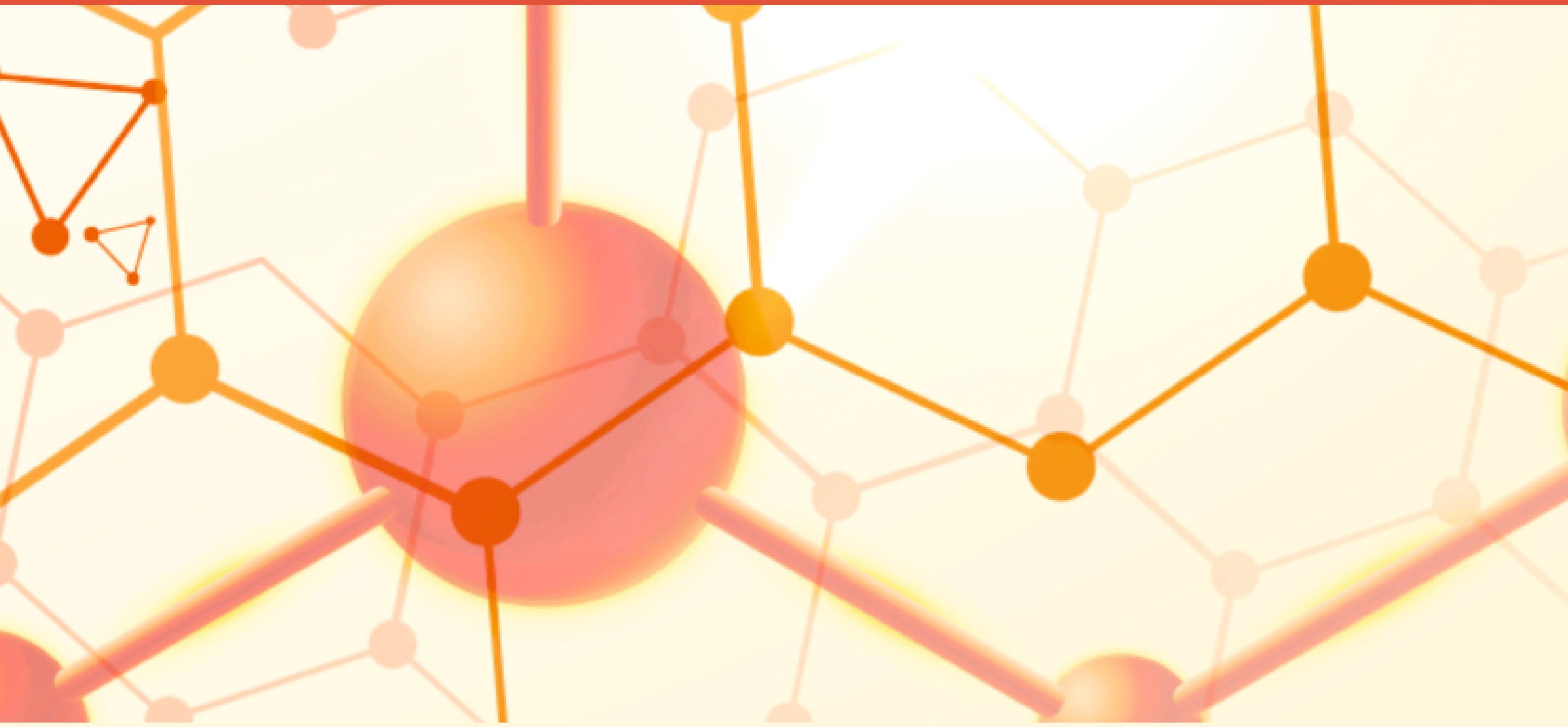
June 17-21, 2024



ABSTRACTS

Vladimir, Russia

Boreskov Institute of Catalysis
N.D. Zelinsky Institute of Organic Chemistry RAS
Lomonosov Moscow State University
Siberian Branch of the Russian Academy of Sciences
NTI Center of Excellence "Hydrogen as a basis of low carbon economy"

XII International Conference
MECHANISMS of CATALYTIC REACTIONS

Vladimir, Russia

June 17-21, 2024

ABSTRACTS

Novosibirsk-2024

УДК 544.47+66.09
ББК 24.54
М45

М45 Mechanisms of Catalytic Reactions (MCR-XII). XII International Conference. / June 17-21, 2024, Vladimir, Russia [Electronic resource]: Abstracts/ eds.:
Prof. V.I. Bukhtiyarov, Prof. O.N. Martyanov, Prof. E.A. Kozlova, Prof. V.V. Kaichev, Prof. Y.V. Zubavichus, Dr. A.A. Gabrienko, Dr. I.E. Soshnikov
– Novosibirsk: BIC, 2024.
– URL: http://www.catalysis.ru/resources/institute/Publishing/Report/2024/Abstracts-MCR-XII_2024.pdf
– ISBN 978-5-906376-56-5

В надзаг:
Boreskov Institute of Catalysis, Novosibirsk
N.D. Zelinsky Institute of Organic Chemistry RAS, Moscow
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Siberian Branch of the Russian Academy of Sciences, Novosibirsk
NTI Center of Excellence "Hydrogen as a basis of low carbon economy", Novosibirsk

The main topics are:

- Study of catalysts and catalytic reactions at the atomic-molecular level
- Kinetics of catalytic reactions
- Advanced methods for study the mechanism of catalytic reactions
- Theoretical methods in catalysis
- Young Scientists Section

УДК 544.47+66.09
ББК 24.54

ISBN 978-5-906376-56-5

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- Siberian Branch of the Russian Academy of Sciences, Novosibirsk
- NTI Center of Excellence "Hydrogen as a basis of low carbon economy", Novosibirsk

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PLENARY LECTURES

PL-1 ÷ PL-6

PL-1

Single-Atom and Nano-Scale Catalytic Systems Studied with Artificial Intelligence

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Integration of artificial intelligence (AI) algorithms into chemical research has become increasingly pivotal due to the rapid growth in experimental data volumes, the complexity of correlating phenomena at molecular and nanoscale levels, and the urgent need for a qualitative leap in the development of universal chemical technologies [1]. This report focuses on the application of AI in the field of catalysis, specifically in the design of new catalysts. We explore cutting-edge trends in the development of AI applications for the creation of next-generation synthetic methods [2,3], the analysis of experimental data [4], and the understanding of the mechanisms of formation and operation of chemical micro-reactors [5]. Particular emphasis is placed on the use of AI to develop universal photocatalysts [6], highlighting how these technologies enable unprecedented precision and efficiency in catalyst design. This approach not only promises to enhance current catalytic processes but also to discover novel catalysts with optimized activity and selectivity. In this presentation, single-atom and nano-scale catalytic systems studied with artificial intelligence will be the main focus.

Acknowledgment: Supported by the Russian Science Foundation (grant 22-13-00247).

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PL-2

Increasing Activity of Heterogeneous Catalysts by Metal-Oxide Interactions

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The choice of oxide support material for transition metal nanoparticles is well-known to critically affect their catalytic and electrochemical activity. Also, many strategies have been proposed for the promotion of oxide catalysts by transition metals. However, our understanding of metal-oxide interactions in applied catalysts remains limited due to the challenging nature of such studies. In this talk, I will discuss how the combination of cutting-edge simulations and experiments can shed light on the activity of metal-oxide interfaces in various catalysts.

Often nanoparticle-support interactions improve the activity of catalysts due to the altered binding energies of reaction intermediates at the boundary of the nanoparticle-support interface [1], e.g. in Pd/ZrO_2 catalysts for CO oxidation [2]. Another important process taking place on the interface is the transfer of several electrons between the nanoparticle and the oxide necessary to equilibrate their Fermi levels. For example, in Pt/CeO_2 catalysts the electron transfer can induce an average charge up to ~0.1 e on Pt atoms and reduce some surface Ce cations from 4+ to 3+ [3,4].

Such changes in the charge state of oxide cations due to interaction may lead to dramatic changes in their catalytic and electrochemical activities. For example, the electron transfer from Ni support to MoO_x overlayer results in a rather uncommon 3+ oxidation state on Mo centers, making them excellent catalysts for electrochemical H_2 evolution [5]. In turn, the electron transfer from Cu to supported ZnO films does change in the charge on Zn but changes the composition of the films to $ZnOH_{0.8}$ under hydrogenation conditions [6], making them highly active in CO_2 reduction to methanol.

