40/Steel pairs: U equals 1.83 V and 1.79 V properly (6 and 7 variants). The electrolyzer voltage becomes minimal among testing materials when electrodes with mixed oxide coating are examined. Thus in the case of $Fe_xO_y \cdot Co_mO_n/Fe_xO_y \cdot Co_mO_n$ pair it amounts 1.77 V only, that is almost on 0.4 V or 20 % lower in comparison with the traditional electrode material's voltage value (variant 8).

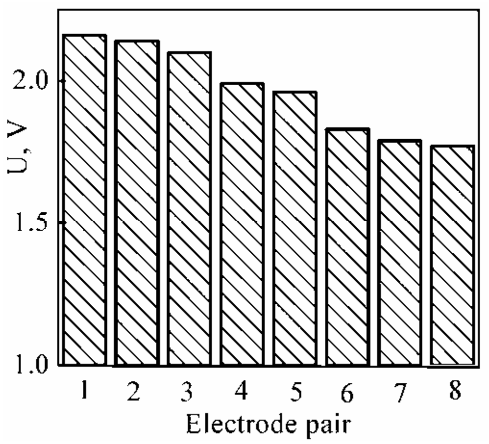

Figure. Electrolyzer voltage for electrode pairs of composition (cathode/anode):
1. Steel/Steel; 2. Ni/Ni; 3. Ni-W29/Ni;
4. Fe-Co20/Ni; 5. Fe-Co20/Steel;
6. Fe-Co20/Fe-Co20; 7. Co-W40/Steel;
8. $Fe_xO_y \cdot Co_mO_n/Fe_xO_y \cdot Co_mO_n$

Such an energy-saving effect is achieved due to the hydrogen evolution overvoltage decline for the Fe-Co20/Fe-Co20 pair and the oxygen one – for the Co-W40/Steel and $Fe_xO_y \cdot Co_mO_n/Fe_xO_y \cdot Co_mO_n$ pairs.

Electrolytic Fe-Co, Ni-W and Co-W alloy coating corrosion resistance investigation has proved these materials can be referred to resistant group of metals and alloys as far as in alkaline environment (pH 11) their corrosion deep indexes does not exceed 0.07 mm/hear. Such a property together with the low electrolyzer voltage value allows recommending synthesized coatings as electrode materials for hydrogen production by means of water-alkaline electrolysis.

PP-IV-33

THE CATALYTIC HYDROGENATION OF COAL WITH ADDITIVES OF WIDE FRACTION OF COAL PITCH

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Nowadays works on processing coals to obtain liquid synthetic fuel by destructive hydrogenation method is widely spread. According to this search of effective technologies of chemical processing heavy and hard hydrocarbon raw-material is actual. The aim of the nesearch was studying processes of the catalytic hydrogenation of coal with catalytic additives. As a hydrogen processes don a wide fraction of coal pitch from Shubarkol coalfield's (Kazakhstan) coals was used in half-cocking process. Before carrying out the catalytic hydrogenation the coal pitch was mechanochemically processed in cavitation-wave field.

By the obtained data we can talk about high conversion degree of organic mass of coal and output of liquid products of coal: yield of fraction until 300°C is 60,4%, hydrogenate – 40,5%.

Pyrite is an active catalyst, stechiometric pyrrotine is a working state of iron-sulfide catalyst in the process of hydrogenation and as a result of reaction with molecular hydrogen atomic hydrogen is generated. However in /1-2/ works it is shown that iron sulfate is more active and surface sulfate $Fe_2O_3[SO_4^{2-}]$ that is formed by oxidation of sulfide is active site of catalyst on the base of iron in coal hydrogenation processes. Thus, high activity of catalysts is also explained by formation of iron complex $Fe_2O_3[SO_4^{2-}]$. Formation of given complex acting as an active catalyst it is determined that with the help of electronic microscopy.

Thus, comparative analysis of data on process of coal hydrogenation shows that chosen fraction of coal pitch by donor ability can be compared with traditional donor of hydrogen – tetraline. Also, it is determined that possibility of using new bifunctional catalysts for coal hydrogenation and wide fraction of coal pitch which have high selectivity to output of light and middle fraction (300°C) with low amount of polycyclic hydrocarbons.

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PHOTOCATALYTIC WATER SPLITTING WITH HYDROGEN EVOLUTION IN Ce^{3+}/Ce^{4+} SYSTEMS

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Hydrogen as environmental friendly and high-energy fuel has attracted attention all over the world for the last decade. Photocatalytic emission of hydrogen from water solution of organic compounds is a very promising and interesting method of hydrogen obtaining. Quantum efficiency of hydrogen emission per one electron can exceed 10% over photocatalyst platinized titania. Unfortunately we can produce only mixture of hydrogen and carbon dioxide using organic donors. It is more profitable for pure hydrogen production to use inorganic donors, for example Ce^{3+} ions. The use of the two-step photocatalytic and photochemical splitting of water to oxygen and hydrogen using semiconducting metal oxides and system Ce^{3+}/Ce^{4+} is considered imperative because of its promising application in solar energy conversion systems [1]. In our work, we used solution of $Ce_2(SO_4)_3$ for hydrogen production and solution of $Ce(SO_4)_2$ for photocatalytic oxygen production. Bare and platinized titania was used as a photocatalyst.

Photocatalytic hydrogen and oxygen emission from $Ce_2(SO_4)_3$ and $Ce(SO_4)_2$ solution was carried out by the following method. Water suspension with catalyst and the initial compound was placed in a sealed thermostated reactor under argon atmosphere and illuminated by a 1000-W high-pressure mercury lamp under continuous stirring. The concentration of $Ce_2(SO_4)_3$ or $Ce(SO_4)_2$ was varied from 1 to 2 mM, catalyst concentration was 0.75 g/L, temperature 20 °C. Concentration of hydrogen and oxygen was measured by means of a gas chromatograph LChM-8, that of Ce^{3+} and Ce^{4+} by means of Lambda 35 Perkin-Elmer UV/Vis-spectrometer. Bare and platinized commercial TiO_2 Degussa P25 and Hombifine N, and self-synthesized rutile were used as catalysts. Ruthile was synthesized by Degussa P25 calcination at 950 °C (R1) and by hydrolysis of titanium tetraisopropoxide (TTIP) in 1M HCl solution with calcination at 350 °C (R2). Noble metals were deposited by soft chemical reduction (SCR) and photodeposition (PD) techniques.

We have carried out experiments for oxygen production from water solution of $Ce(SO_4)_2$. Fig. 1 shows the initial rate of oxygen production for six catalysts.

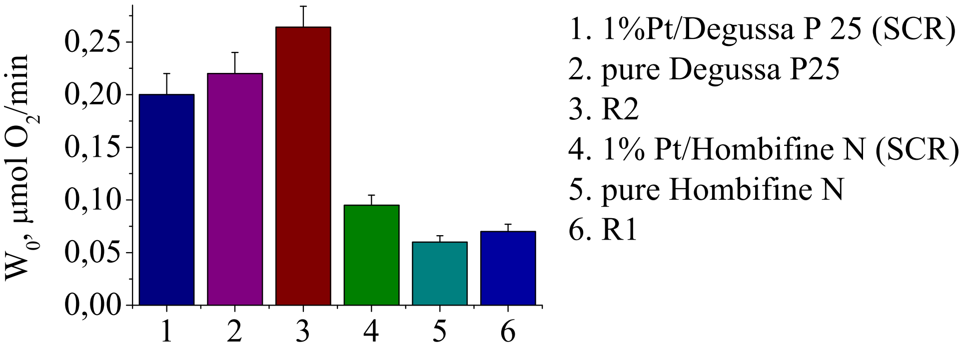

Fig. 1. The initial rate of oxygen production over different catalysts.

One can see that the best catalyst is rutile synthesized by TTIP hydrolysis in hydrochloric acid solution. This catalyst consists of rutile, which is the best phase of TiO_2 for photocatalytic oxygen production [2], and has quite high surface area (~100 m^2/g) due to low temperature of calcination. Pure and platinized Degussa P25, which consists of two phases – anatase and rutile – show a very high activity, too. The activity of pure rutile R1 is very low likely due to the very low specific surface area (~5 m^2/g). Small amount of hydrogen was detected in the case of platinized specimens. So rutile (R2) and pure Degussa P25 are the best photocatalysts for individual oxygen production.

Hydrogen can evolve only on platinized titania [3] so only platinized Degussa P25 and Hombifine N were used for photocatalytic hydrogen production. The hydrogen emission rate on 1%Pt/P25 (SCR) was 0,01 µmol/min. It exceeds that in the case of 1%Pt/Hombifinene N by a factor of three. The rate of hydrogen evolution for 1%Pt/P25 (PD) is lower than for 1%Pt/P25 (SCR) and it is equal to 0,0081 µmol/min, despite many researchers in the field suppose that the photodeposition (PD) of platinum is preferred. Thus, using self synthesized rutile and platinized commercial Degussa P25 we can produce oxygen and hydrogen from water solution of ceric and cerious salts, respectively. Combining two photocatalytic reactors and enter changing the reaction solutions of Ce^{3+} to Ce^{4+} we manage to obtain a cycle for photocatalytic water splitting.

Acknowledgements

The authors want to acknowledge NATO grant SfP-981461 and ISTC grant 3305.

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Section 5.

Catalytic processing of renewable sources: fuel, energy, chemicals

PP-V-1

INFLUENCE OF ICE ON MEAs OF PEM-FCs

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PEM-FCs are being recognised to be as one of the best candidates as pollution-free and energy-saving power sources for electric or hybrid vehicles because of their high energy conversion efficiency (~50%) and zero or nearly zero emissions. At present, significant introduction of PEM-FCs is limited by their cost, their behaviour in sub-freezing conditions, the unavailability of an H_2 distribution infrastructure and the rather low amounts of H_2 gas that can be safely stored on board vehicles. The start-up and stationary behaviour of PEM-FCs below 0°C is one of the most challenging tasks to be solved before commercialisation: freezing of water inside the PEM-FC could form ice layers in the electrodes and in the gas diffusion layer (GDL). Therefore the cell reaction is limited or even inhibited. The automotive industry started to develop solutions to reduce the start-up time of FC systems: the strategies varied from H_2 catalytic combustion on the electrode catalyst to fuel starvation or external stack heating to increase the stack temperature [1].

This study investigates the phenomena of water freezing below the freezing point in PEM-FCs. In particular, the analysis was focused on the effects of ice into the MEA, as mechanical stress, and the decay of the polarization curve. Such an effect was investigated on a single cell PEM-FC using a 5 cm^2 MEA from Electrochem (Nafion membrane, catalysed with 20% wt Pt 1.0 $mg \cdot cm^{-2}$ supported on Vulcan XC-72R Carbon Black) with carbon paper as GDL. The MEAs, in both hydrated and de-hydrated status, were conditioned for 48 h at -10°C by placing them into a thermostatic chamber (Angelantoni UC 600-70 model), to assure the complete ice formation within the various MEA layers. After re-conditioning at

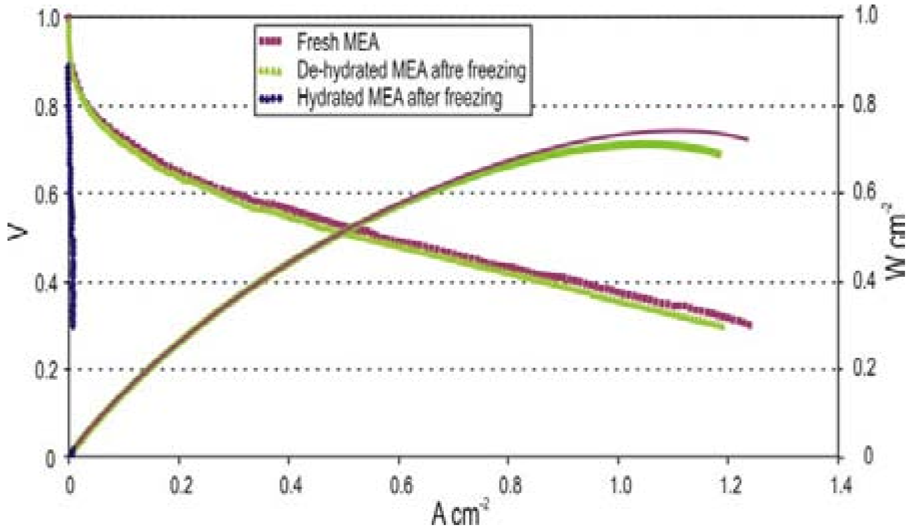

Fig. 1: polarization curves of the various MEAs.

room temperature for other 48 h, each single MEA was then characterized in a special PEM-FC test-bench, by feeding humidified H_2 and O_2 flows (100 Nml·min^{-1}). The obtained polarization curves are reported in Figure 1 and compared with the fresh MEA, used as reference: irreversible performance losses were found on the hydrated MEA, whereas the de-hydrated MEA completely recovered its performance compared to the fresh one. The ice formed into the hydrated MEA during the freezing conditioning, probably produced breaks and cracks into the MEA structure, leading thus to a strong decay of the power output. Instead, such a phenomenon did not occurred with the de-hydrated MEA due to the absence of water during the freezing conditioning.

To better investigate what happened to the MEAs structures, the MEAs were then removed from the FC test-housing and inspected by SEM analysis (Figure 2): significant damage to the hydrated MEA and backing layer was observed, in terms of cracks, fibers fractures and catalyst delamination from both the membrane and the GDL, leading presumably to H_2 crossover [2] and consequent performance loss. Moreover, the fibers showed plastic deformations probably caused by the presence of ice crystal in the membrane. The de-hydrated MEA appeared in the same status of the fresh one, without any visible effect of its permanence in sub-freezing conditions. The presence of water in the PEM-FC in freezing conditions may cause severe damages, mainly due to the formation of ice crystals causing breakage of the MEA structure, pores clogging and limitations in the transport of reactant gases [3] with a drastic performance loss. More details will be presented in the full paper. A possible strategy to avoid such an undesired effect is to remove water from the FC before the shutdown, otherwise the successive start-ups can result impossible.

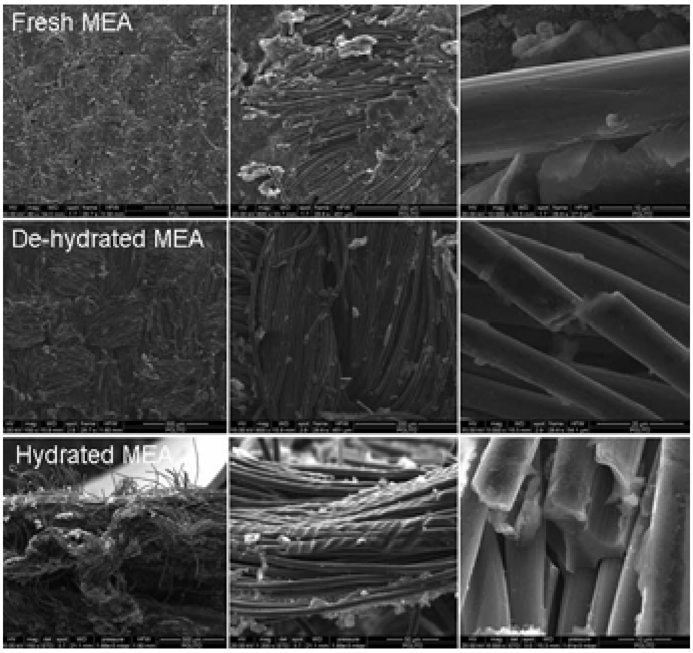

Fig. 2: SEM images of the anodic side of the various MEAs.

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DIRECT OILS HYDROGENATION TO ALCOHOLS AND HYDROCARBONS

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The processing of natural oils consisting of triglycerides is a topical problem at the present time, due to the need to obtain renewable sources of fuel and important chemicals. One such product is fatty alcohol which is used as a solvent, detergent, and foam inhibitor and as an additive to motor fuels.

The most investigated method of fatty alcohol production is the hydrogenation of lower molecular alkyl esters of fatty acids, obtained by the trans-esterification of natural triglycerides or by the esterification of the fatty acids obtained by the hydrolysis of these triglycerides [1]. In the 1990s Shell Oil and Henkel published patents relating to copper-containing catalysts for the direct processing of triglycerides to alcohols [2, 3]. Each of them displays very high conversion to fatty alcohols (about 90% of the theoretical) and high selectivity for 1,2-propanediol (of approximately 90% of the theoretical) and 10% of high-molecular products.

In this work the reaction of tristearin (glyceryl tristearate) hydrogenolysis was carried out in a fixed-bed gas reactor at a hydrogen pressure of about 2 MPa in the temperature range 280-350 °C. A permeable porous membrane was used to increase the gas-liquid interface for more effective saturation of the gas phase with reactant vapors. The hydrogen bubbled through this membrane in the oil vessel. By introducing a catalyst into the membrane the hydrogenation process may be carried out using the membrane itself as a reactor. In the literature there are several examples of using membranes, containing the appropriate catalyst, in such a way for carrying out three-phase processes [4-6].

The authors of the above patents [2, 3] used copper-zinc catalysts (in the patent to Shell a rare earth promoter was introduced to the catalyst composition). At the same time the precursor structure affects the catalytic properties of copper particles in the hydrogenation and dehydrogenation reactions [7, 8]. For example specific activity of oxide catalysts in the methanol synthesis increases according to the sequence: CuCr < CuSi < CuZnSi ≈ CuZnAl (spinel structure) << CuZnAl (wurtzite-like structure) and in the reaction of methanol dehydrogenation to CO and hydrogen specific activity increases according to the sequence:

CuZnAl < CuZnSi << CuSi ≈ CuCr. An important question is the effect of the precursor structure and copper state on the catalytic properties in the reaction of triglyceride conversion.

The interaction of triglycerides with hydrogen over copper-containing catalysts with different precursor compositions and structures ($CuCr_2O_4$ (tetragonal distorted spinel), $Cu_2H_2[Si_2O_5](OH)_4{\cdot}nH_2O$ (chrysocolla), $(Cu,Zn)_3[Si_4O_{10}](OH)_2{\cdot}nH_2O$ (copper-zincsilite), (Cu,Zn)O (wurtzite-like structure)) was investigated in the present work.

The condensed phase products were analyzed using the NMR ^{13}C and ^{1}H method. This method allows the determination of tri-, di- and monoglyceride, fatty acid, alcohol, saturated and non-saturated hydrocarbon content and of the nature of acid residue, glycerol and propanediol content in the liquid phase. Low-molecular reaction products in the gas phase were analyzed using the chromatographic method.

We showed that the triglycerides hydrogenation reaction leads to fatty acid formation over Cu-Si-containing catalysts. Over Cu-Cr and Cu-Zn catalysts fatty alcohols C_{18} are formed. These alcohols are partly hydrogenated to C_{18} hydrocarbons. Glycerol formed in the reaction is hydrogenated to propanediol, propanols and light hydrocarbons due to severe reaction conditions. When using permeable membrane containing metallic copper as a reinforcing component, a significant conversion of triglyceride is achieved over the membrane itself even without introducing any specific catalyst.

Thus copper-containing catalysts can be used for direct triglyceride hydrogenation to alcohols and hydrocarbons. It is possible to increase the efficiency of this process by decreasing mass transfer inhibition by using membrane reactors with permeable composite catalysts.

This work was supported by RFBR-ofi-07-03-12159. A.A. Khassin is grateful to the Russian Foundation for Science Support for financial support.

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DEVELOPMENT OF Pd/SIBUNIT CATALYSTS PREPARATION TECHNIQUE FOR SYNTHESIS OF CHEMICALS FROM RENEWABLES

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Supported palladium catalysts are widely used as catalysts for various industrial processes including several transformations of renewable resources. Although Pd catalysts preparation based on PdII salt hydrolysis followed by deposition of palladium hydroxide at pH 5 - 6 on a carbon support was studied in the literature, complete information about catalysts obtained via palladium hydroxide deposition at pH 8 – 10 is still unavailable. It is known that the higher pH of the catalyst precursor solution contacting with a support particle the more palladium is located on its periphery [1]. In this work a set of 1% (wt) Pd/C and 4% (wt) Pd/C samples was prepared by three deposition procedures at pH 8 – 10 (Methods I – III) and for comparison by deposition at pH 5 – 6 (Method IV). Na/Pd molar ratio (χ) was varied from 5 to 21 in Methods I-IV. Samples were washed, dried at 373 K and reduced by hydrogen at 423 K. Catalytic activity and efficiency of the catalyst particles were tested in a model reaction, liquid-phase hydrogenation of cyclohexene at 273 K and PH2 =1 atm. Pd distribution throughout the carbon grain was estimated by XPS measurements. The dispersion of Pd particles was determined by the pulse CO-chemisorption technique at 298 K.

1% (wt) Pd/C catalysts were applied in rapeseed oil hydrogenation. Products of this reaction are used in frying oils, margarines, etc. According to the literature *cis-trans* isomerisation of fatty acids occurs readily since both reactions, double bond hydrogenation and isomerisation, occur *via*

Table 1. Rapeseed oil hydrogenation over 1% (wt) Pd/C catalysts at 373 K.

Method (Na/Pd molar ratio of 21)	Pd distribution throughout the catalyst grain	D (Pd), nm	Activity, ml (H_2)/mg_{cat}·sec	*Trans*/*Cis*-ratio
I	Uniform	2.0	$3.8 \cdot 10^{-4}$	3.8
II	Egg-shell	1.7	$3.8 \cdot 10^{-4}$	1.7
III	Egg-shell	3.2	$2.8 \cdot 10^{-4}$	2.9
IV	Egg-shell	1.9	$6.4 \cdot 10^{-4}$	2.2

half-hydrogenated inter-mediates. Harmful influence of *trans*-isomers on human's health is well known. The tendency of a metal to promote one of the routes is closely related to particle size of the active metal and metal distribution throughout the support grain. In this work hydrogenation of rapeseed oil was carried out at 373 K, P_{H2} =6 atm in an autoclave under efficient stirring. Products were analyzed by GC and FTIR-spectroscopy. The obtained results (**Table 1**) indicate that in order to avoid *trans*-isomers formation it is necessary to decrease Pd particle size and to provide egg-shell distribution of Pd throughout the support grain.

1% (wt) Pd/C and 4% (wt) Pd/C powdered catalysts were tested in selective oxidation of lactose into lactobionic acid (LBA). Since oxidation of sugars is very sensitive to the composition of the adsorbed layer, «in-situ» measurements of electrochemical catalyst potential during a reaction reflect the oxygen coverage on the catalyst surface [2]. In this work kinetic measurements for a variety of Pd/C catalysts with different metal loading and different preparation techniques in comparison with a commercial catalyst (Degussa) were presented (**Figure 1**).

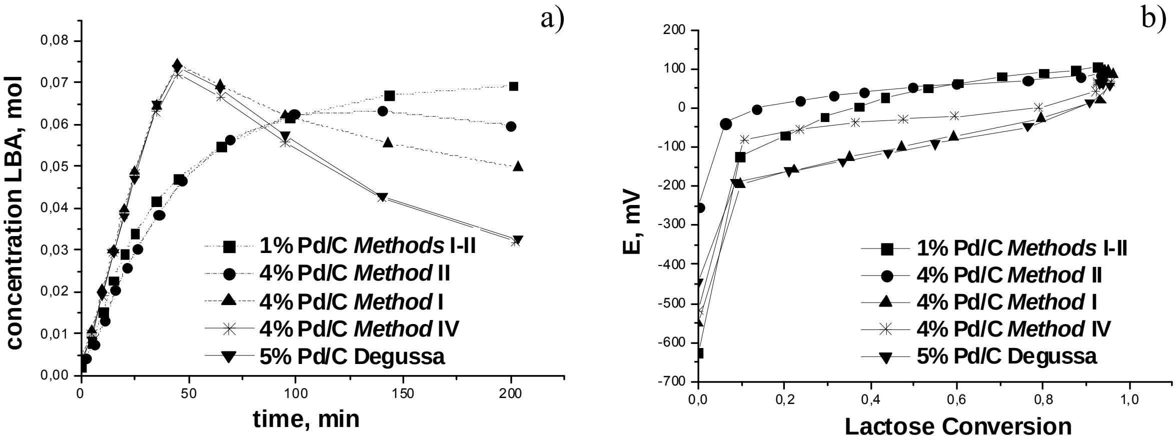

Figure 1. Lactose oxidation over palladium catalysts at 343 K, pH=8.
a) Concentration *vs* time, b) Catalyst potential *vs* conversion.

Significant differences in catalytic behavior and catalyst potential responses during lactose oxidation can be noticed from **Figure 1**, reflecting the nature of catalytic systems. The strong relationship between the metal dispersion, metal loading and the catalyst performance was found. More details on the relationship between the metal dispersion, metal loading, support properties and the catalyst performance will be provided in the presentation.

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PP-V-4

Pt NANOPARTICLE-HOLLOW POROUS CARBON NANOCOMPOSITES AS THE MICROREACTOR FOR REDUCTIVE AMINATION

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Introduction

It is well-known that the metal nanoparticles (MNPs) are very active catalysts because of their large surface area and a great ratio of atoms remaining at the surface. However, the MNPs are usually stabilized by organic ligands such as polymers and surfactants to prevent coalescence to the bulk metal. This results in the coverage of their active metal surface by organic ligand. Consequently, their intrinsic high catalytic activity is inhibited. Therefore, the syntheses of MNPs-based heterogenous catalyst, which has the original catalytic activity of MNPs are strongly desired. Numerous stabilized MNPs have been prepared by various methods, e.g., MNPs encapsulated in the mesoporous material and dendrimer, and have been proved to catalyze a variety of reactions1). Recently, we reported the fabrication of Pt nanoparticle encapsulated in hollow porous carbon (Pt@*hm*C) and its high catalytic activity for olefin and nitrobenzene hydrogenations2). This material is examined to have a suitable structure leading to the intrinsically high catalytic activity. The unique structure of Pt@hmC overcomes the above mentioned problems of MNPs. In this study, the expansion of catalytic function of Pt@*hm*C for the reductive amination of aldehydes and ketones in the microreactor provided by the hollow porous shell is investigated.

Experimental

The typical preparation procedure of Pt@*hm*C is described in our previous paper2). The catalytic reactions of reductive amination of aldehydes and ketones were performed in a closed test tube equipped with H_2 balloon at room temperature.

Results and discussion

Fig. 1 shows the TEM image of Pt@*hm*C. The Pt@*hm*C consists of Pt nanoparticle of average particles size of 2.1 nm and a hollow carbon (45 nm diamieter with a shell thickness of 10 nm). By FT-IR and N_2 sorption analysis we confirmed that the Pt nanoparticles are naked without covered by organic ligands and the carbon shell has the bimodal pore structure with a mesopore system centered at 2.0 nm and a micropore system of <1.0 nm in diameter.

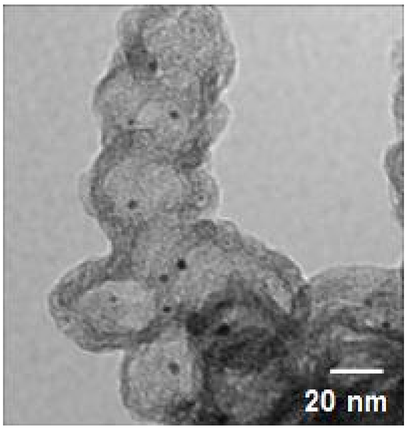

Fig. 1. TEM image of Pt@*hm*C.