Finally, the catalytic activity may be increased by the spillover of the reacting species through the metal-oxide interface. For example, the increased activity of Zn-ZrO_2 catalysts for CO_2 hydrogenation to methanol upon Pd doping was attributed to the ability of Pd to activate H_2 molecules consumed in large quantities during methanol synthesis [7]. Upon Pd doping, the reaction rate becomes limited not by the scarcity of surface H* species, but by the high activation barriers for their diffusion towards the active sites on the Zn-ZrO_2 surface. Such high barriers limiting the spillover kinetics can be alleviated by engineering a distribution network for H* within the catalyst in the form of carbon nanotubes supporting Pd nanoparticles [8].

The obtained understanding of metal-oxide interactions helps to propose various strategies for the improvement of catalytic activity in other reactions and accelerates the pace of catalyst development.

PL-2

Acknowledgment: These studies received funding from the National Research Foundation of Singapore under the NRF Fellowship NRFF13-2021-0126, European Community (FP7-NMP.2012.1.1-1 project ChipCAT, Reference No. 310191), King Abdullah University of Science and Technology, SABIC, and National University of Singapore through Flagship Green Energy program (R-279-000-553-646).

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PL-3

Synchrotron Radiation Techniques for the Atomic-Level Studies of Catalysts: New Capabilities to be Empowered by SKIF

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X-ray techniques, such as X-ray powder and single-crystal diffraction (XRD), X-ray absorption spectroscopy (XAFS), X-ray photoelectron spectroscopy (XPS), etc., provide essential atomic-level insights into the mechanisms of catalytic reactions, which can be exploited as a basis for the knowledge-driven design of next-generation catalytic systems with improved and balanced set of catalysis-relevant characteristics (activity-selectivity-stability against deactivation under reaction conditions). Modern synchrotron radiation facilities bring this idea to life to the full extent due to the complementary use of different techniques in particular implemented in advanced modes, e.g., time-resolved, microprobe, in situ/operando, and so forth. The high brilliance of synchrotron sources enables studies of minute quantities of rare and transient species as well as combinatorial high-throughput screening of extended sample series. Synchrotron techniques could reconcile bulk and surface sensitivity, long- and short-range order zooming the region-of-interest from a whole catalytic reactor down to single atoms.

During last few years, the Boreskov Institute of catalysis has been coordinating the construction of a modern synchrotron radiation facility called SKIF, which is located in the science city of Kol'tsovo nearby Novosibirsk. Major civil works are to be completed by the end of December 2024 (Fig. 1). The construction site covers the area of 30 hectares. The accelerator complex designed by the Budker Institute of Nuclear Physics will include a 200 MeV linac, a full-energy booster, and a 3 GeV main storage ring with a circumference of 476 m featuring a record-low horizontal emittance of 75 pm·rad [1].

Three out of six first-priority beamlines were specifically designed to meet needs of catalysis-related research. These include 1-2 «Structural diagnostics», 1-4 «XAFS spectroscopy and magnetic resonance», and 1-6 «Electronic structure».

The report outlines the current status and roadmap of the project implementation. Main directions of the SKIF scientific program relevant to catalysis are described. Prospective capabilities of the synchrotron radiation facility are illustrated with recent examples on concerted use of XRD, XAFS, XPS, and other related techniques to unveil atomic-level structure of catalysts and its evolution in response to environmental parameters (temperature, reactive gas atmosphere).

Fig. 1. An aerial view of the SKIF construction site as of May, 2024: 1 – injector building, 2 – main storage ring building, 3 – beamline 1-3 "Fast processes" external building, 4 – beamline 1-5 "Hard X-ray diagnostics" external building, 5 – building of stands and testing facilities, 6- building of engineering facilities

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for SRF SKIF, Boreskov Institute of Catalysis.

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PL-4

Heterogeneous Hydrogenations of Alkynes and Alkenes – From Mechanisms to Operando Spectroscopy of Model Reactors

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The hydrogenation processes of unsaturated hydrocarbons are of major importance, both fundamental and applied. Homogeneous hydrogenations with H_2 catalyzed by transition metal complexes in solution are generally well-understood in terms of the reaction mechanism. They often involve the oxidative addition – reductive elimination stages, whereby the two H atoms that are added to an unsaturated reactant come from the same H_2 molecule (pairwise H_2 addition). In contrast, heterogeneous hydrogenations are usually expected to involve addition of random H atoms (non-pairwise) – the key aspect of the mechanism for hydrogenation on metal surfaces formulated by Horiuti and Polanyi [1], which is now generally accepted. However, as novel and improved analytical techniques are developed, new mechanistic information becomes available. In 1987 it was shown [2] that the use of parahydrogen (p-H_2) in homogeneous hydrogenations can lead to a major (1000-fold and more) enhancement of the NMR signals of reaction products and intermediates. Observation of this effect requires pairwise hydrogenation mechanism, in agreement with what is expected for metal complexes in solution. However, in the past 15 years it was experimentally established that pairwise hydrogenation is also possible on supported metals as well as on many other types of heterogeneous catalysts [3].

Pairwise H_2 addition mechanism is observed to operate concurrently with the main (non-pairwise) hydrogenation mechanism (such as Horiuti-Polanyi) and can contribute measurably (5-10 % in some cases) to the reaction conversion. The combined experimental and DFT study clearly demonstrates that pairwise H_2 addition is improbable for any reaction mechanism that involves the formation of H* adatoms on a catalyst surface. This is particularly true for the Horiuti-Polanyi hydrogenation mechanism operating via dissociative H_2 chemisorption and participation in the reaction of H* adatoms randomized on the catalyst surface by diffusion. Currently, the search for the alternative reaction pathway which, unlike the dominating Horiuti-Polanyi mechanism, can achieve pairwise H_2 addition to an unsaturated hydrocarbon, continues.

In addition to mechanistic studies, the spectroscopic and imaging modalities of NMR are also promising for advanced in situ and operando characterization of catalytic processes and operating reactors under relevant reaction conditions [4]. However, this area of research has to overcome the existing obstacles. One major problem of NMR is its intrinsically low sensitivity. Furthermore, in the studies of liquids and gases in catalysts and reactors, the heterogeneous nature of such objects leads to another major problem – poor spectroscopic resolution and the associated loss in chemical specificity. Thus, efficient approaches are required to minimize distortions of spectra and images of liquids and gases in highly inhomogeneous media and to boost the sensitivity of NMR and MRI in catalysis research and beyond.

One efficient approach to improve spectral resolution is the optimization of reactor geometry. By optimizing a packed catalyst bed structure, the linewidth of ^1H NMR signals of fluids were reduced by more than 10-fold (Figure 1a), which also improved detection sensitivity. A more dramatic sensitivity boost is provided, as mentioned above, by the use of p-H_2, which is particularly suited for the studies of hydrogenations and other catalytic processes that use H_2. Furthermore, hydrogenation with p-H_2 naturally produces multiple-quantum nuclear spin coherences that are useful for implementing a different NMR line-narrowing approach. Yet another, non-intuitive, possibility to improve spectral resolution for heterogeneous media is to perform experiments at zero- or ultra-low magnetic fields, where chemical specificity is available through the characteristic line patterns associated with nuclear spin-spin couplings in molecules. This regime is characterized by small (sub-Hz) NMR linewidths which are totally insensitive to sample heterogeneity (Figure 1b). Besides, NMR and MRI studies of samples in metal containers become possible [5].