The reductive amination of acetone with aniline as a model reaction was performed by various Pt catalyst under atmospheric pressure of H_2 at room temperature to produce *N*-isopropylanilin. Results are summarized in Table 1. Owing to the naked metal characteristic of Pt@hmC which provides a large effective Pt metal surface to induce the catalytic reaction, Pt@hmC achieved the highest turn over frequency (TOF). Commercial Pt/AC composite and Pt-PVP in which the surface of Pt is covered by PVP ligand demonstrated poor activity. Besides, the reductive amination of other ketone with aniline also proceeded smoothly to corresponding products under present system. Moreover, since Pt@*hm*C shows high catalytic acitivity for nitrobenzene hydrogenation to aniline as previously reported, one-pot synthesis of *N*-isopropylaniline directly from nitrobenzene and acetone is expected.

Table 1. Reductive amination of aniline and acetone.

entry	catalyst	Pt / μmol	TOF / h^{-1}
1	Pt@*hm*C	0.025	3700
2	Pt-PVP*	0.025	100
3	Pt/AC**	0.25	420

Conditions: aniline 0.5 mmol, acetone 1 cm^3, H_2 (balloon), room temperature.
TOF: mol of product per mol of total metal per 1 h.
* Pt nanoparticles protected PVP
** Pt/AC was perchased from N.E.Chemcat.

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PP-V-5

THE PROCESS FOR PRODUCING ORGANIC ACIDS BY MEMBRANE BIOREACTOR SYSTEM

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Introduction

Lactic acid has been manufactured by employing the batch-type fermentation process which comprises the steps of culturing lactic acid bacteria for more than 60 hours after inoculation and isolating lactic acid from the culture medium. The batch process has an advantage of high-concentration lactic acid production of over 120 g/L, though it has revealed a critical shortcoming of low volumetric productivity of less than 5 g/L/h. To compensate for the low productivity, the fermentation volume is enlarged, which in turn increases the cost for the construction of fermentation facilities and the maintenance of the facilities. As an alternative approach to overcome the low productivity of batch-type fermentation process, cell-recycling process by which microorganisms are concentrated in a fermenter to increase the productivity, has been suggested.

Results and conclusions

According to present experiments, the lactic acid and other organic acids can be produced in a simple and inexpensive manner, so as to eliminate the disadvantages of the prior processes discussed above. It has been surprisingly found, that if to create such conditions at which growth rate of cells is minimal but sufficient for replacement cells death, in this case decrease of the specific consumption of carbohydrates per unit of lactate is take place.

The growth rate of cells can be reduced by increase of temperature and decrease of pH up to critical and supercritical values for each microorganism and as well by decrease of amounts nutrients fed into the fermenter and by use of additives bacteriostatics.

It has been surprisingly found, that for each microorganism there are optimal conditions - temperature, pH, amounts of nutrients and bacteriostatics fed into the fermenter, at which growth rate of cells is minimal but sufficient for replacement cells death.

Preferably, the optimal growth rate of cells is reached by combination of temperature, pH, by amount of used nutrients and bacteriostatics fed into the fermenter.

Concentration of cells of microorganisms has been reached about 100 g/L (dried cell weight) and more, in the membrane recycle bioreactor system. With combinations of parametres described above, we can get volumetric productivity more then 100 g/L/h.

REACTORS FOR SYNTHESIS OF LACTIDE

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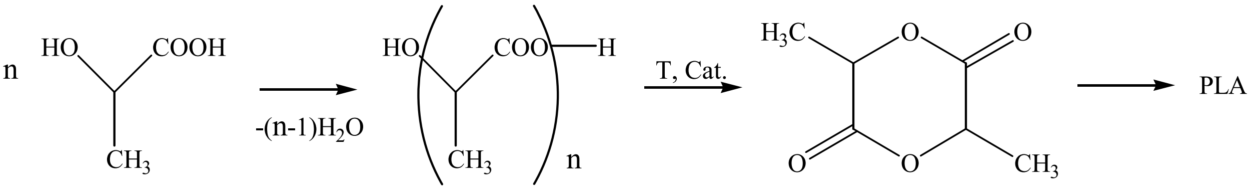
Introduction

The best solution of the problem of polymeric wastes is replacement of “iternal” petrochemical polymers with bio-degradable polymers. One the most promising of such polymers is polylactic acid (PLA) which can be synthesized from biotechnologically produced L-lactic acid (LA). At present the most economical way to produce PLA is known to be polymerization of L-Lactide which in tern can be synthesized by depolymerization of oligomers of lactic acid (OLA). So the general chemical chain can be shown as follows:



The aim of presented work was to compare different types of reactor for first and second stages of chemical chain clown above: oligomerisation of LA and synthesis of lactid.

Experiment

For both of reactions three types of reactor were investigated:

1. Vertical tubular flow reactor with fixed bed.
2. Semibatch mixed reactor.
3. Rotor film evaporator.

Different reaction conditions were being varied for these reactor in both processes: temperature, pressure, type of catalyst, contact time, medium.

Results

The best results on synthesis of OLA were obtained in the semibatch mixed reactor. The process can be carried out as catalytically ant without catalyst under temperature 170-180 °C. Reaction should be conducted preferably under continuous flow of N_2 in order to facilitate water removing. This method provides to produce OLA with degree of oligomerisation in the range n = 2-20; with yield up to 99% and specific capacity about 80-90 g (OLA)/(l×h).

The best results on synthesis of lactide were obtained in the rotor film evaporator working in the continuous flow regime. The process preferably was carried out in presence of catalyst (i.e. tin octoate) under vacuum (pressure = 12-15 torr) and temperature 220-225 °C. This method provides to produce lactide with yield up to 88 % and specific capacity of reactor (concerning evaporation surface) 1.2 kg(lactide)/(m^2×h).

Conclusions

The three types of reaction units were examined for two reactions: oligomerisation of lactic acid and formation of lactide. The best reactor type and reaction condition were experimentally determined for both of processes.

METHOD FOR COMPLEX PROCESSING OF POLYMERIC WASTES INTO FUEL FRACTIONS

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Introduction

At present time one of the main ecological problems is permanently growing volume of polymeric wastes. There are several methods for utilization or treatment of those: recycling, burial, combustion, processing into useful products. Evidently the burial and combustion are eco-faulty technologies and recycling and processing are more ecological friendly ones. The problem is that only a limited part of plastics can be recycled. Hence it would be preferred the rest amount of wastes to be converted into useful products. Today the main trend in development of such technologies is toward processing of polymeric wastes into hydrocarbon material which can be used as source for fuel fractions.

In this report two lab-scale installations for thermal-catalytic processing of some polymers are presented.

Experimental section

Two installations were built up: (1) Reaction-distilling unit consists of batch-type reactor supplied with stirrer and reflux column. Thermal-catalytic destruction proceeds at temperature 380-430 °C. The reflux column provides to output target fraction of products having boiling point lower then 350 °C. (2) Screw-type unit contains reactor and product's separating system. The cylindrical horizontal reactor is supplied with screw which allows feeding with different capacity depending on speed of rotation of screw. This reactor is very suitable while polymer destruction is accompanied by higher coke formation (more then 2%) and while feed stock contains solid filler materials.

As a feed stock the following materials were used: PE, PP, PS, tire-cover rubber (total sulfur content is 1.3-1.4 %) and isoprene rubber (total sulfur content is 0.7-0.8 %).

As a catalyst we tested solid materials based on chromium oxide, zinc oxide and magnesia supported on solid carrier. As an adsorbent for sulfur-containing substances we tested solid systems containing Ca, Mg, Zn, Al and their oxides.

Results

The presented technology provides almost 100 % conversion of organic part of feed stock. At that the yield of liquid products is 85-90 % for polyolefins and PS, and 45-60 % for rubber material (the content of sulfur in products is 0.4-1.1 %). Liquid products have a composition and boiling point range close to those of fuel fractions.

Products' composition varies depending on type of raw materials. In case of PS the liquid products contain 85-95 % of alkyl-aromatics; in case of PP – 70-80 % of highly branched saturated and unsaturated hydrocarbons; in case of PE – 60-85 % of saturated and unsaturated linear hydrocarbons. The liquid products of destruction of rubber boiling below 185 °C contain about 55-65 % of uncondensed aromatics and fraction boiling in the range 185-300 °C contain about 10-20 % of condensed aromatics.

In order to convert products of polymers' destruction into components of fuel fractions it was necessary they undergo the hydrotreating for hydrogenation of olefins and hydrodesulfurization. The hydrotreating was carried out in the autoclave. The hydrogenation of unsaturated hydrocarbons was carried out under 220-240 °C and 25-35 bar in the presence of Ni-containing heterogeneous catalyst that provided 80-95% conversion of double bonds. The hydrodesulfurization was carried out under 300-340 °C and 25-40 bar in the presence of Al-Co-Mo heterogeneous catalyst that resulted in 80-95 % degree of sulfur removing.

Conclusion

The results obtained allow formulation of general approach to technology of thermal and thermal-catalytic processing of polymeric wastes into fuel fractions.

THE METHOD FOR PRODUCING OF MOTOR FUEL COMPONENTS FROM VEGETABLE OILS AND ANIMAL FATS

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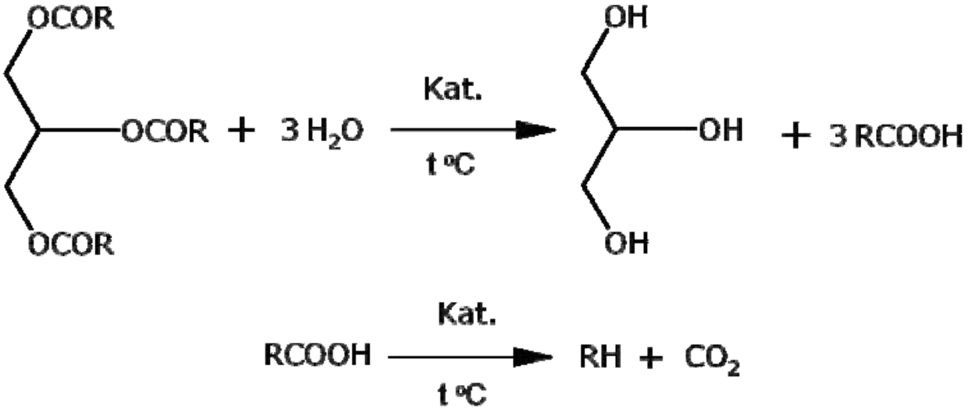
Introduction

The world's fossil fuel resources – including crude oil, natural gas and coal – are huge; however they will be exhausted sooner or later. There is already fossil fuel deficit leading to a rise of motor fuel prices. As a result the use of renewable energy sources expands steadily.

At present biodiesel is extensively produced both in the USA and Europe. This fuel consists of methyl esters of the fatty acids (FAME) of the parent oil and fat. Biodiesel is better than petrodiesel in terms of sulphur content, flash point, aromatic content and biodegradability. But biodiesel is a better solvent than petrodiesel, and has been known to break down deposits of residue in the fuel lines of vehicles that have previously been run on petrodiesel. Another disadvantage of biodiesel is that it has lower energy content, since diesel engines inject equal volumes of fuel so power drops 8%. These disadvantages can be avoided if not FAME but hydrocarbons are produced from triglycerides of oil or fat.

Results

Proposed method includes two-stage process for production hydrocarbon fuel that is identical to petrodiesel. At the first stage glycerol is removed from the molecule of triglyceride by hydrolysis. At the next processing step the fatty acids formed in first stage undergo the decarboxylation resulting in paraffin and olefin formation.



It was determined that decarboxylation is greatly accelerated by oxides and hydroxides of alkali- and alkali-earth metals as well as alumina. It was shown that oxides of the metals whose carbonates decompose below 380-400 °C, such as magnesium oxide and alumina, are the most effective catalysts. Conversion of fatty acids approaches to 100 % with applying of these oxides. The target reaction is accompanied by ketonization, cracking and polymerization reactions. All of these side reactions lead to yield decreasing and obtaining undesirable products.

This report displays influence of catalyst type and process conditions on the yield of liquid hydrocarbons and product composition.

UPGRADING OF FCC-GASOLINES ON Pt,Pd/ZEOLITE CATALYSTS

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In the last years sulphur content of engine gasolines was stepwise reduced to 50(10) mg/kg in the European Union [1]. This is mainly caused by environmental protection reasons (acid rains, preserve exhaust gas after treatment systems from sulphur compounds). Sulphur oxides, sulphurous acid and sulphuric acid can cause the corrosion of the exhaust gas system, furthermore, by entering into engine oils these compounds can decrease the basic reserve of the engine oils [2]. Nitrogen content of engine gasolines was not limited yet, however during the combustion they form nitrogen oxides, thus they definitely increase the NOX emission of vehicles [3].

By the use of neither the conventional, nor the new generation catalysts - developed for the sulphur reduction of FCC gasolines - reduction of both sulphur and nitrogen content of FCC gasolines is not possible with low octane loss (≤ 3 units) [4,5].

Based on the foregoing the objective of our research work was to find a catalyst which is suitable to produce low sulphur containing (≤ 10 mgS/kg) and practically nitrogen-free (≤1 mgN/kg) FCC gasoline with low octane loss (≤ 3 units). The experiments were carried out in reactor system consisting of a down-flow fixed bed tubular reactor working without back-mixing. During the investigation of several catalysts having different composition we found that the expediently selected Pt,Pd/zeolite catalysts are suitable for aims.

Under expediently selected process conditions (T = 265-280°C; ptotal = 30 bar: LHSV=1.2-2.0; H_2/hydrocarbons ratio: 300 Nm^3/m^3), the investigated PtPd/USY catalyst is able to produce nitrogen free FCC gasolines of ca. 10 mg/kg sulphur content from FCC gasoline feedstocks containing 50-150 mg/kg sulphur, 10-25% olefins and less than 50 mg/kg nitrogen with a lower loss of octane number (2-2.5 units) compared to those produced over conventional (4.5-5.5 units) and new (3-3.5 units) CoMo/alumina catalyst. This is a new possible application field of PtPd/USY catalyst. Use of this product is advantageous for reduction of nitrogen-oxides emitted by gasoline-fuelled passenger cars.

Neither the low sulphur content (<50 mg/kg), nor the high sulphur content (>150 mg/kg) of the feedstock does not favor the selective hydrodesulphurization ability (high HDS activity but moderate olefin and aromatics hydrogenation activity and thus low level of octane number loss) of the PtPd/USY catalyst. Accordingly, the reason of the selective hydrodesulphurization ability is the inhibiting effect of sulphur compounds and the resulting hydrogen sulphide on olefin hydrogenation, while high concentration of sulphur compounds inhibits hydrodesulphurization.

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TRIGLYCERIDES ALCOHOLYSIS CATALYZED BY HETEROGENEOUS CATALYSTS FOR BIODIESEL PRODUCTION

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Introduction

Biodiesel is an attractive renewable fuel due to the similar main characteristics shared with conventional diesel and to its environmentally friendly use. Currently, the fatty acid methyl ester mixture *(biodiesel fuel)* is produced by alkali-catalyzed transesterification of vegetable oils with methanol. The main used catalysts are the homogeneous basic ones, such as sodium hydroxide, potassium hydroxide and sodium or potassium methoxide [1]. The homogeneous basic catalysis show a very fast kinetic of reaction but also a collateral saponification reaction that reduces the *bio*diesel production efficiency. By contrary, the acid transesterification allows to obtain a *bio*diesel production without formation of by-products. The drawbacks of an acid transesterification are the corrosive homogeneous used catalyst (H_2SO_4, HPO_4, HCl) and the slow reaction rate that can be increased by high temperature and pressure [2].

In this contest, our work focus on the possibility to use silicates (with acid and base properties) and acid zeolites (Beta, MFI, FAU-X) as catalysts for the transesterification of fatty acids with methanol to *bio*diesel. These type of catalysts allow combining the advantages of the alkaline and acid transesterification with those of heterogeneous catalytic process. Besides the usual zeolites characterization techniques (XRD, TG-DTA, SEM, EDX), FT-IR and NH_3-TPD analyses have been carried out on the catalysts in order to identify the nature and the strength of the catalytic active sites.

Experimental part

The acid zeolites H-BEA, K-Silicalite-1, H-Silicalite-1, Na-Silicalite-1 and Fau-X have been prepared by conventional procedures. The silicates used have been the potassium and sodium ones, in powder form. The transesterification reaction catalyzed by silicates and acid zeolites have been carried out at reaction temperatures ranging between 40÷150 °C and using a molar ratio of triglycerides to methanol ranging between 1:6 ÷1:50. The *bio*diesel composition (methyl esters, mono-, di and triglycerides content) was determined by GC-analysis using tricaprin as internal standard.

Results and discussion

In the performed reaction conditions (140°C, 24 hours, 15% wt of catalyst respect to oil, oil:methanol molar ratio equal to 1:10) the potassium silicate shows the highest oleic acid conversion value (93%), followed by the sodium silicate with a conversion value of 88%. Among the zeolites, the K-Silicalite-1 allows to reach the 50% of conversion, with respect the 20% of the Fau-X. To achieve a conversion value comparable with the basic catalyst, the acid zeolites require the increasing of the temperature and methanol amount. These results suggest that the faster reaction rate achieved using silicates could be due to the presence of base sites on amorphous surface of these catalysts. At the same time, the weak acid sites also present on silicates surface allow to achieve an acid esterification of the free fatty acid, avoiding the soap formation.

In the transesterfication of an olive oil with the following fatty acid composition: 74% of oleic acid, 12,3% of palmitic acid, 3,5% of stearic acid and 7,7% of linoleic acid and 2,5% of myrisitc acid, the selectivity of the silicates catalyst has been compared with that of the conventional alkaline homogeneous catalyst KOH. The sodium silicate catalyst shows a higher selective towards the long chain fatty acids (Figure 1). The maximum content of methyl palmitate, methyl oleate and methyl linoletae (C18) increases and no myristic acid conversion occurs at the end of the reaction catalyzed by the sodium silicate.

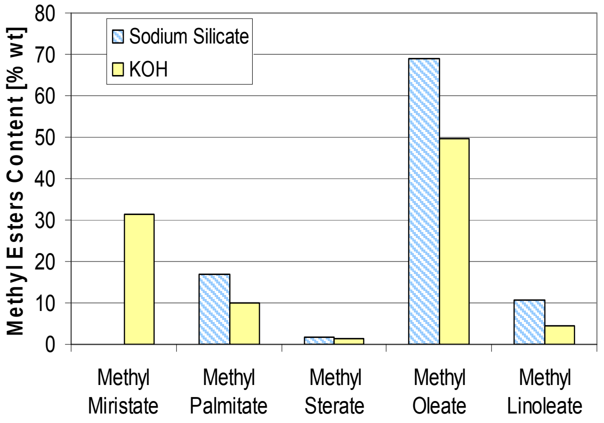

Figure 1. Methyl esters content obtained by transesterification reaction catalyzed by KOH and sodium silicate.

Finally, some of the most important parameters of *bio*diesel quality (monoglyceride, diglyceride and triglyceride content, total glycerol level and acid value) for reactions using each catalyst have been evaluated. For example, the acid value of the *bio*diesel produced by potassium silicate is equal to 0.23 mg KOH/g (0.5 mg KOH/g is the maximum value defined by the European Union Draft Standard prEN 14214).

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BIOETHANOL CONVERSION ON ZEOLITE CATALYST: EFFECT OF WATER TO ETHANOL RATIO

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Nowadays, as a result of the depletion of petroleum resources and specific ecological requirements, more attention is given to renewable energy sources which are able to substitute crude oil. One of the prospective sources of hydrocarbons is ethanol obtainable from biomass and other bioorganic wastes. The convenient bio-ethanol is not pure; It rather has a high water content depending on its natural source, production technology and further distillations. The production cost of ethanol depends on its purity and grows exponentially with degree of purity from water, especially after 88% point.

However, a large quantity of water (~ 40% mass) is formed during the main reaction:

$$CH_3CH_2OH \rightarrow C_xH_y + H_2O \qquad (1)$$

which means that the water influence can be negligible in the case of diluted ethanol. To check this hypothesis we have tested the conversion of different ethanol water mixtures on the HZSM-5 catalyst modified with ZnO and low quantity of iron oxide (Si/Fe > 500). The conversion of 96% grade ethanol (which is used in medicine) on this catalyst at 350 °C gives up to 50% of liquid hydrocarbons selectivity during first 8 h of reaction with near complete ethanol conversion. Dependence of product composition from ethanol space velocity is shown on table 1. The increase of ethanol space velocity leads to decrease in liquid hydrocarbons formation and increase of ethylene formation. Another important point is the stability of products composition. Looking on ethylene (C_2) concentration in the outlet of the

Table 1. The influence of space velocity on product composition of ethanol conversion on $ZnO/FeO_x/HZSM-5$ catalyst (T = 350 °C, P = 1 atm)

WHSV, h^{-1}	Liquid HC, %	C_2 (1), % mass	C_2 (2), % mass	C_3 (1), % mass	C_3 (2), % mass	C_4 (1), % mass	C_4 (2), % mass
1.4	33	3	3	20	18	43	45
2	49.5	6	5	15	12	28	32
4	35	14	14	14	12	35	37
6	29	10	22	14	10	43	34
10	28	15	35	15	8	38	23

1) after 1 hour of reaction 2) after 4 hours of reaction

reactor we can see that its concentration increases after 4 hours of reaction at WHSV > 4 h^{-1} which means that the catalysts loses selectivity in its oligomerization reaction leading to C_4-hydrocarbons and liquid products.

Water addition to ethanol flow decreases the amount of liquid hydrocarbons formed during ethanol conversion on ZnO/FeO_x/HZSM-5. The conversion of ethanol also decreases to 90% at 1:5 ethanol-water (e/w) conversion with the increase of diethyl ether concentration. At ratios lover than 1:4 e/w diethyl ether formation was also observed consuming up to 10% of ethanol. The rise of ethylene concentration within 4 hours of reaction has been found with water concentrations higher than 25%. High concentration of C_4 products means that oligomerization of ethylene either stops at this stage or leads to C_6-species which are transformed to the mixture of C_2, C_3 and C_4 via cracking routes.

In our opinion the main deactivation role of water in this zeolite catalyst is blocking of activation site for oligomerization and aromatics production. The high concentration of water molecules inside the pores of zeolite lowers the acidity of the catalyst and moves adsorbed ethylene species from active centers back to gaseous phase before their oligomerization. In proving this conception it is necessary to mention that after short activation of the catalyst (1hr) in air stream, its properties regenerate almost completely.

But if we are concerned with optimizing yields of C_3-C_4 or ethylene instead of liquid products we can conclude that water addition to ethanol plays an important role in changing catalyst selectivity without altering the catalyst and technological equipement.

Table 2. The influence of water on product composition of ethanol conversion on ZnO/FeO_x/HZSM-5 catalyst (T = 350 °C, P = 1 atm)

WHSV ethanol, h^{-1}	WHSV water, h^{-1}	Liquid HC, %	C_2 (1), % mass	C_2 (2), % mass	C_3 (1), % mass	C_3 (2), % mass	C_4 (1), % mass	C_4 (2), % mass
2	2	2	27	44	21	16	50	35
2	4	0	44	47	15	15	35	33
2	6	0	45	60	10	8	18	12
2	10	0	50	70	22	10	22	10
4	2	10	25	27	19	17	51	49
6	2	5	20	50	20	11	55	33

1) after 1 hour of reaction 2) after 4 hours of reaction

PRODUCTION OF METHYL FORMATE AND FORMALDEHYDE BY CATALYTIC METHANOL CONVERSION

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Nowadays, due to continuous price growth for oil and latest worldwide tendencies of decreasing the dependence and in long term even repudiation from raw oil, the aim to develop synthesis of valuable organic compounds from alternative raw materials becomes one of the most relevant goals in chemical technologies. One of the best examples is the methanol produced from synthesis gas which further can be utilized for methyl formate and formaldehyde production the valuable intermediate products for organic synthesis. Methyl formate production is the first step in the synthesis of acetic acid, N,N-dimethylformamide and hydrogen cyanide.

Commercial process of methyl formate production has a number of following essential drawbacks: 1) the system is operated at a pressure of carbon monoxide highly above atmospheric, 2) the system is operated in the presences of catalysts rather sensitive to impurities that demands greater expenses for stage of starting material purification.

Gas phase dehydration of methanol being the most investigated way of methyl formate production at present is a heterogeneous catalytic process operated at the atmospheric pressure in the flow reactor.

As methyl formate derived form methanol dehydration easily take part in side reactions then to increase competitiveness it is necessary to create effective catalytic systems.

Our recent studies have shown copper catalysts based on composite carbon material sibunit developed in Institute of catalysis named after G.K. Boreskov of the Siberian department of the Russian Academy of Science to be highly effective for methanol dehydration.

Methanol conversion products analysis has shown that besides methyl formate producing there is significant amount of formaldehyde to be formed in the high temperature range. Formaldehyde derived thus may be used as marketable product and raw material in polymer synthesis.

Currently formaldehyde is received either oxidation or oxidative dehydration over silver catalysts or oxide catalysts based on iron molybdate. Formaldehyde thereby received contains water that sharply narrows opportunities of its further processing into high-quality products.

Recent studies lead in this area, have shown, that alternative to existing process of non oxidizing methanol dehydration not only meets modern requirements of ecology and safety of manufacture, but also it appears to be more profitable. Hydrogen to be formed during the methanol dehydration can be used as an end product or to be involved in carbon dioxide hydrogenation for methanol production to return last to recycle. Involving carbon dioxide in reaction of methanol production using of hydrogen released will allow to solve the important ecological problem of recycling CO_2, reducing thereby a greenhouse effect.

This study addresses an opportunity to increase efficiency and stability copper catalyst based on sibunit by chrome promoting agent introduction.

The temperature influence on methanol conversion in the presence of chrome catalyst and chrome-promoted copper catalysts was investigated.

The effect of added chrome on the behavior of copper catalysts for the gas phase dehydrogenation of methanol has been investigated for two chrome contents (0,1 and 0,5 wt.%).

Possible directions of methanol conversion over chrome-based and chrome promoted copper-based catalysts were proposed. It is stated that in presence of chrome-based catalyst, dimethyl ether is the main product and no methyl formate or formaldehyde has been formed. By contrast, in the presence of copper-based and chrome-promoted copper catalysts no dimethyl ether has been chromatographically observed.

For the reason of observed methanol conversion, promoted catalysts was stated to reveal higher activity then copper-based catalyst.

The chrome introduction significantly influences methyl formate selectivity. In the presence of 0,1wt.% chrome promoted catalyst selectivity reveal extreme behavior with maximum value in temperature range 325-350 °C. When adding 0,5wt.% chrome maximum selectivity value was reached at 150 °C and was high as 80%. Thus, maximum methyl formate yield was observed over 0,5wt.% chrome promoted copper catalyst in range 175-200 °C.

With chrome present, the selectivity of formaldehyde decreased with increasing amounts of chrome and reveal extreme behavior reaching 95% at 300 °C over unpromoted copper catalyst. However, the highest formaldehyde yield values were observed in presence of 0,1%wt. chrome promoted catalyst at temperatures below 400 °C for the high activity of the last one.

Thereby chrome promoted copper catalysts may be used in methanol conversion to either methyl formate or formaldehyde in dependence of used conditions.

INVESTIGATION OF HYDRODEAROMATIZATION OF GAS OILS ON NOBLE METAL/SUPPORT CATALYSTS

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Diesel fuel specifications are continuously tightening and its demand is also growing, especially in the European Union. Sulphur limit of diesel fuels is currently 50 mgS/kg in the European Union that will be reduced to 10 mgS/kg from 2009. However, ultra low sulphur (lower than 10 ppm) diesel fuels shall already be made available regionally in a geographically balanced manner [1]. Not only sulphur limits but also aromatics content is expected to become stricter. The limit of polycyclic aromatic content of diesel fuel is currently 11% in the standard, but a maximum specification for total aromatics content is likely to be established beside the limit for polycyclic aromatics. Reduction of the aromatic content of diesel fuels is relevant, because aromatic hydrocarbons have low cetane number and cetane index, contributing to the increase of vehicle HC and PM emissions. Technologies applied in the refining industry can be divided into the following categories [1].