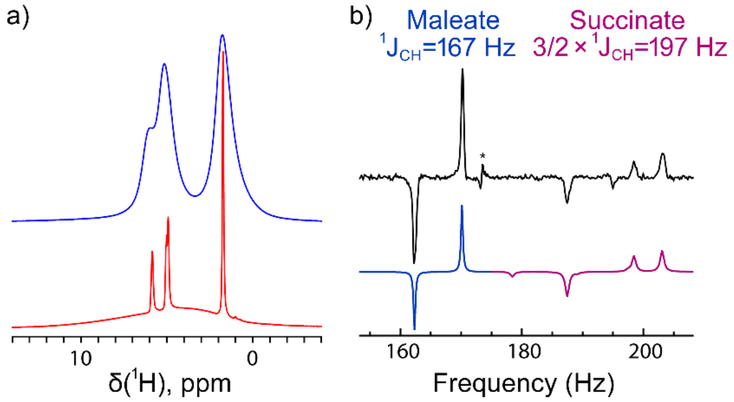

Fig. 1. a) ^1H NMR spectra (300 MHz) of propylene in a granular bed with a regular (upper blue trace) and optimized (lower red trace) structure. b) Experimental ZULF NMR spectrum (upper black trace) detected during catalytic hydrogenation of dimethyl acetylene-dicarboxylate in a titanium reactor under uninterrupted bubbling of p-H_2, and the predicted spectrum (lower color-coded trace) showing spectroscopically resolved contributions of hydrogenation products - dimethyl maleate (blue) and dimethyl succinate (pink).

Acknowledgement: This work was supported by the Russian Science Foundation, grant 22-43-04426.

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PL-5

New Opportunities for Mechanistic Investigations in Catalysis Using Routine Kinetic Data

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Kinetic studies are among the most efficient research methods for the investigations of the complex catalytic reactions. However, as “kinetic investigation can be a painstaking job” [1], it is often ignored when establishing mechanistic details. In our opinion, it is associated to a considerable degree with experimental difficulties of the correct determination of the reaction rates usually used as the main estimated parameters in kinetic studies. In addition, when the precatalyst activation and the deactivation of the active species proceed (that are the attributes of the majority of the catalytic processes), their complicated connections with the main catalytic cycle lead to the high sensitivity of the observed reaction outcomes to a wide set of uncontrolled factors. This feature results in possible misrepresentations of the observed rate laws. As the way for the overcoming of the circumstance stated above, we have suggested to use the measurements of the relative reactivity or the related value of the differential selectivity in parallel or competing reactions involving the several (at least two) products formation by the same catalyst. Opposite to the reaction rate, the relative reactivity of two substrates as well as the differential selectivity of the active catalyst responsible for their conversion are independent of its concentration (that can vary significantly as a result of controlled variation in the experimental conditions, or due to the action of uncontrollable factors) and are determined by its nature. As the useful method for accurate measurements of both the relative reactivity and the differential selectivity in parallel or competing reactions we have offered to use so-called phase trajectories, being in the simplest case the interdependencies of the concentrations of the products from these parallel or competing reactions [2]. The key feature of this approach is that only primary kinetic data about these concentrations are needed without any differentiation procedure potentially raising additional errors.

Comparing the differential selectivity using the phase trajectories under pointed variations of the reaction conditions, a set of the essential fundamental features of Pd-catalyzed cross-coupling reactions have been revealed [2] concerning the nature of truly active species, the set of realized during the reactions elementary steps and their possible rate-determining character. However, the analysis of the patterns of the relative reactivity and of the differential selectivity for the elucidation of the mechanistic details of the complex catalytic reactions can be provided by the similar approach in the course of the sole catalytic experiments. As the main analyzed parameter in this case the shape of the phase trajectory should be considered. Depending on the complexity of the reaction under consideration, by the choice of the appropriate mathematical treatment of raw kinetic data it becomes possible to provide the linearity of the phase trajectories. In such case any deviation of the experimentally obtained phase trajectory from linearity will indicate a change in the active catalyst responsible for the formation of the products of the catalytic reaction.

Another approach can be realized to track possible changes in the nature of the active catalyst in the course of the reaction. The matter is the comparison between the experimental phase trajectory and the simulated one by numerical integration procedures for differential equations described the trajectory under the specific mechanistic hypothesis. A divergence of any area of the simulated and experimentally obtained phase trajectories unambiguously indicates the inconsistency of the proposed hypothesis and experimental patterns. Analyzing the character of such divergence and carrying out checking experiments it becomes possible to establish the mechanistic patterns of the catalytic reaction [3].

Another alternative for the identifying of the fine mechanistic details of catalytic reactions with only integral kinetic data in hand on the concentrations of the products of competing reactions are the recently used time-resolved Hammett correlations [4]. Comparative studies of such patterns can be used to obtain essential information about mechanistic peculiarities of the complex catalytic reactions.

The individual examples of the approaches stated above are discussed in the report. Using the combinations of these approaches with the recent opportunities provided by machine learning algorithms it becomes potentially possible to reveal fine mechanistic details of the complex catalytic reactions with available equipment and limited experimental efforts.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 24-23-00382.

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PL-6

Artificial Intelligence Methods for Catalytic Properties Descriptor Identification and Catalyst Design

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Activity and selectivity of a catalyst are in general difficult to predict, in particular from first principles. The problem lies in the extreme complexity of the relation between the atomic composition of a material and its catalytic properties at realistic temperatures and pressures. We demonstrate how to bridge this complexity with artificial intelligence (AI) on several examples.

Single-atom metal alloy catalysts (SAACs) have recently become a very active new frontier in catalysis research. The simultaneous optimization of both facile dissociation of reactants and a balanced strength of intermediates' binding make them highly efficient and selective for many industrially important reactions. However, discovery of new SAACs is hindered by the lack of fast yet reliable prediction of the catalytic properties of the sheer number of candidate materials. We address this problem by applying a compressed-sensing symbolic-regression approach [1,2] parameterized with density-functional inputs. Besides consistently predicting high efficiency of the experimentally studied SAACs, we identify more than two hundred yet unreported candidates [3]. Some of these candidates are predicted to exhibit higher stability and efficiency than the reported ones. Our study demonstrates the importance of finding descriptors directly from data, as well as provides a recipe for selecting best candidate materials from thousands of transition-metal SAACs for various applications.

Moreover, using subgroup discovery, an artificial-intelligence approach that discovers statistically exceptional subgroups in a dataset, we develop a strategy for identification of most important parameters of a catalytic material and competing mechanisms of a catalytic reaction. The approach is used to develop physical understanding of hydrogen activation at SAAC's, address the problem of converting CO_2 to fuels and other useful chemicals [4], and design novel electrocatalysts for oxygen evolution reaction based on transition-metal-organic frameworks.

Acknowledgement: This research was supported by Ministry of Science and Education of Russia, agreement RF-2251.63222X0004 (13.2251.21.0194, 075-10-2022-119).

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KEYNOTE LECTURES

KL-1 ÷ KL-8

KL-1

Mechanisms of C_2–C_4 Alkene Transformation on Zeolites Modified with Metal Cations

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Light alkenes (C_2–C_4) are important building blocks [1-4] used to produce valuable chemicals, such as simple aromatic hydrocarbons (benzene and toluene), higher alkenes, unsaturated carbonylic and carboxylic compounds, etc. Among others, zeolites modified with metal cationic species are considered to be perspective catalysts for light alkene transformation with high conversion and selectivity. Further development of industrially relevant catalysts requires the mechanisms of C_2–C_4 alkene transformation of metal-modified zeolites to be understood. In particular, the role of metal-containing cationic sites has to be clarified and the key surface intermediates have to be identified.

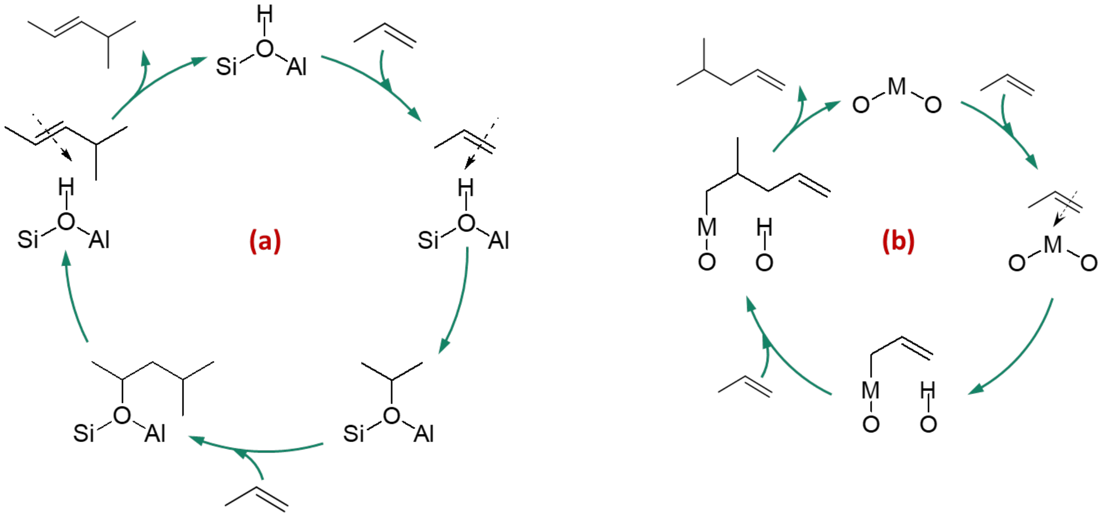

Fig. 1. Alkene Oligomerization with the Assistance of
(a) Zeolite Brønsted Acid Sites (Si–O(H)–Al) or (b) Metal-Containing Cationic Sites (M)