One-step processes are used for converting feeds having high sulphur, nitrogen and aromatic content on transition metal (NiMo/alumina or CoMo/alumina) catalysts (deep heteroatom removal and partially aromatic-hydrogenation).

Two-step processes are used for converting feeds having high sulphur, nitrogen and aromatic content: in the first stage deep heteroatom removal and partially aromatic-hydrogenation on transition metal catalysts (NiMo/alumina or CoMo/alumina) occurred and in the second stage further deep heteroatom removal and deep aromatic reduction of previously hydrodesulphurized feeds on monometallic (Pt/alumina) or bimetallic (Pt,Pd/USY, Pt,Pd/HY zeolite) noble metal catalysts occurred.

For these reasons, in recent years, sulphur and nitrogen tolerant (up to 50-200) precious metal catalysts have attracted much attention for the hydrogenation of aromatics in diesel fuels in the second stage of the two-step processes [2]. In case of monometallic noble metal catalysts (e.g. Pt or Pd), the sulphur (≤10 mgS/kg) and nitrogen (≤1 mgN/kg) content in the feedstock must be strictly reduced before the catalyst comes in contact with the feedstock due to their poor sulphur and nitrogen tolerance. Bimetallic catalysts (e.g. Pt-Pd/USY) and/or appropriate acidic support can be used to increase the sulphur tolerance, which depends on electron deficiency of noble metal particles [3]. The tolerance to nitrogen is also an important issue because most petroleum feedstocks contain basic nitrogenous compounds [4,5], which are strongly adsorbed on the catalyst support.

The main objective of our study was to find a noble metal/support catalyst suitable for the hydrodearomatization of high sulphur and nitrogen containing gas oils from Hungarian and Russian crudes. Additionally the effect of key process parameters (temperature, pressure, LHSV, hydrogen-to-hydrocarbon volume ratio) on the hydrodearomatization efficiency of prehydrogenated gas oil fraction was investigated, too. The experiments were carried out in a high-pressure reactor system consisting of a down-flow fixed bed tubular reactor of 100 cm^3 effective volume. The 100 cm^3 tube reactor was working without back-mixing. It contains all the equipments and devices applied in the reactor system of hydrotreating plants (pumps, separators, heat exchangers, as well as temperature, pressure and gas flow regulators). The operation was mixed phase.

The main goal of our experiments was to find a bimetallic Pt,Pd/USY catalyst suitable for deep hydrodearomatization of relatively high sulphur (up to 300 mgS/kg) and nitrogen (up to 200 mgN/kg) containing feeds with Pd/Pt ratio of 4:1. In case of optimal process parameters (T = 310°C, P = 60 bar, LHSV = 1.0-1.5 h^{-1}, H_2/hydrocarbon volume ratio = 600 Nm^3/m^3) low aromatic (<10%), practically sulphur and nitrogen free products (≤10 mgS/kg and ≤1 mgN/kg) having high cetane number (54-58) could be produced which are environmentally friendly diesel fuel blending components.

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SIMULATION OF TRANSESTERIFICATION REACTORS TO BIODIESEL PRODUCTION FROM BIOETHANOL AND PALM OIL

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Thanks to its weather and geographic conditions Colombia has a great potentiality, in terms of natural resources plantations, to generate biofuels; it counts with around 298 and 210 thousands hectares of palm and sugar cane respectively[1-3], offering alternatives of joint biofuels productions. The transesterification reaction, using palm oil and bioethanol has not been explored deeply because of, among others, the difficulties presented in the stages of later separation. These operational problems are largely attributed to the effect generated by the catalyst type (acidic or basic). Different studies have been carried out using different oils as raw material, different alcohol as well as different catalysts. In this work we made a simulation of the alternative that could be used to produce biodiesel from palm oil and bioethanol with basic and acidic catalysts and compared with experimental results of enzymatic catalyst reported in literature.

Biodiesel is obtained from the conversion of triglycerides presents on vegetable oils like palm, soy, sunflower and rapeseed, among others, with a given alcohol (methanol, ethanol, and others) into methyl or ethyl esters by means of a transesterification reaction. In this process, the three chains of fatty acids of each molecule of triglyceride react with the alcohol in presence of a basic catalyst to obtain the alkyl ester (biodiesel) and the glycerol. We can see a scheme in three steps of transesterification reaction of triglyceride with ethanol proposed by Freedman *et al.*[4].

$$TG + 3ROH \xrightarrow{CATALYST} G + 3E \tag{1}$$

$$TG + ROH \Leftrightarrow DG + E \tag{2}$$

$$DG + ROH \Leftrightarrow MG + E \tag{3}$$

$$MG + ROH \Leftrightarrow G + E \tag{4}$$

TG: Triglycerides, DG: Diglycerides, MG: Monoglycerides, G: Glycerol, ROH: Ethanol, E: Biodiesel.

PP-V-14

Alkali catalyst. For a basic catalyst, either sodium hydroxide (NaOH) or potassium hydroxide (KOH) should be used with ethanol as well as any kind of oil. The reason why there is a great interest in the alkali process is it is more efficient and less corrosive than the acid process, making it a preferred catalyst to be used in industries. The limits of this technology are due to the sensitivity that this process has to purity of reactants, to the fatty acid, as well as to the water concentration of the sample.

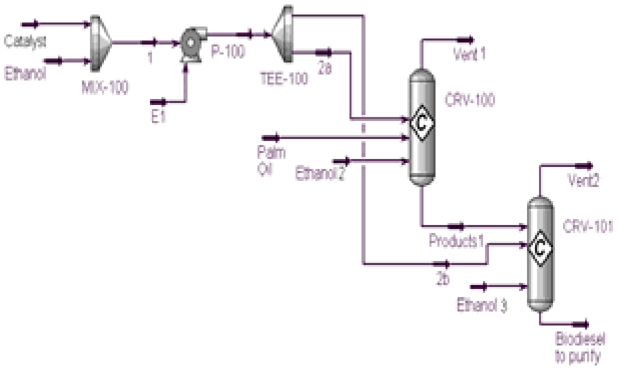

Fig. 1. Transesterification stage to biodiesel production.

Acid catalyst. This type of catalyst gives a very high yield in esters but the reaction is very slow. The acid most commonly used is sulfuric acid with temperature range from 55 to 80 °C. A kinetics modeling for soybean oil has been made by Freedman *et al.* [4].

Lipase as catalyst. Lipases are enzymes used to catalyze some reaction such as hydrolysis of glycerol, alcoholysis and acidolysis, but it has been discovered that they can be used as catalyst for tranesterification and esterification reactions too.

The simulated reactors in this work are shown in Fig. 1. The palm oil was chosen for the transesterification process considering the average percentage of fatty acids in Colombia variety. The following composition in fatty acids: 45% palmitic acid, 40% oleic acid and 15% linoleic acid was defined for the process simulation. The reaction was carried out with ethanol using NaOH and KOH as catalysts to 60 °C, H_2SO_4 to 70 °C and 150 kPa and the results were analyzed and compared with those of Nelson *et al.*[5] and Shimada *et al.*[6] using immobilized *C. antarctica lipase*. Several differences were founded in reaction conditions, yield of biodiesel obtained and velocity of production depending upon the catalyst used. Nevertheless, all processes were designed properly and with high efficiency.

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THE KINETICS OF METHANOL STEAM REFORMING

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Methanol is nowadays considered as a fundamental building block in the production of many chemicals such as, for example, formaldehyde and acetic acid or, alternatively, as a low-cost energy vector like in MTBE and biodiesel productions. Moreover, methanol is regarded as an hydrogen reservoir in fuel cells applications, in which methanol represents an efficient solution for hydrogen transportation- and storage-related problems. With this approach is possible to produce high purity hydrogen, compatible with fuel cells technology, through the catalysed steam reforming reaction. The catalytic steam reforming of methanol is based on the following reaction [1-7]:

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$$

In this work the kinetics of methanol steam reforming (MSR) have been studied in experimental conditions similar to the ones used in industrial applications and by using a commercial catalyst with a shape of cylindrical pellets. The used catalyst, very active and selective, is a mixture of Cu-Zn-Al oxides and is usually employed, in industry, for low-temperature CO water-gas-shift (WGS) reaction:

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

In a first phase of the study, different kinetic models have been tested in the description of experimental runs performed in a CSTR Berty-type reactor and reported in our previous work [8,9]. In this way the detrimental effect of water and/or hydrogen concentration on the reaction rate has been established, also in comparison with the results reported in the literature by other authors [1-7]. With this approach the more reliable kinetic law has been selected for the description of experimental data and for the subsequent scale-up towards the packed-bed pilot reactor.

In a second phase of the research different runs have been performed on a tubular pilot-scale packed bed reactor (Fig. 1) operated in non-isothermal and non-adiabatic conditions. The kinetic law developed for the run in the CSTR reactor runs has then been used for the simulation of these second kind of continuous experiments, also taking into account for both mass and heat balance along the reactor and inside the catalytic particles [10]. Effectiveness factor of the pellets has been evaluated, by rigorous calculation [10], along the reactor axis obtaining the related profile and a comparison with experimental values will conclude the paper.

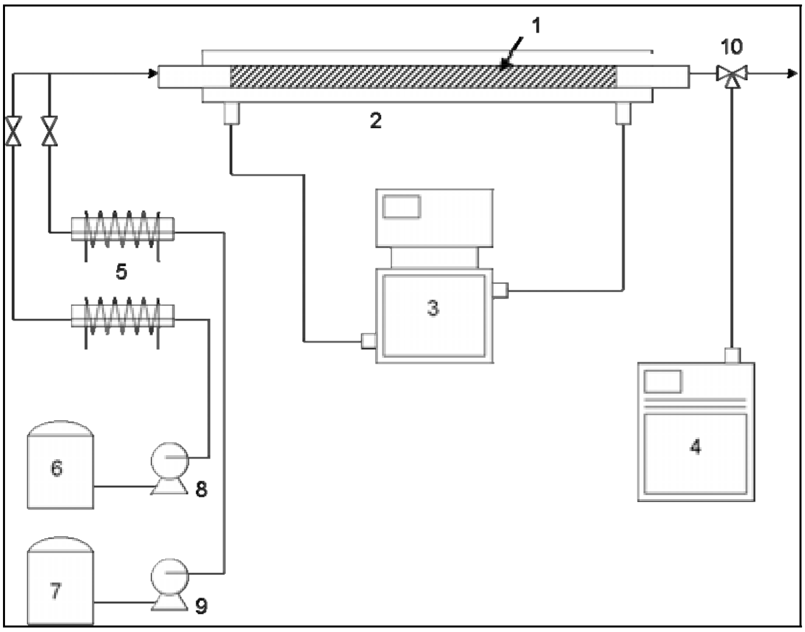

Figure 1. Pilot reactor scheme. 1 – catalytic bed, 2 – heating/cooling jacket, 3 – circulation thermostat, 4 – GC for analysis, 5 – water and methanol vaporizers, 6 – methanol reservoir, 7 – water reservoir, 8 – methanol feeding pump, 9 – water feeding pump, 10 – sampling valve.

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SYNGAS PRODUCTION BY PARTIAL OXIDATION OF METHANE OVER $Rh/LaMnO_3$ HONEYCOMB CATALYSTS

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Syngas is the row material for the production of H_2 and also clean fuels through gas-to-liquid processes (like methanol and Fischer-Tröpsch syntheses). In order to produce syngas more efficiently, catalytic partial oxidation (CPO) of methane has received an increasing interest during last decades [1]. Through CPO syngas can be produced with no energy consumption, no coke formation and at relatively low temperature, thus avoiding NO_x emissions. Although more expensive than Ni-based catalysts, noble metals appear to be very attractive because of their high activity (allowing the development of processes at short contact time) and no coke formation [2]. On precious metal catalysts (especially on Rh) the effects of the support morphology [3], the addition of oxygen carriers to the support [4] or the nature of the support [5] have been investigated. However, this class of catalysts suffer from deactivation due to the formation of hot spots [6], caused by the rapid CH_4 oxidation leading to H_2O and CO, as proposed by Lyubovsky et al. [7]. Recently we proposed a bi-functional $Rh/LaMnO_3$ honeycomb catalyst for CPO of methane [8, 9]; these catalysts showed better performances than Rh only catalysts. In this work the effect of Rh loading on catalytic performance under several operating conditions is presented; moreover, at fixed catalyst composition, the effects of honeycomb features (cell density and material) have been studied.

$Rh/LaMnO_3$ catalysts have been prepared according to the procedure described elsewhere [8]. The active phase is composed of Rh (0,1% - 1% wt.) and $LaMnO_3$ (30% wt.). Commercial cordierite and SiC honeycombs (cell density: 200 - 1200 cpsi) were used as substrates. Catalytic tests were conducted under adiabatic conditions using the experimental rig described in [8]. The effects of CH_4/oxidant ratio, oxidant type (air or oxygen), space velocity and CO_2 addition were studied.

Catalytic tests conducted over samples containing different Rh loading showed that catalytic performance slightly increased with increasing noble metal content. As an example, in figure 1 the catalytic performances of bi-functional catalysts (substrate: cordierite, 600 cpsi) containing 0,1%, 0,5% and 1% wt. Rh as a function of CH_4/O_2 ratio are reported. Methane conversion decreases with increasing CH_4/O_2 ratio for all the samples, but the curves related to different samples are near each other. It appears that activity is directly related to the amount of Rh, responsible for the reforming activity. Investigating the effects of other reaction parameters, not reported, showed that catalytic performance slightly increases with increasing Rh content at each reaction condition. The effect of cell density has been studied using several cordierite monoliths. The results (not reported) showed that the catalytic performance depended not monotonically by channel dimensions. This behaviour is related to two countered effects, an increase in the amount of catalyst and a decrease in space velocity (catalytic performance is directly related to space velocity) by increasing cell density. Moreover, it appears that the activity towards Reverse Water Gas Shift reaction is favoured by decreasing the channel dimension, thus changing H_2/CO ratio. The use of SiC monoliths instead of cordierite ones allowed to increase catalytic performance of $Rh/LaMnO_3$, without changing the other parameters. This is in consequence of the different temperature profile (fig. 2) due to the different thermal conductibility of the substrates. High thermal conductivity generates higher temperatures in the second part of the reactor, where endothermic (reforming) reactions occur; moreover, the heat transfer from high temperature towards "cold" zones results in a decrease in the peak temperature, thus reducing or avoiding deactivation phenomena.