When metal cationic species are present, the catalytic properties of a zeolite change remarkably as compared to unmodified H-form zeolite performance [5-8]. Therefore, it is reasonable to suggest a change in the transformation mechanism (Figure 1). However, the ability of metal-containing sites (Lewis acid sites, LAS) to catalyze alkene transformation has been debated, with the key role often given to zeolite Brønsted acid sites (BAS) [9, 10]. In this report, the recent spectroscopic and theoretical studies will be discussed which provide certain evidences speaking in favor of LAS involvement in alkene transformations. In particular, the results obtained by ^{13}C MAS NMR, FTIR spectroscopy, and DFT calculations on C_2–C_4 alkene transformation on ZSM-5 and BEA zeolites modified with the metals of 11–13 groups (Zn, Cu, Ag, In) will be presented.

KL-1

Based on the available data, the key surface intermediates of alkene transformation as well as the main reaction pathways will be highlighted. As obtained for different metals, the primary intermediate is the metal-alkene π-complex, and the properties of such π-complexes are different depending on the nature of the metal cationic site. The other important intermediate is the metal-allyl species which provides alkene oligomerization and aromatization or, for some metal species, oxidation to yield such valuable compounds as benzene and toluene or acrolein. The suggested mechanisms of light alkene transformation with the assistance of LAS will be discussed in this report.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 22-13-00029.

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KL-2

Multispectral Diagnostics of Catalytic Reactions in Microfluidic Systems

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Optimization of the reaction conditions is an important step for improving efficiency of the catalyst utilization and meeting strict environmental aspects. The catalytical reactions benefit from reducing noble metal concentrations, improving their TONs, using nontoxic solvents and milder conditions. Microfluidic systems offer unique capabilities for high-throughput screening. Reduced reagent consumption and the ability to quickly change the composition of incoming streams and the operating mode make microreactor systems convenient for screening the influence of many parameters on product yield and process selectivity. The general workflow for autonomous microfluidic system is shown in Fig. 1. It is based on initial guess of the reaction parameters (0) and the loop (1–4) with the feedback from online spectral diagnostics of the catalyst and products (3). A rational search for optimal experimental conditions should be based on the analysis of a large amount of available literature data and preliminary numerical experiments

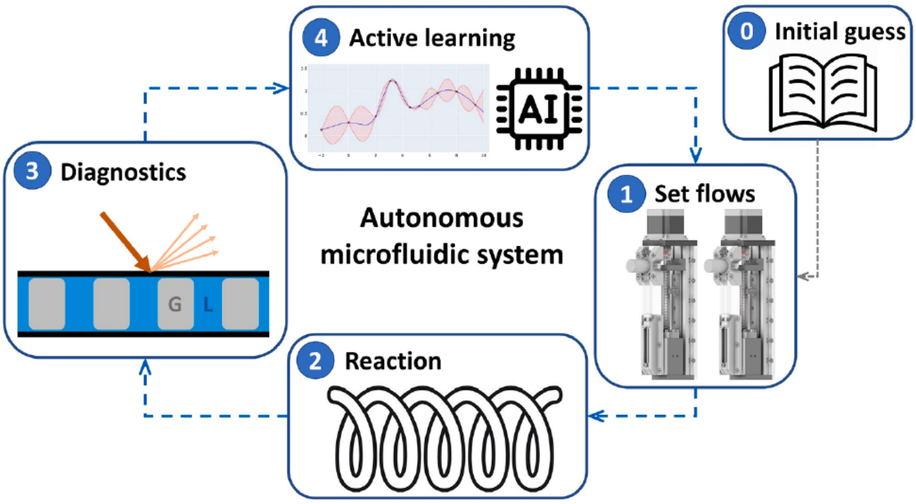

Figure 1. The scheme for autonomous microfluidic system, combining recommendation system, syringes for variation of reagent concentrations, delay line enabling needed reaction time, spectral feedback analyzed by machine learning methods.

Feedback in the autonomous system is provided by spectral data measured from the capillary in situ. The development of new spectral monitoring cells and their integration with microfluidic systems allows online monitoring of both the composition of the reaction mixture via IR-Fourier and Raman spectroscopy methods and the state of metal centres by using X-ray absorption spectroscopy. The knowledge about current and target descriptors of the catalytic system (reagent concentrations or metal local environment) is supplied to the optimisation that balance via exploration and exploitation in the space of reaction parameters and find their optimal combination. In this work we discuss in details integration of spectral monitoring to two industrially important homogeneous catalytical reactions.

Homogeneous hydroformylation is applied for aldehyde and alcohols production. Rh metal complexes allow tandem one pot reactions for converting olefins directly into alcohols and more often such reactions are performed in microfluidic flow regime both relevant from academic research and industrial automatization. The reaction yield depends on the coordination of Rh atoms or formation of Rh clusters, therefore knowledge about local atomic and electronic structure of active sites under industrial conditions is important. Rh K-edge X-ray absorption spectroscopy (XAS) is unique tool to probe coordination of Rh, however up to date there were no reports of application of this methodology to hydroformylation in microfluidic biphasic flow. Our work demonstrates the experimental setup and transmission cell developed for segmented flow operando measurements. The quantitative analysis of XAS data was performed with the library of theoretical spectra computed for relevant monomeric, dimeric and small clusters species. We demonstrate that under segmented flow presence of amine species in the reaction prevents formation of Rh clusters in favor of Rh dimers.

Hydrosilylation of alkenes is another industrially important catalytic reaction for producing organosilanes. This process is often based on the homogeneous Pt-catalysts. Given the high cost of platinum and its irretrievable "scattering”, the new approaches that can reduce its consumption is an important goal in the modern chemistry. Heterophase (biphase) catalytic systems for hydrosilylation offer additional advantages in terms of high activity, product separation and recycling. However, large-scale synthesis in heterophase conditions is complicated by constrained mass and heat transfer. The droplet microfluidic regime is of particular interest due to improved mass and heat transfer while being compatible with many diagnostic devices. The reaction rates were higher in capillaries due to increased specific area between catalyst and reactants, and easy separation of catalyst and product phases was achieved. We found Raman spectroscopy to be an convenient tool for online monitoring of the conversion from each droplet. Finally, we demonstrated the application of 3D-printed microfluidic reactors that provide compact design of reaction units with complex topology. These results open new perspectives for process automation and industrial applications of biphasic hydrosilylation reactions in droplet flow mode.

Acknowledgement: The research was supported by the Strategic Academic Leadership Program of the Southern Federal University ("Priority 2030").

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KL-3

Coadsorption Phases of Oxygen and Chlorine on Silver Surfaces and their Role in the Ethylene Epoxidation Reaction

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Adsorption of chlorine and oxygen on silver surfaces has been studied since the beginning of the 1970s [1,2]. The research works in this field are related with the industrial reaction of ethylene epoxidation [3,4], in which chlorine-containing species play role of promoters.

The noticeable progress have been achieved in separate studying of O/Ag(111) and Cl/Ag(111). On the first stage of research, the structure of chlorinated silver (111) surface has been studied by low-energy electron diffraction (LEED), room-temperature scanning tunnelling microscopy (RT-STM) and extended x-ray adsorption fine structure spectroscopy (EXAFS) [5,6]. The application of low-temperature scanning tunnelling microscopy (LT-STM) in a combination with density functional theory (DFT) calculations makes possible recognition of all atomic structures formed by chlorine on Ag(111) [6]. In particular, it has been shown that complex patterns observed by many authors may be explained by the formation and evolution of the domain walls in the chemisorbed chlorine layer, by the surface reconstruction (3×3) and by the appearance of surface chloride clusters Ag_3Cl_7 at saturation [6].