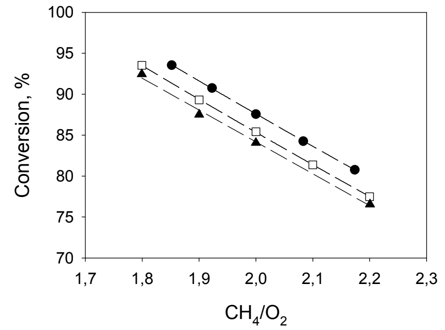

Fig. 1 – Catalytic performance of $Rh/LaMnO_3$ (Rh: 0,1% [▲], 0,5% [□], 1% wt. [●]) as a function of CH_4/O_2. Oxidant: O_2; T_{pre}: 500°C; GHSV: 38000 h^{-1}.

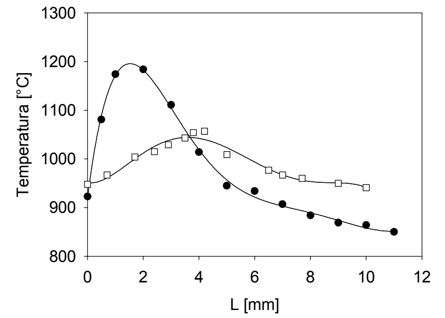

Fig. 2 – Temperature profiles measured inside $Rh/LaMnO_3$ catalysts with cordierite (●) and SiC (□) substrates. $CH_4/O_2 = 1.7$; oxidant: O_2; T_{pre}: 500°C; GHSV: 50000 h^{-1}.

In conclusion, experimental results showed that using bi-functional catalysts it is possible to obtain good high conversion and selectivity even introducing very small amount of Rh into the active layer. Moreover, catalytic performances can be modified changing geometrical features of the substrate. The use of a substrate showing high thermal conductivity can increase both catalytic performance and durability.

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DEHYDROGENATION/DEHYDRATION OF ISOPROPANOL OVER BIMETALLIC COPPER-METAL (m = Ni, Co, Fe) CATALYSTS

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The replacement of copper-chromite systems with more environmentally benign copper catalysts, such as silica supported Cu, is of current interest because of the prohibition of chromite disposal in landfills by the EPA. Cu is highly selective for alcohol dehydrogenation but suffers from low activity and a propensity to sinter; thus, the addition of a second metal may not only increase dehydrogenation activity and catalyst lifetime and still maintain high selectivity, but also facilitate reduction of the Cu precursor to metallic Cu. The bimetallic Cu-Ni/SiO_2, Cu-Co/SiO_2 and Cu-Fe/SiO_2 catalysts investigated here were prepared by the addition of Ni, Co, and Fe to a prereduced Cu/SiO_2 catalyst and then characterized by their BET specific area, X-ray diffraction (XRD), Infra-Red spectroscopy (XPS), and temperature programmed reduction (TPR). Dehydrogenation and/or dehydration of isopropanol to acetone and/or propylene respectively over a family of silica-supported Cu, and bimetallic Cu–Ni, Cu–Co, Cu–Fe catalysts revealed that Ni (99%), Co (99,3%) and Fe (98.8%) were more active than copper monometallic and that all catalysts were 100% selective to acetone when supported on a high-temperature treated silica possessing weak acidic surface groups. In contrast, a silica support with a surface rich in acidic, oxygen containing functional groups allowed a dehydration pathway to form propylene. The different studies have provided evidence of the dissociative adsorption of isopropanol and the formation of isopropoxide species which decompose at high temperature to acetone and/or propylene. A Langmuir–Hinshelwood mechanism assuming that removal of the first hydrogen atom from the hydroxyl group was rate-determining fit the data well, provided physically and thermodynamically meaningful rate parameters, and explained the decrease in apparent energy (Eapp) at higher temperatures. In addition to hydrogen and acetone, which produced small rate inhibitions, inclusion of isopropanol (IPA) in the site balance was supported by in situ diffuse-reflectance infrared spectra. The heats of adsorption for IPA, H_2, and acetone obtained from the adsorption equilibrium constants in the rate expression were consistent with values reported by surface science and adsorption studies.

PP-V-18

STUDY OF THE CATALYTIC ACTIVITY OF CALCINED Ni/Mg/Al(La) HYDROTALCITES FOR METHANE DRY REFORMING REACTION

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Introduction

Considerable attention has been paid to the catalytic reforming of CH_4 with CO_2 to synthesis gas in recent years. This reaction (Eq.1) has very important environmental implications since both CH_4 and CO_2 contribute to the green house effect:

$$CH_4 + CO_2 \rightarrow CO + 2H_2 \quad (1).$$

They are also two of the most important abundant carbon-containing materials. Therefore, converting these two gases into a valuable synthesis gas may not only reduce atmospheric emissions of CO_2 and CH_4, but also satisfy the requirement of many synthesis processes in the chemical industry [1,2].

Great efforts have been focused on the development of catalysts which show high activity and stability. These catalysts are conventionally prepared by the wet impregnation method of different supports. This method is not fully reproducible and may give rise to some inhomogeneity in the distribution of the metal particles. Therefore, a new concept of catalyst may be required. Layered double hydroxides (LDH) are a class of synthetic two-dimensional nanostructured anionic clays. These types of catalysts also show interesting properties such as high surface area, memory effect and basic character [3]. The particular properties of these materials have been applied to several reactions such as CO_2 reforming of methane. In this paper, we intend to study NiAl-T hydrotalcites derived catalysts where T, represents calcination temperature, for methane dry reforming reaction.

Experimental

The NiAl-T hydrotalcite type catalysts were prepared by coprecipitation at constant pH of 11.0 with $(M^{2+})/(M^{3+})$ =2 (M = Ni, M^{3+} = Al) using an aqueous solution of $Ni(NO_3)_2\cdot 6H_2O$ and $Al(NO_3)\cdot 9H_2O$. The hydrotalcite-like materials were calcined for 8h at various temperatures, such as 500°C, 600°C, 700°C and 800° (θ = 5°C/min). The Chemical composition of the samples was determined by ICP method. X-Ray powder diffraction patterns were recorded in a X' PERT PRO MPD diffractometer. FTIR spectra were obtained with a PERKIN-Elmer spectrometer in the region of 4000-400 cm^{-1}. The BET surface areas were determined with a NOVA 2000e apparatus. The study of the reaction of methane reforming by carbon dioxide in presence of these catalysts was carried out into a tubular «U»-shaped quartz reactor at various temperatures (400°C-700°C). The catalyst were pretreated under hydrogen at 650°C for 12 h. Reaction mixture in proportion $CH_4/CO_2/Ar$ = (20/20/60 %), at a flow rate 20 ml/min was used.

Results and Discussion

The data obtained by chemical analysis results confirmed that the M(II)/M(III) mole ratio was close to the intended value of 2.

The XRD patterns exhibit the characteristic diffractions of hydrotalcite-like layered double hydroxide materials on NiAl non calcined catalyst case and no other crystalline phases are present. The thermal treatment of NiAl-T resulted in the disappearance of part of the layered structure of hydrotalcite and the formation of peaks attributed to the NiO and $NiAl_2O_4$ were detected.

By infrared spectroscopy, in the non-calcined sample, the obtained spectra reproduce the general features often reported for hydrotalcites-like compounds.

We have studied the reaction of dry reforming of methane by carbon dioxide in presence of the various catalysts at temperatures ranging from 400 to 700°C. At 650°C, the NiAl-T catalysts show significant conversions such as 41.2 %, 63.0%, 69.0% and 70.0% respectively on NiAl-500, NiAl-600, NiAl-700 and NiAl-800 for CH_4 conversions. The studied catalysts exhibit catalytic performances at 650 °C, which vary in the following sequence: NiAl-800 > NiAl-700 > NiAl-600 > NiAl-500.

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BIOMORPHIC CATALYSTS ON THE BASIS OF CERIUM-ZIRCONIUM MIXED OXIDE FOR SOOT COMBUSTION IN DIESEL ENGINES

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In the past decades, special attention has been paid to the oxidation of soot particulate emitted from diesel engines due to its harm to the environment and human health [1-4]. Systems on the basis of cerium-zirconium mixed oxides recently gained attention on the utilization for soot oxidation because of their high oxygen storage capacity [2]. In the present work CeO_2-ZrO_2 mixed oxide was synthesized with the use of waste biomass.

CeO_2-ZrO_2 (1:1) mixed oxide was prepared in the following way: pine sawdust (wood biomass with the approx size of 0.63-1.25 mm) was impregnated by solutions of corresponding nitrates in the ratio sawdust:mixed oxide = 10:1. Samples were dried and calcinated in air at 600 °C for 4 hours. The catalysts with 1, 3 or 5 % of manganese were prepared by impregnation, followed by drying and calcinations in air at 600 °C for 30 min.

Samples were characterized by methods BET, SEM and catalytic activity was measured in oxidation of model soot (carbon black (CB): N330n Degussa). 10% of CB was mixed with 90% of catalyst in zirconia ball miller for 40 min. Oxidation tests were held in NETZSCH STA 409 apparatus. Samples were heated from room temperature to 1000 °C (5°/min) in air flow (75 ml/min).

The results of surface area analysis and characteristic temperatures of carbon black combustion in the presence of various catalysts are shown in the Table.

Sample		$Ce_{0.5}Zr_{0.5}O_2$			
		pure	Mn, %		
			1	3	5
BET(m^2/g)		90	77	72	64
T_{max}, ^{0}C	1st peak	281	281	274	266
	2nd peak	372	369	356	353

It is important to mention that values of the surface area are rather high. For example, similar systems prepared by sol-gel method give the value of surface area equal to 48 m^2/g [5]. Pure support exhibits higher value of surface area than modified samples and increasing the content of modifier leads to decreasing the value of the surface area.

The combustion of carbon black occurs at 632 °C [3]. Pure cerium-zirconium oxide decreases the temperature of soot oxidation to 281 and 372 °C. Impregnation catalyst with Mn leads to further lowing of CB combustion temperatures (Table). Despite that surface area of Mn-modified catalyst is less than of the pure support, it is more active than pure CeO_2-ZrO_2, so manganese noticeably promotes soot oxidation. The positive influence of manganese in the process of CB combustion is also mentioned in the work [4]. Presence of two peaks on the DTA curves is discussed in literature [6]. We suppose them to be influenced by various factors: external surface area of the catalyst, which is available for the soot; extent of immediate contact CB with catalyst; oxygen mobility of the system.

High catalytic activity of examined systems can obviously be explained taking into consideration method of catalyst preparing. As it's known there are some mineral inclusions in the pine sawdust [7], in particular ions K^+ and Ca^{2+}, which are supposed to promote catalytic oxidation of soot [2]. So the support is initially provided with these actives species due to the method of synthesis. Besides according to data obtained with the help of SEM (Fig.1), using sawdust as matrix for preparing the catalysts leads to biomorphic structure of the final mixed oxides [8], i.e. they completely repeat the structure of the cellulose component of the wood. Thus obtained oxides exhibit besides high surface area also heightened shortness, which favours improving contact between soot and catalyst and in this way decreases the temperature of soot combustion.

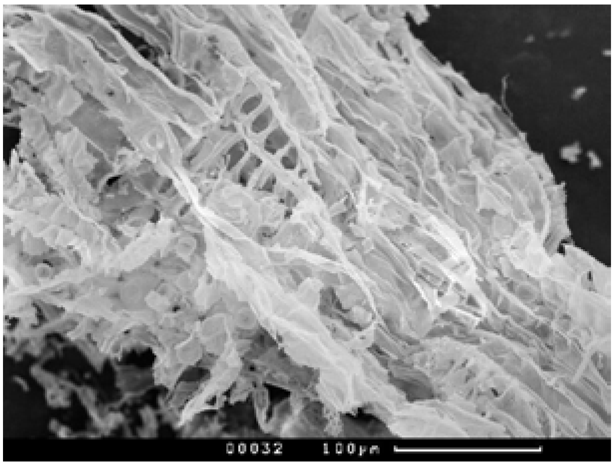

Fig. 1. SEM image of biomorphic CeO_2-ZrO_2.

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PP-V-20

Al,Cu-PILLARED CLAYS AS CATALYST IN ENVIRONMENTAL PROTECTION

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Introduction

Toluene is pollutant classified into the group of extremely dangerous compounds to the environment. Since toluene is a common contaminant in waters in the vicinity of oil refineries and the amount of toluene in drinking water should not exceed 1 ppm, preventing toluene from getting to water streams is an important task. The techniques usually adopted to achieve water purification from toluene are largely based on the use of phase separation methods and/or adsorption on active suspended materials as well as biodegradation [1]. There are several drawbacks of these methods, including the inability of quantitative removal of pollutants or the fact that they are time consuming and effective only at low concentration levels [2, 3]. Oxidation of toluene into nontoxic carbon dioxide and water might be the optimal solution.

In order to perform water purification from toluene Al-Cu pillared clay (PILC) was synthesized and tested as catalyst in the oxidation of toluene in two different catalytic reactions at moderate temperatures: catalytic wet peroxide oxidation (CWPO) using synthesized Al-Cu PILC as catalyst and electrooxidation in acid solution using Al-Cu PILC as electrode material.

Experimental

Smectite clay (≤ 2 μm) was pillared using procedure given by Kloidas *et al.* [4], while CWPO of toluene was carried out at 310 K analogue to the procedure given for phenol degradation [5]. The initial toluene and H_2O_2 concentrations were 2 mM and 40 mM, respectively. Aliquots were taken at predetermined periods of time and, after filtration analyzed by gas chromatography.

For the purpose of electrocatalytic reaction the synthesized Al PILC and Al-Cu PILC were enriched with carbon black, suspended in Nafion solution and deposited on glassy carbon. The reference electrode was Ag/AgCl in 1M KCl, while a platinum foil served as a counter electrode. The electrocatalytic activity of the PILC based electrodes were analyzed in 0.1 M H_2SO_4 containing 1 – 5 mM toluene solution using cyclovoltammetry.

Results and Discussion

In Fig. 1. are given the results obtained using gas chromatography for the monitoring of CWPO of toluene.

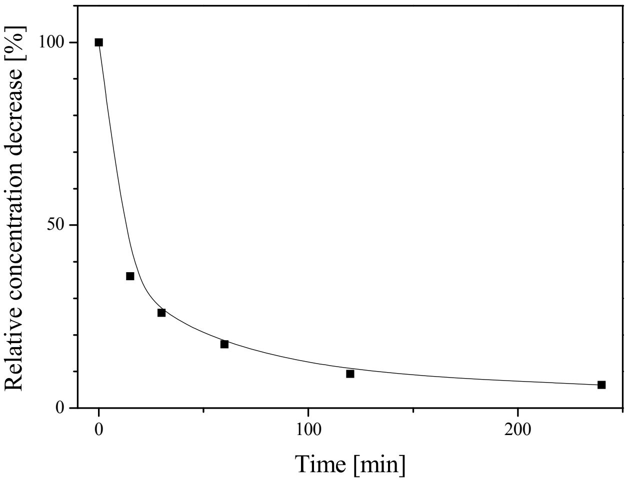

Fig. 1. Toluene degradation vs. reaction time

From the diagram can be concluded that approx. 90% of toluene initially present in the reaction system was removed within the first two hours of the reaction.

Satisfying results were obtained in the electrochemical process as well. The investigation carried out using carbon glass electrode and Al-PILC based carbon glass electrode showed no peak corresponding to the toluene oxidation.

On the other hand, each steady state voltammogram obtained using Al-Cu PILC based electrode in 0.1 M H_2SO_4 and in different concentration toluene solutions as a variable, showed broad anodic peaks at around 0.5V vs. Ag/AgCl. This peak current increased along with the increase of toluene concentration. The obtained anodic peaks can be ascribed to the electrooxidation of toluene. According to these results only Al-Cu PILC showed to be active for the toluene electrooxidation under the experimental conditions.

Conclusion

Both CWPO and electrooxidation confirmed the possibility of the use of synthesized Al-Cu PILC in the toluene oxidation reaction and should be employed in the environmental protection.

Acknowledgements

This work was supported by the Ministry of Science of the Republic of Serbia (Projects TR6712B and 142019B).

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PP-V-21

KINETICS OF THE HYDROXYMATAIRESINOL HYDROGENOLYSIS OVER PALLADIUM CATALYSTS

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Introduction

Knots, e.g. the part of the branch that is embedded in the tree, are harmful in pulp and paper manufacturing and should be removed before pulping [1]. Some years ago, large quantities of the lignan hydroxymatairesinol (HMR) were discovered in Norway spruce (*Picea abies*) knots [2]. Since lignans have anticarcinogenic [3] and antioxidative [4] effects, the waste material from pulping industry can be used for synthesis of pharmaceuticals and technical antioxidants. No other lignan has been found in substantial amounts in nature, therefore other lignans that are of great interest and importance should be synthesized starting from HMR. The lignan matairesinol (MAT) has high application potential. In our previous studies related to HMR hydrogenolysis, we have investigated the influence of support acidity for palladium catalysts supported on carbon [5], zeolites [6] and carbon nanofibres (CNF) [7]. It was concluded that the acidity of the support material has a great influence on the activity; for carbon and CNF supported palladium catalysts, the activity increased when the acidity increased. For palladium supported by H-Beta zeolites, having higher concentration of acid sites than carbon materials, the activity decreased with the acidity increase. Since the choice of catalyst support and the concentration of acid sites on the support have a great influence on the hydrogenolysis to HMR, it is important to study the effect of reaction conditions. The influence of mass transfer, temperature, reactant concentration and hydrogen pressure was studied.

Results and discussion

The main reaction network is presented in Fig. 1. There are two diastereomers of HMR, the isomer with RRR configuration (HMR 1) and the one with RRS configuration (HMR 2). The influence of hydrogen pressure was studied using a 5% Pd/C catalyst (Degussa) in an autoclave at hydrogen pressures from 5 to 40 bars. At low pressures the reaction rate increased, but at pressures higher than 25 bar the reaction rate decreased dramatically. It can be concluded that there is an optimum in activity not only as a function of acid site concentration but also as a function of hydrogen concentration. These observations are in agreement with the reaction mechanism presented in [5], where the first step is protonation of the hydroxyl group (with proton coming from the support material) followed by water abstraction and a hydride addition (hydrogen adsorbed on the catalyst surface) resulting in MAT. Too high concentration of acid sites or excess hydrogen retards the reaction.

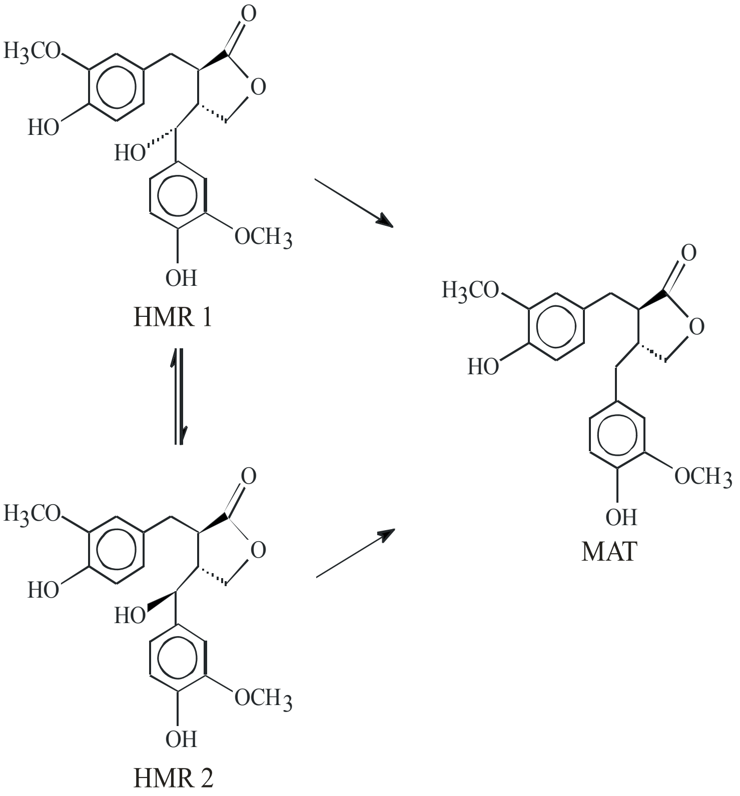

Fig. 1. The main reaction, hydrogenolysis of hydroxymatairesinol (HMR) to matairesinol (MAT).

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PP-V-22

THE NEW METHOD OF OBTAINING OF PURE HYDROGEN WITH USING CaO

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The method of steam conversion of fuel is a cheap and perspective method of obtaining of pure hydrogen. The obtained hydrogen is polluted by carbon contained gases, such as CO, CO_2 and CH_4. The calcium oxide may be effective using as a sorbent [1].

In the present work comparative analysis of using of calcium oxide as a sorbent for purification of hydrogen, obtaining from methane or methanol has been done. One has been done the complete thermodynamical modeling of equilibriums in the systems CaO – fuel – H_2O at the atmosphere pressure, and in the temperature interval of 700-900K, where fuel – CH_3OH or CH_4. The ratios CaO/fuel and H_2O/fuel have been changed at the calculations. The equilibrium compositions of gas and solid phases have been obtained.

The results show that optimal conditions of hydrogen purification at using as a fuel methane are $CaO/CH_4 = 2$ and $H_2O/CH_4 = 5$, and temperature 800K. Optimal conditions of hydrogen purification at using as a fuel methanol are $CaO/CH_4 = 2$ and $H_2O/CH_4 = 3$, and temperature 800K. But there is possible to achieve CO content equal 17 ppm at decreasing temperature to 750K at using methanol as a fuel.

The equilibrium compositions of gas phases of the systems CaO – fuel – H_2O are given in the table 1.

Table 1. Equilibrium composition of the systems CaO – fuel – H_2O at 800K, mol%.

Fuel	C(H_2)	C(CO)	C(CO_2)	C(CH_4)
CH_4	60,00	0,009	0,026	0,164
CH_3OH	65,20	0,012	0,027	0,313

The content of table 1 shows that, the purification depth from CO and CO_2 has been achieved identical for both of types of fuel. At the methanol using the more hydrogen reach mix is obtained. But this mix contains more methane. Since the methane is not catalytic poison, the methanol is more useful as a fuel.

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ONE-STAGE PRODUCTION OF HIGH QUALITY DIESEL FROM SUNFLOWER OIL OVER Pd/SAPO-31

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Introduction

In last decade production of biofuels from renewable sources has become more and more important and this tendency is expected to continue. There are many benefits of biofuels including domestic production of fuels, decreased greenhouse gas emissions, decreased dependence on fossil fuels, improvement of rural economies and increased national security.

Nowadays the mixture of vegetable oil fatty acid methyl esters produced by transesterification of various vegetable oils was found to be suitable to operate diesel engines. However this technology has numerous disadvantages [1]. These drawbacks can be eliminated if the vegetable oils are converted to a paraffin-rich mixture of hydrocarbons over conventional NiMo/Al_2O_3 and CoMo/Al_2O_3 catalyst. However this mixture consists of n-paraffins (90-95%), it is solid and possesses unfavorable cold flow properties, so it requires to be isomerized over suitable catalysts.

This work presents results on one-stage production of a diesel hydrocarbons with improved temperature characteristics from sunflower oil using Pd-SAPO-31 catalyst.

Experimental

SAPO-31 material was synthesized according to [2]. The calcined silicoaluminophosphate was Pd loaded by wet impregnation method followed by drying at 120 °C for 4 h and calcining at 600 °C for 3 h in air. Hydroconversion of sunflower oil was carried out using a fixed-bed, downflow, tubular SS reactor at $P = 1.2\text{-}3.0$ MPa, $T = 320 – 360$ °C, WHSV=0.9-1.7 h^{-1} and H_2/feed volume ratio = 1000-2000.

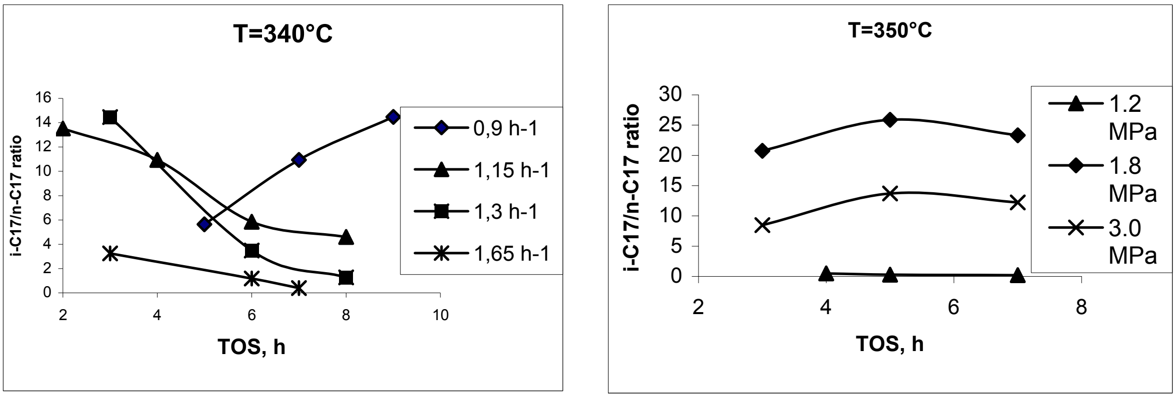
Results and discussion

Obviously, diesel production over Pd/SAPO-31 catalyst from vegetable oil is rather complicated process, the following reactions take place: hydrogenation of double bonds and C-O bonds in the molecules on the metallic sites, decarboxylation, dehydration and isomerization on the acid sites. Hydrogenation and decarboxylation of sunflower oil results in a formation of n-C17 paraffin predominantly, which is isomerized on acid sites of the catalyst as described in [3]. The yields of both diesel hydrocarbons and C_{17} fraction as well as i-C_{17}/n-C_{17} ratio in dependence on reaction conditions are shown in Table 1. The diesel fraction containing mono- and di-substituted isomers is essentially obtained at temperatures 340-350 °C and WHSV= 0.9-1.2 h^{-1}, the resulting product possesses high cetane number (>80) [1] and good temperature characteristics, in this case pour point of the product is as low as <-50 °C. It is seen (Table 1) that raise either reaction temperature or WHSV of the feed decreases yield of paraffins, and formation of oxygen-containing compounds is observed in this case what is unfavorable for diesel fuel.

Table 1. Yields of diesel hydrocarbons, C_{17} fraction and i-C_{17}/n-C_{17} ratio in resulting product in dependence on reaction conditions. Time-on-Stream = 6 hours.

T,°C	WHSV, h^{-1}	C_9^+ paraffins yield (from theoretical value)	C_{17} fraction	i-C_{17}/n-C_{17}
330	1.65	98.4	61.5	1.1
340	0.9	85.7	60.4	10.9
	1.15	85.7	68.6	5.9
	1.3	96.4	68.9	3.5
	1.65	99.9	68.4	1.2
350	0.9	79.0	56.7	11.7
	1.2	87.3	56.2	25.8
	1.5	98.8	72.6	0.5
360	0.9	69.5	46.0	16.8
	1.2	92.2	54.6	0.8
	1.5	90.2	65.2	0.2

It is seen also (Fig. 1) that isomerization activity of the catalyst depends on reaction conditions as well: a fast deactivation of Pd-SAPO-31 is observed at high WHSV and low reaction pressure. However, at optimal conditions stable performance of the catalyst is possible what permits to produce high-quality diesel from sunflower oil in a single reactor.