As for the oxygen adsorption on Ag(111), Rovida et al. [1] reported formation of the (4×4) structure in LEED after the prolonged dosing of molecular oxygen on Ag(111) at 200 °C, for which oxide-like structural models have been suggested [7]. In the 2000s, LT-STM has been applied to the O/Ag(111) system [8]. As a result, an $Ag_{1.83}O$ oxide-like model appeared for the *p*(4×4) phase [8]. In 2006, a new structural model for the *p*(4×4) phase containing two triangles of six silver atoms within the unit cell (Ag_6) has been suggested [9-10]. However, recently, Andryushechkin et al. [11] revised the Ag_6-model and unambiguously demonstrated the existence of two types of the *p*(4×4) reconstruction, which can be described as Ag_3O-O_x (x=0÷6) and Ag_6O models, respectively.

Coadsorption of chlorine and oxygen remains poorly studied for so far. In particular, the first experimental real-space studies of the structures formed by Cl and O on silver (111) surface have been reported in 2018 [12]. The authors found that molecular chlorine dissociates on the Ag(111)-*p*(4×4)−O surface at both 300 and 77 K, preserving the unchanged period of the reconstruction. At 300 K, chlorine atoms tend to replace oxygen atoms from the ditches between the Ag_6 -triangles. At 77 K, chlorine atoms adsorb mainly in the centres of the Ag_6 triangles forming likely the Cl--O bonds.

In the present work, coadsorption of chlorine and oxygen on the Ag(111) surface has been studied with low-temperature scanning tunnelling microscopy in a combination with DFT calculations. Chlorinated Ag(111) surface was exposed to molecular oxygen with a pressure of 1 Torr for 140 minutes at sample temperature of 500 K. Depending of amount of preadsorbed chlorine, we have discovered a series of new well-ordered coadsorbed structures containing both oxygen and chlorine atoms: (5×5), (7×7), (4√3×4√3)R30°. The DFT analysis has shown that all the structures correspond to the reconstruction of silver (111) surface (see Fig.1, as an example). Moreover, the reconstruction is formed by silver triangles with atoms occupying either fcc or hcp positions. Most of chlorine and oxygen atoms occupy nearly fourfold positions similar to those in the (4×4)-O and (3×3)-Cl reconstructions. A characteristic feature of all coadsorbed structures is the presence of bright objects, which we associate with

Cl_3-O, and Cl-O complexes. Using DFT, we calculated positions of O 1s XPS line for all oxygen atoms in the structures. Oxygen atoms in the fourfold positions correspond to the XPS peak at 528 eV (as in the Ag(111)-*p*(4×4)-O), while oxygen in the Cl_3-O, and Cl-O complexes corresponds to the XPS peaks at 531 eV and 530 eV, respectively.

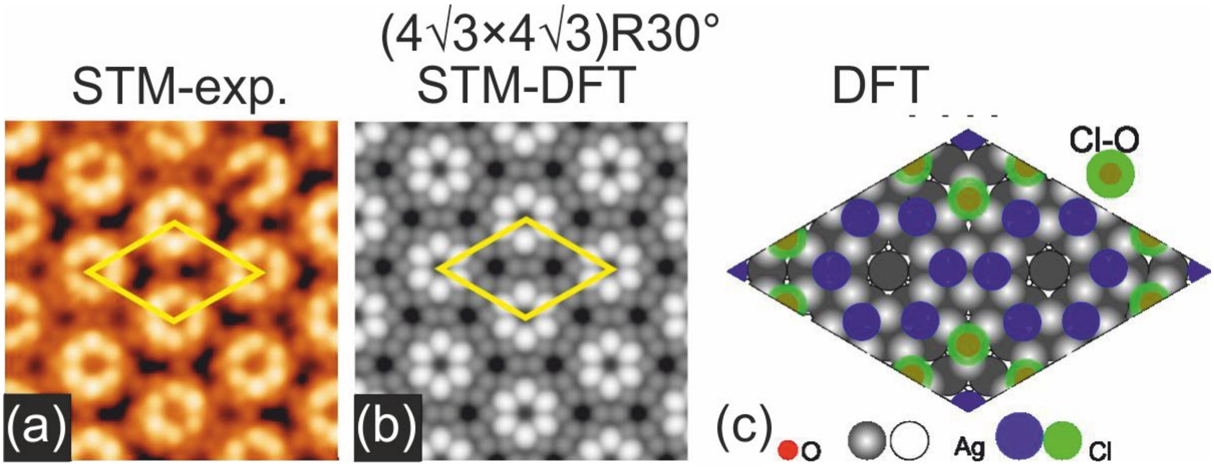

Fig.1. *The experimental (a) and theoretical (b) STM images of the (4√3×4√3)R30º structure. (c) The DFT-optimized model of the (4√3×4√3)R30º structure. The appearance of bright rosettes is associated with the formation of Cl-O type structures.*

Thus, we demonstrated that chlorine replaces oxygen in the fourfold positions at temperature close to the reaction conditions. We can conclude that the role of chlorine in the reaction of ethylene epoxidation is in the formation of Cl-O bonds, in which oxygen appears to be electrophilic. Our result may provide key information into the establishing of the promoting role of chlorine in the epoxidation process.

Acknowledgement: This study was supported by the Russian Science Foundation under grant No. 24-63-00037. We also thank the Joint Supercomputer Center of RAS for providing the computing power.

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KL-4

"Metal – Oxygen Vacancy" Interfaces as Active Sites of M/$Ce_{1-x}Zr_xO_2$ (M=Ni, Ru, Rh, Pt) Catalysts

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In recent years, there has been a growing interest in the study of catalytic systems containing metal centers and oxygen vacancies in close contact. The unique properties of Ni-, Ru-, Pt- and Rh-containing catalysts supported on cerium-containing oxides in a number of industrially important reactions were demonstrated to be related with ease of red-ox transitions of ceria-based oxides. Our studies have been carried out aimed at establishing correlations between the structure and catalytic properties of M/$Ce_{1-x}Zr_xO_2$ catalysts in three reactions in which the organization of interphase boundaries plays a major role: methanation of CO and CO_2 (M = Ni, Ru, Rh) [1] and water gas shift (M = Pt) [2-4]. For the catalysis of all three reactions, the active centers are apparently metal-oxygen vacancy pairs in the region of the metal/oxide interface. To experimentally test this assumption, the catalytic properties were compared with data on the length of metal/support interfaces and the degree of reduction of support crystallites. The reaction mechanisms were studied by joint analysis of the results of macrokinetic measurements (the effect of temperature, reagent concentrations), *in situ* IR spectroscopy and DFT modeling. To carry out the proposed work, it was necessary to ensure the homogeneity of the composition, structure and morphology of both $Ce_{1-x}Zr_xO_2$ carrier nanoparticles and supported metal nanoparticles.

Modern methods of X-ray diffraction, spectroscopy and electron microscopy were used to determine the structure of the catalysts and especially the metal/oxide interfaces. Particular attention is paid to studying the structure of samples under conditions of catalytic reactions in the *in situ* mode or samples after catalytic experiments in the *ex situ* mode. Original methods have been developed for analyzing the dynamics of diffraction and PDF patterns of catalyst samples in reduction/oxidation cycles, allowing us to clarify the nature of the interaction between the support and deposited metals. Quasi *in situ* XPS was used to study the state of Ce and deposited metals under the catalytic conditions.

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KL-5

Study of the Mechanism of Photocatalytic CO_2 Reduction over Semiconductor Photocatalysts

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The current trend towards carbon footprint reduction as well as growing energy consumption requires the creation of new or modernization of existing energy production systems. Realization of this concept includes development of renewable energy sources, reduction of greenhouse gas emissions, and improvement of energy efficiency of processes. The introduction of CO_2 in the production of new fuels will close the carbon cycle and contribute to addressing both greenhouse gas emissions and increased energy demand. Traditional catalytic technologies for carbon oxide transformation require elevated temperatures and pressures, which implies significant energy costs. The development of photoinduced processes driven by solar irradiation will reduce the costs and carbon footprint of CO_2 reduction processes. Photocatalytic reduction of CO_2 to form alcohols and hydrocarbons is a promising process that mimics the function of natural photosynthesis [1].

The main factor hindering the practical implementation of photocatalytic processes is the lack of efficient and stable heterogeneous photocatalysts operating under the influence of visible light. Recently, more attention of researchers has been attracted by an organic polymer material - graphite-like carbon nitride g-C_3N_4, which has the properties of a semiconductor with a band gap of 2.7 eV and a band structure suitable for photocatalytic reduction of CO_2 [2]. For the successful development, modification and subsequent implementation of these photocatalysts, it is necessary to understand the nature of the catalytic action and an understanding of the mechanism of activation of the CO_2 molecule, the cleavage of the C-O bond, and knowledge of key intermediates and elementary reactions occurring on the surface of the catalyst. The first step in this direction is the *in situ* study of catalysts during the activation of the CO_2 molecule, both in the absence and presence of water.

The lecture systematizes data on approaches applied to the synthesis of photocatalysts based on graphite-like carbon nitride. The relationship between the characteristics of materials based on graphite-like carbon nitride and their activity and selectivity for organic products in the reduction of carbon dioxide is discussed. In addition, the study of the mechanism of the CO_2 reduction reaction using DRIFTS and XAS methods in *in situ/operando* mode will be considered.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 24-13-00416.

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KL-6

Mechanism of Catalytic Transformation of White Phosphorus Tetrahedron in the Coordination Sphere of Transition Metal Complexes

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The development of modern phosphorus chemistry proceeds in various priority directions focused on creation and design of new ecologically friendly methods for preparation of phosphorus compounds and materials with practically useful chemical and physical properties [1]. White phosphorus (P_4) is main source for preparation of phosphorus derivatives which allows access to practically important phosphorus ligands and biologically active materials. However, the industrial pathway usually involves an environmentally unsafe P_4 chlorination process accompanied with the formation of huge amounts of toxic P-Cl by-products.

Transition-metal mediated white phosphorus activation and functionalization are currently attracting increasing attention as an ecological alternative for preparation of important phosphorus products [2,3]. However, the mechanism of catalytic transformation and follow up functionalisation of white phosphorus tetrahedron in the coordination sphere of transition metals has not well studied and currently not fully understood.

Herein, we report the investigation of the mechanism of catalytic activation and transformation of white phosphorus tetrahedron in the coordination sphere of transition metal complexes. It has been found that P_4 tetrahedron can be transformed to the zig-zag-*PPPP* chain and can act as η^1-ligand in the coordination sphere of Co-subgroup complexes [4,5]. Moreover, the nature of the ligand at the metal centre can adjust the reactivity of the metal atom in this process and help to stabilize new unknown oligophosphorus intermediates derived from starting P_4 molecule assisting their following functionalization [5-7].

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-13-00427.

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KL-7

Design of CrO_x-ZrO_2-SiO_2 Catalysts for Non-Oxidative Propane Dehydrogenation

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Production of propylene via thermal and catalytic cracking of hydrocarbons doesn't satisfy the growth of its industrial demands, and the gap is continuously widening. Therefore, propane dehydrogenation processes become increasingly important. The advantage of the oxidative dehydrogenation of propane is its exothermic nature, while the formation of oxidation products and explosion hazard make it less attractive. Non-oxidative propane dehydrogenation (NPDH) has been implemented in industry (Oleflex processes that use platinum catalysts and CATOFIN processes that employ chromium oxide catalysts), but the development of new catalysts with the reduced content of toxic chromium, enhanced selectivity, stability and regeneration ability remains an urgent task.

This work focuses on the design of CrO_x-ZrO_2-SiO_2 catalysts of NPDH . The effectiveness of a shot-time oxidative treatment for the regeneration from carbon deposits was also studied. Several ways of catalyst modification were proposed:

1. "One-pot" simultaneous synthesis of all components was found to be promising for uniform distribution of active sites in contrast to traditional impregnation methods that produce large Cr_2O_3 particles inactive in NPDH. Raman, XRD and XPS analysis were used to reveal the interaction between components. SiO_2 co-precipitated with other components acts both as a textural promoter and stabilizer that prevents crystallization of Cr_2O_3 and ZrO_2. This method provides high dispersion of Cr^{n+} and coordinatively unsaturated Zr^{4+} sites. As a result, transformation of Cr^{6+} species to Cr^{3+} doesn't lead to the sintering and/or crystallization of the catalyst particles. The reducibility of Cr^{6+} species was studied by TPR-H_2 and XPS.

2. The catalyst efficiency was increased by altering the synthesis of the active component. CrO_x-ZrO_2 was co-precipitated on rice husk-derived SiO_2 (CrZr/SiO_2) or directly to rice husk followed by calcination (CrZr/RH). Both methods ensured high CrO_x-ZrO_2 dispersion and increased catalytic activity. The CrZr/SiO_2 sample turned out to be the most efficient in NPDH at 500 and 550°C. Cr/ZrSi prepared by impregnation showed the lowest activity because of the large size of Cr_2O_3 crystallites, which made them inactive in NPDH.

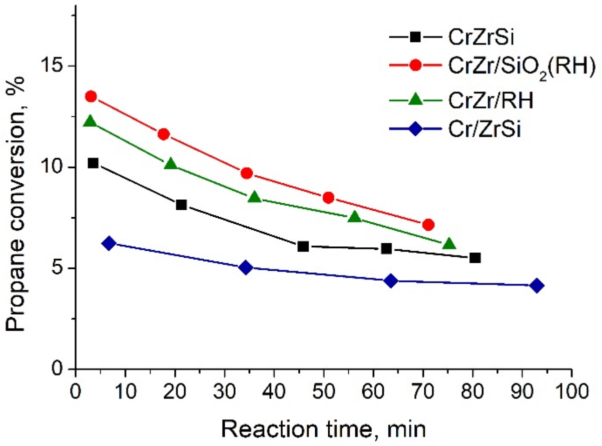

Fig. 1. Propane conversion for NPDH (550°C) catalysts prepared by different methods.

3. Modification with a small amount (0.05, 0.5 and 1 wt.%) of Ru or Pt enhanced the catalyst performance. The close interaction with a noble metal decreased the activation energy of Cr^{6+} reduction from 79.2 to 77.7 kJ/mol. Appearance of CO_2 and carbonate bands in the FTIR spectra of adsorbed CO confirmed the high activity of the catalyst sites. The catalyst surface was modified by the glow-discharge plasma treatment. According to the FTIR of adsorbed CO data the plasma treatment strongly decreased the bridging adsorption of CO on Ru, i.e. increased the Ru dispersity.

A glow-discharge plasma treatment of the 1RuCrZr/SiO_2 catalyst increased the conversion of propane at 500°C not compromising its high selectivity to propylene formation. The 5%H_2/Ar plasma appeared to be more efficient than the pure Ar one. Thus, treating the catalysts in the low-temperature glow discharge plasma is an effective way to form active sites of NPDH.

A shot-time oxidative treatment was applied for catalysts regeneration. The degree of carbon deposit removal was analyzed by the differential scanning calorimetry and Raman spectroscopy. The proposed procedure allows the efficient regeneration of the catalyst in the same reactor, which eliminates the loss of the catalyst and reduces the cost of its loading and unloading.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 22–23–00445. The authors acknowledge support from the Lomonosov Moscow State University Program of Development for providing access to the XPS instrument.

KL-8

The Paradigm of Single-Atom Alloy Catalysts in the Selective Hydrogenation of Alkynes

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Single-atom alloy (SAA) catalysts are a type of catalyst that refers to highly dilute alloys in which atoms of the catalytically active metal (Pd, Pt, Ru) are isolated from each other by atoms of a second (host) metal (Zn, Cu, Au, Ag, Ga, In) that is inactive or of low activity in the target process [1-4]. This isolation leads to the formation of single-atom active sites with identical adsorption and catalytic properties on the surface of the alloy or bimetallic nanoparticle and prevents the formation of multiatomic sites. As a result, the degree of uniformity of the active sites of SAA catalysts is much higher than that of mono- or bimetallic counterparts. Furthermore, the selectivity of the catalyst is significantly increased. As a result, SAA catalysts are attracting increasing attention for use in a variety of catalytic reactions.

This lecture will focus on our recent progress in the development of SAA PdAg/Al_2O_3 catalysts for selective hydrogenation reactions.