A). P=1.8 MPa. B). WHSV=1.2 h^{-1}.

Fig. 1. i-C_{17}/n-C_{17} ratio in resulting product in dependence on WHSV of the feed (A) and reaction pressure (B).

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AUTOCLAVE ENGINEERS COMPANY

SYSTEMATICAL APPROACH IN SELECTING A CATALYTIC REACTOR

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Selecting the right apparatus undoubtedly is of fundamental importance for competitive catalyst research. The choice of equipment should be not occasional but systematical especially for long-term and complex catalytic investigations. Since 1945 engineers of Autoclave Engineers Company (AE) have been continuously working at quality reactors for catalytic research [1]. Nowadays a practical system is developed by AE to help the investigator to choose a right catalytic reactor of any size (from miniature to pilot), pressure (vacuum to several hundred bar), temperature (sub-ambient to hundreds °C), materials (stainless steel and assorted high temperature, corrosion resistant alloys). Reactors can be also supplied with control systems of all levels. Only a part of examples is shown in Table 1.

Table 1. Application selection guide

Reactors	***Reactants***			***Typical Reactions***						
	Liquid/Solids	Gas or Vapor/Solids	Gas/Liquid/Solids	Hydrogenation	Liquefaction	Oxidation	Hydrotreating	Catalyst Testing	Hydrocarbon / Petroleum Studies	Hydro Liquification
Fixed Bed Reactors	+	+	+	+		+	+	+		
Continuous Stirred Tank Reactors	+		+	+	+	+	+	+		
Berty Stationary Catalyst Basket		+		+		+		+		
Berty «Micro» Stationary Catalyst Basket		+		+		+				
Robinson-Mahoney Stationary Catalyst Basket	+		+		+		+	+		
Robinson-Mahoney «Micro» Stationary Catalyst Basket	+		+		+		+	+		
Mahoney-Robinson Spinning Catalyst Basket			+	+	+			+	+	+
Carberry Spinning Catalyst Basket	+	+	+	+	+	+	+	+		
Harshaw Stationary and Falling Catalyst Basket			+	+		+		+		
Caldwell Stationary Catalyst Basket		+		+		+		+		

Usually a researcher should ask the following questions when selecting the right apparatus for his research:

1) Are the kinetics of the reaction relatively fast or is the process you are trying to simulate a continuous flow process? If either are true, consider tube (fixed bed) reactor based systems like BTRS-Jr.® or BTRS 900.

2) Can a fluid be the dominant component of the mixture (perhaps a process solvent) and is unsupported catalyst a viable possibility? If yes, consider a High Pressure Laboratory (Batch) Reactor.

3) Is fluid the dominant component and are you using supported catalysts? If yes, select the Robinson-Mahoney stationary catalyst basket design as the preferred tool for most applications.

4) Do you need sequential reactions where first the solid catalyst interacts with the gaseous reactants followed without interruption by a reaction where the solid catalyst is immersed in a liquid phase? If yes, consider the Harshaw «Falling Basket» design [Fig.1]. This reactor design is especially appropriate for kinetic measurements, because you definitely know the moment of beginning of the reaction.

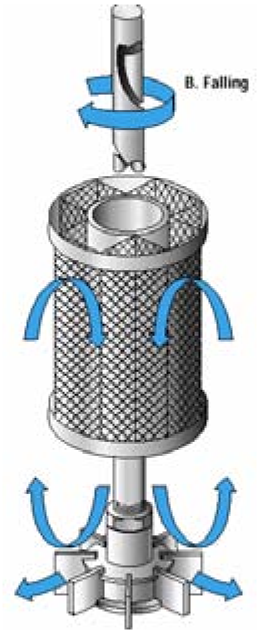

Fig.1. Harshaw «Falling Basket».

5) Is your reaction a Solid-Gas reaction where the reaction kinetics are relatively slow? There are three designs to consider, Berty, Carberry and Caldwell.

Sometimes your catalytic research may require special equipment. AE has a long history in custom design that fulfills the customers need.

References

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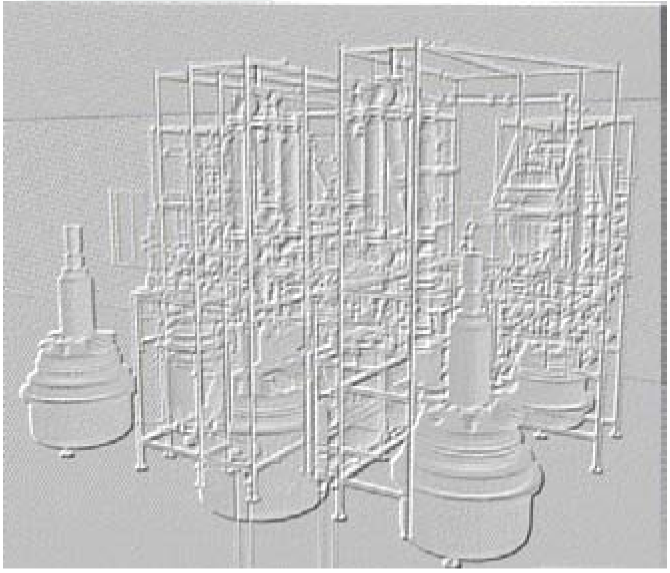
GROUP OF CATALYSTS TESTING



The group of catalysts and supports testing performs: comparison and lifetime tests, studies of catalytic process kinetics and catalysts activity in the catalysts deactivation processes, tests of laboratory samples, experimental batch catalyst samples and commercial samples (fresh and unloaded from commercial setups).

An approach to control of catalytic properties is primarily determined by the fact that catalysis is a kinetic phenomenon which is associated with an increase of chemical reaction rates under catalysts action. For this reason, it is reasonable to use specific rate of a chemical reaction calculated per unit catalyst volume (weight, volume, surface) as a criterion of catalytic activity.

The flow-circulating method involving different modifications and improvements of schematic diagrams of a technological setup, associated with process peculiar features, is the most promising method of determining catalysts

Catalytic processes performed on the setup of the department

Amination of aromatics

NOx reduction by ammonia and syngas

SO2 reduction by methane

Gas-phase nitration of aromatics

Hydrocracking

Hydrolysis of COS and HCN during cleaning of syngas

Oxidation of binary liquid hydrocarbons

Oxidative dimerization of methane

Oxidation of hydrocarbons, ammonia, sulfur dioxide, hydrogen sulfide

Oxidative ammonolysis of propane (propylene) into acrolein

Purification of ethylene (propylene) from acetylene fractions

Steam and air reforming of methane

Dehydrogenation of hydrocarbons

Fischer-Tropsch process

Steam conversion and oxidation of CO

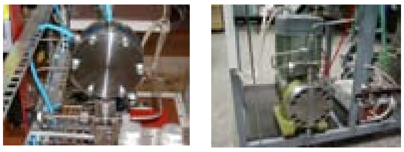
Steam reforming of methanol (ethanol)

Synthesis of ammonia, methanol, vinyl acetate

Synthesis of unleaded gasoline from gas condensate and by-products of oil refining

Tests are performed in the setups supplied with reactors, 1 to 100 ml in volume, at atmospheric pressure and under conditions of increased pressure (to 100 bar) and maximal temperatures as high as 850 C

The reactor designs allow investigations of granules of commercial catalysts as well as honeycomb catalysts reinforced with a stainless steel net or their fragments



To obtain reliable data on catalyst activity, we use differential reactors with an external steam-gas mixture circulation

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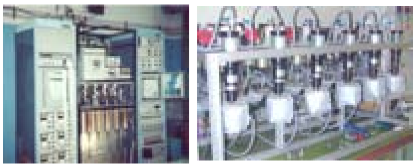
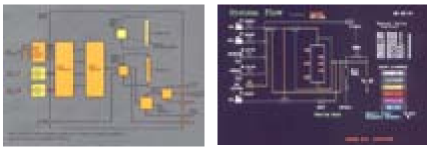


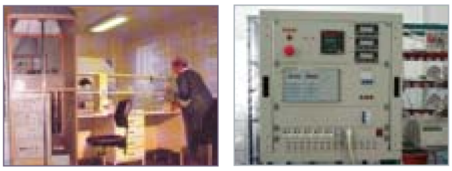
For shorten the time of choice of new catalysts and to increase efficiency of life tests, the group uses multi-reactor automated setups



Experiments can be controlled either by local control devices or a PC

To prevent condensation of initial reagents and reaction products, the testing technique is installed in a thermal box with calorifer

To provide security of the personnel from injurious substances, the systems are placed in transparent sealed boxes



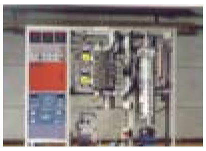
The setups are supplied with a signaling and blocking systems to provide twenty-four-hour testing without personnel, safe performance of the process, especially at high pressuer

Turn-key automated catalytic systems are developed and manufactured for own requirements and supplied on order

SETUP FOR OIL REFINING PROCESSES

"BIFORMING"

"DEWATERING OF HYDROGEN-CONTAINING GAS DURING REFORMING"



"REFORMING"

"THERMAL-STEAM STABILIZATION OF CRACKING CATALYSTS"

"HYDROREFINING"

"UTILIZATION OF CASING-HEAD GASES/OIL GASES INTO LIQUIDS UNDER CONDITIONS OF BARRIER DISCHARGE"

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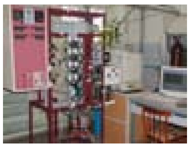
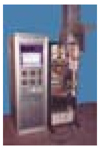
DEVICES FOR STUDYING PROCESSES OF NITROGEN AND NITROGEN COMPOUND MAKING INDUSTRY

"AMMOXIDATION"

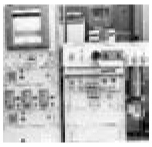
"STEAM/AIR CONVERSION
OF METHANE AND CO"



"STEAM/AIR CONVERSION
METHANE AND CO
AT HIGH PRESSURES"



"AMMOXIDATION ON
MONOLITH CATALYSTS"



"METHANATION"

SYSTEMS FOR OTHER PROCESSES

"EPOXIDATION OF ETHYLENE
(PROPYLENE)"

"OXIDATION OF
SULFUROUS ANHYDRIDE"

"CLEANING OF
TEREPHTHALIC ACID"

"REDUCTION OF SO2
WITH METHANE"

"REDUCTION NO$_x$
WITH AMMONIA (SINGAS)"

SETUP FOR CIRCULATION AND PULSE IMPREGNATION AS WELL AS ACTIVATION AND REGENERATION OF CATALYSTS

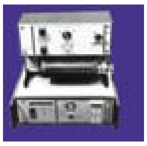
"CIRCULATION IMPREGNATION
OF REFORMING CATALYSTS"

"CIRCULATION AND PULSE IMPREGNATION
OF CATALYSTS AT A PRESSURE OF 10 BAR"

"CATALYSTS IMPREGNATION WITH
AUTOMATIC SOLUTIONS PROPORTIONING"

"STUDY OF ACTIVATION AND
REGENERATION OF CATALYSTS"

SPECIAL-PURPOSE SYSTEMS FOR UNIVERSITIES AND CHEMICAL COLLEGES



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WE PROVIDE: OPTIONAL DESIGN OF SEPARATE UNITS AND DEVICES, DELIVERY OF LABORATORY, RESEARCH FACILITIES, MANUFACTURING EQUIPMENT AND DEVICES

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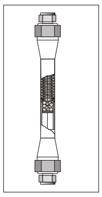
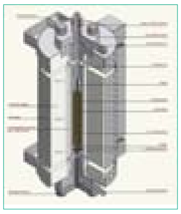
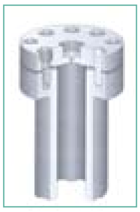
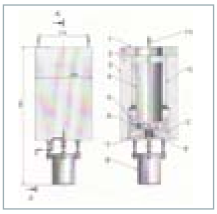




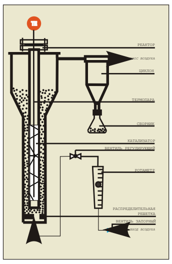


DESIGN AND MANUFACTURING OF DIFFERENT ASSIGNMENT LAB FURNACES



"FAST-RESPONSE FURNACE WITH A FAN"

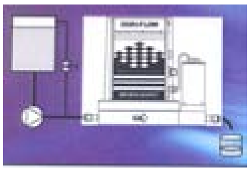
"OPEN FURNACE"



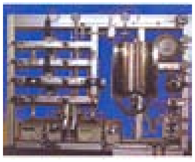
"FURNACE WITH A FLUIDIZED LAYER"

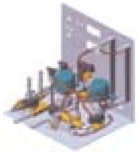
"TUBE FURNACE"

DEVELOPMENT OF GAS AND LIQUIDS DOSING SYSTEMS



DEVELOPMENT OF DEVICE CONSTRUCTS





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XVIII International Conference on Chemical Reactors

CHEMREACTOR-18

Editor: Professor Alexander S. Noskov

The abstracts are printed as presented, and all responsibilities we address to the authors. Some abstracts underwent a correction of misprints and rather mild editing procedure.

Compilers: Tatiana V. Zamulina

Computer processing of text: Natalia A. Tsygankova

Cover design: Nina F. Poteryaeva

Disk maker: Alexey A. Spiridonov

Подписано в печать 12.09.2008 Формат 60×84/8
Печ.л. 69,75 Заказ N 70 Тираж 250

Отпечатано на полиграфическом участке издательского отдела
Института катализа им. Г.К. Борескова СО РАН
630090, Новосибирск, пр. Академика Лаврентьева, 5