Several aspects will be discussed:

1) Preparation and characterization of powdered PdAg/Al_2O_3 SAA catalysts.

2) Effect of Ag:Pd ratio on the efficiency of powdered SAA catalysts in the liquid-phase hydrogenation of substituted alkynes and the gas-phase hydrogenation of acetylene.

3) Preparation, characterization and catalytic properties of novel PdAg/Al_2O_3 SAA catalysts with «egg-shell» distribution for industrial application in acetylene hydrogenation.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-13-00301.

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ORAL PRESENTATIONS

Section 1: Study of catalysts and catalytic reactions at the atomic-molecular level
OP-I-01 ÷ OP-I-26

Section 2: Kinetics of catalytic reactions
OP-II-01 ÷ OP-II-16

Section 3: Advanced methods for studying the mechanism of catalytic reactions
OP-III-01 ÷ OP-III-05

Section 4: Theoretical methods in catalysis
OP-IV-01 ÷ OP-IV-04

Young Scienists section
OPs-01 ÷ OPs-20

OP-I-01

Abatement of VOCs over Non-Noble Metal Catalysts at Near-Ambient Conditions by Ozon-Catalytic Oxidation (OZCO)

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Total catalytic oxidation processes with atmospheric oxygen are commonly used to eliminate volatile organic compounds (VOCs) from waste gases emitted by industrial plants and vehicles [1]. Highly active noble metal catalysts can effectively remove VOCs when the temperature of the exhaust gases exceeds 200-250°C. (fig.1 (1) - Pd/Al_2O_3). However, in many cases, the temperature of the exhaust gases is insufficient to complete oxidation with atmospheric oxygen. This is specific problem for catalytic purification of the exhaust gases of automobile engines during their cold start or at idle, as well as the exhaust gases of paint and varnish industries. Therefore, VOCs removal from gas streams at temperatures below 200°C is a significant challenge.

The problem can be solved by using ozone as an oxidizing agent. Gas-phase oxidation of VOCs can occur in the presence of ozone at temperatures as low as 200-250°C (see fig.1 (2) gas-phase oxidation by ozone). The use of a catalyst can significantly decrease the temperature of VOC oxidation by ozone enabling VOC abatement at near-ambient temperature range (fig.1 – (3) Mn/Al_2O_3). This process is known as ozone-catalytic oxidation (OZCO) and is currently under intensive global study [2,3].

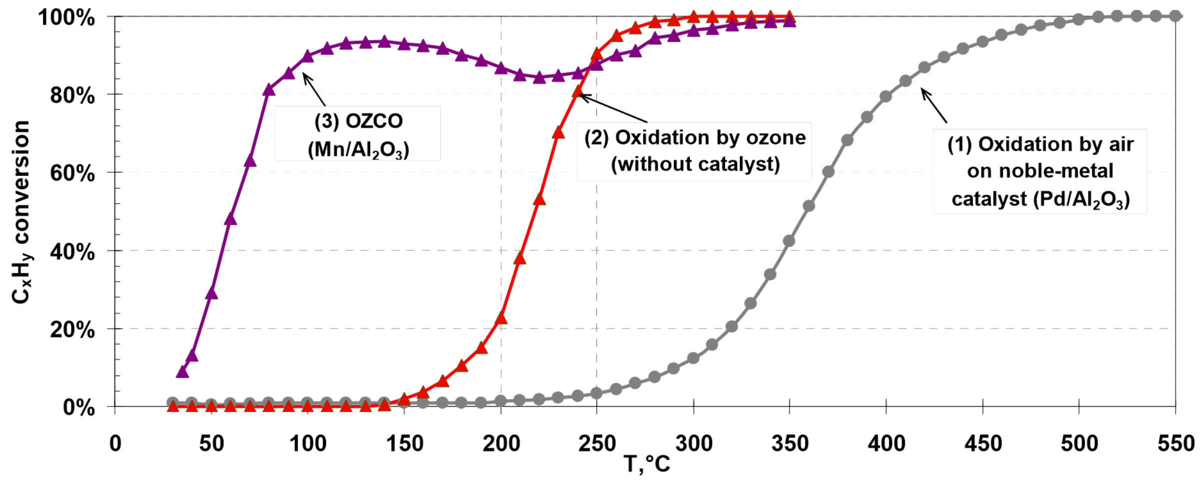

Fig. 1. Efficiency of C_xH_y removal (n-butane was used as a model VOC) from air flow as a function of temperature at GHSV = 150 000 h^{-1} in a course of: (1) - convention catalytic oxidation by molecular oxygen; (2) - oxidation by O_3 in gas-phase; (3) - ozone-catalytic oxidation (OZCO).

Excellent efficiency of ozone-catalytic oxidation at 20-100°C can be explained on the basis OZCO process mechanism, which includes three main stages:

$$O_3 \rightarrow O_2 + O^* \qquad (R1)$$

OP-I-01

$$O^* + O^* \rightarrow O_2 \qquad (R2)$$

$$O^* + C_xH_y \rightarrow xCO_2 + y/2H_2O \qquad (R3)$$

According to this scheme ozone easily decomposes to highly reactive oxygen species O* (stage R1) on the surface of the appropriate catalyst favoring their further reaction with VOC molecule (stage R3).

Our study focused on the relationships between catalyst performance in the OZCO process and its activity in O3 decomposition. A number of supported catalysts containing oxides of V, Cr, Mn, Fe, Co, Ni, Cu and Zn have been studied. The data obtained suggest that optimum catalytic performance can be achieved by balancing the reaction rates at the R1 and R3 stages and minimizing the contribution of O* recombination (stage R2).

Our results clearly show that the appropriate design of the OZCO catalyst can significantly decrease ozone consumption and provide efficient VOC abatement at near-ambient conditions.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-13-00214.

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OP-I-02

Insight into the Mechanism of Hydrogen Evolution Reaction over Dark TiO_2 – Based Photocatalysts

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Development of TiO_2 with a highly defective structure, named as black or dark titania [1,2], is an important approach in the field of photocatalysis today since this opens good opportunities for practical applications. In the modern literature, this field is widely presented for individual and composite photocatalytic systems. To prepare the dark TiO_2 materials, the following methods were used: (1) high-temperature H_2 treatment (or high pressure H_2 treatment, etc.); (2) application of Ti^{3+}-based precursors (mainly, $TiCl_3$) followed by thermal treatment. The pulsed laser ablation (PLA) technique is a promising approach to prepare dark TiO_2 as well as wide spectra of photocatalytic composites. The PLA method allows organizing both stabilized oxygen vacancies and interstitial Ti^{3+} cations which are uniformly distributed in the crystalline lattice of titania.

The present work is focused on the detailed study of the role of Cr^{3+}-containing sites as a promoter of stabilized defect structure possessing high catalytic properties of dark TiO_2 prepared by PLA in the hydrogen evolution reaction (HER).

Dark TiO_2 samples were prepared by PLA technique using Nd:YAG laser (LOTIS TII, LS2131M-20 model) with a wavelength of 1064 nm [3]. Two main series of black TiO_2 photocatalysts with varying Cr^{3+} promoter additives were studied using XRD, Raman, FTIR, DRS, and photoluminescence spectroscopy, and also O_2-TPO and H_2-TPR techniques. The catalytic properties were tested in the HER in 20 % glycerol-water solution as a sacrificial agent under the near-visible irradiation.

It is shown that the Cr-containing sites allow stabilizing the defect structure of the dark TiO_2 and increasing its catalytic activity in comparison with the P25 Degussa TiO_2 and TiO_2 (Hombifine). The behavior of TPO/H_2-TPR profile depends on the Cr-containing promoter in dark TiO_2 as well as pretreatment conditions such as He/air calcinations before the temperature-programmed experiments.

In the report, effect of the Cr-containing promoter on the defect structure, reaction ability toward TPO/H_2-TPR, optical properties, and catalytic activity of the dark-TiO_2 photocatalysts in the HER will be discussed.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 19-73-30026.

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OP-I-03

PdFe Catalysts for Diclofenac Hydrodechlorination in Water: Mild Reduction, Mild Reaction

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Introduction

Hydrodechlorination (HDC) of chlorinated micro toxicants in diluted water solutions is a good method of water cleaning. Thus, the products of diclofenac (DCF) HDC are much less toxic, than diclofenac, and diluted HCl formed as by-product is also environmentally affordable [1]. The properties of the most efficient Pd catalysts can be further improved by the aimed choice of a support, promoter and preparation method. In the literature, little attention is paid to the conditions of palladium reduction from the oxide before catalyst testing in HDC of DCF. Mild reduction at 30°C can be very cost effective, but its efficiency needs to be proven. In this work the influence of support nature (Al_2O_3, ZrO_2, ZrO_2-SiO_2), and addition of iron (0.5 or 10 wt.%) on the ability of PdO to be reduced to Pd^0 was studied using *in-situ* and *ex-situ* XPS, *in situ* DRIFT of adsorbed CO and other methods. Catalytic activity was compared in DCF hydrodechlorination in batch and flow conditions at 30°C.

Materials and Methods

The catalysts were prepared by incipient wetness method using the solution of Pd and Ni nitrates in distilled water, and calcination at 400°C. They were reduced in harsh (320°C, H_2, 2 h) or mild (30°C, H_2, water suspension, 2 h) conditions. Catalytic tests were performed in batch (catalyst 0.05 g, 15 ml of DCF solution in water, 150 mg/L, 30°C, H_2 0.6 L/h) or flow reactor (catalyst 0.1 g, DCF solution in water, 75 mg/L, 30°C, H_2 0.6 L/h). The products were analyzed by HPLC on Agilent 1100 Series instrument with Zorbax SB-C18 column 15 cm (Agilent Technologies Inc., USA), UV detector at 278 nm and 1:1 acetonitrile-0.1M formic acid eluent. The XPS spectra were acquired on an Axis Ultra DLD spectrometer (Kratos Analytical, UK) with a monochromatic AlK* radiation source (h* = 1486.7 eV, 150 W). The compressed catalysts were studied before and after *in-situ* treatment in Ar+5%H_2 at 1 atm in the high-pressure cell connected to the vacuum chamber of the spectrometer. Also dried powdered catalysts were studied after *ex-situ* mild reduction. The catalysts were also characterized by DRIFT spectra of adsorbed CO after in situ reduction in H_2 at 330°C and 180 Torr, temperature-programmed reduction with H_2 (TPR), TEM, SEM, Mössbauer spectroscopy and some other methods.

Results and Discussion

Catalytic properties of Pd in HDC of DCF depends on the support nature, the presence of iron oxide as surface modifier and the reduction conditions. The presence of SiO_2 in the support causes an increase in S_{BET}, but mobile support strongly covers Pd particles and causes depletion of surface with Pd. The same was observed for Pd/Al_2O_3 catalyst. Modification of Al_2O_3 with iron oxides strongly hinders depletion of surface with Pd, improving catalytic properties. No such depletion was found for Pd/ZrO_2. Fe^0 was not found by XPS and Mössbauer spectroscopy in reduced catalysts, only iron oxides.

Table 1. Catalytic properties in DCF HDC, texture and XPS results

Catalyst	**T of reduc-tion/ °C**	**S_{BET}/ $m^2.g^{-1}$**	**XPS results for surface, at.%**			**Batch catalytic test**	**Flow catalytic test**	
			Pd^0/ Pd^{2+}	**Fe^{2+}/ Fe^{3+}**	**Me* /Pd**	**TOF, $1.h^{-1}$**	**t, min**	**X_{DCF} (t)#, %**
Pd/Al_2O_3	30	171±17	2.6	-	203	966	185	88
	320		4.9	-	999	908	275	87
$Pd10Fe/Al_2O_3$	30	153±15	3	1.3	318	1019	225	90
	320		99	1.6	351	1058	225	85
$Pd0.5Fe/Al_2O_3$	30	172±17	0.1	0.2	280	127	-	-
	320		4.6	0.6	242	1039	225	61
Pd/ZrO_2	30	53±6	4.6	-	148	1003	225	15
	320		0,9	-	113	914	225	61
Pd/ZrO_2SiO_2	30	340±34	24	-	47	65	225	10
	320		5.7	-	45	497	225	58

* Me = Al or Zr in the oxide support; # X_{DCF} (t) is integral DCF conversion

Mild reduction for Pd/Al_2O_3, $Pd10Fe/Al_2O_3$ and Pd/ZrO_2 is nearly as efficient as the reduction at 320°C, as it is seen from Pd^0/Pd^{2+} ratios and comparable TOF values (Table 1). DRIFT study of adsorbed CO confirmed increased assortment of Pd adsorption centers in PdFe catalysts. XPS and TPR demonstrated strong interaction between Fe and Pd in bimetallics.

Mild reduction is especially efficient when performed before flow catalytic test in the same reactor where the HDC takes place. Such method provides cost saving and decrease the risks connected with the production and transferring of pyrophoric catalyst after reduction to batch reactor. Pd/Al_2O_3 and $Pd10Fe/Al_2O_3$ were the most stable in flow-type experiment.

Acknowledgement: The study was supported by Russian State Programs 122040600057-3 and AAAA-A21-121011990019-4. The equipment purchased under Lomonosov Moscow State University development program was used.

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OP-I-04

Understanding of Surface Oxygen Species on the Catalysts for Oxidative Coupling of Methane

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For many years the oxidative coupling of methane (OCM) providing direct methane to ethylene conversion within one process was the target of scientific and commercial interest. Various oxide catalysts have been explored aiming to enhance the low yield arising from poor conversion and selectivity to reach the requirements for industrialization [1]. In spite of a large number of publications, the nature of the active centers responsible for methane activation as well as the reaction pathway are not clear and still under debate [2.3]. The catalyst activity in OCM reaction is correlated with specific surface oxygen sites demonstrating basic properties. For modern multicomponent OCM catalysts, like Na-W-Mn/SiO_2 it is challenging to clarify the nature of surface species responsible for methane activation due to coexistence of different oxides and salts on the catalyst surface. Among single metal oxide catalysts reported in literature, La_2O_3 is the most promising where different oxygen species $O_2^{\bullet-}$, O_2^{2-}, and O^{2-} were considered as active centers. The surface peroxide (O_2^{2-}) was first proposed as active center in 1985 by Lunsford [4]. However, so far there is still no evidence confirming there are peroxide species stable at the reaction temperature (about 750°C) which function as CH_4 activation centers.

The investigation of La_2O_3 catalyzed OCM reaction was performed by online MS (in high temperature microreactor), by *in situ* XRD and XPS equipped with high pressure gas cell (HPGC) and using specially designed sampleholder stage which enables XPS analysis at temperatures up to 800°C.

On the *in situ* cleaned La_2O_3 surface the specific surface oxygen species detected by XPS are correlated with the catalyst activity in OCM reaction. The online MS results suggest that for this gas-solid interface reaction, there should be a substantial structure change of the catalyst surface at the temperature around 600°C. The *in situ* XRD and XPS reveal the competition between surface carbonate and the specific oxygen species in this temperature range. *In situ* XRD coupled with online MS indicate that the formation of carbonate by interaction with CO_2 (the product of full oxidation) results in deactivation of the catalyst, quantitatively correlating with the C_2 light-off temperature and selectivity.

To understand the nature of the specific oxygen species (O*) its reactivity to different OCM related reactants and products is tested indicating that the O* species is an intrinsic surface structure sensitive to the presence of surface carbon containing species. None of the treatments could form a surface without carbon (including carbonate), hydroxyl or O* species demonstrating their competition. The OH groups formed by H_2O adsorption on La_2O_3 are characterized by 531.8 eV peak in O 1s spectra, which is very close to the binding energy of

O* peak, 531.4 eV. To exclude the assignment of O* to highly stable hydroxyl species TPD and FTIR heating experiment on the clean La_2O_3 surface are performed. Both experiments clearly demonstrate no hydroxyl groups on the catalyst surface containing O* species. It is interesting that after Ar^+ etching XPS reveals the clean La_2O_3 surface without O* species (cannot be prepared by other methods). While keeping this surface in vacuum the O* species is subsequently formed due to the intrinsic surface reconstruction within some minutes. Fig. 1A shows the time dependent O 1s spectra obtained immediately after Ar^+ etching. The charge balance analysis (Fig. 2B) (considering the oxidation states of La is +3 and that of lattice oxygen is -2) provides a formal oxidation state of oxygen in O* species -1, *indicating it as peroxide*.

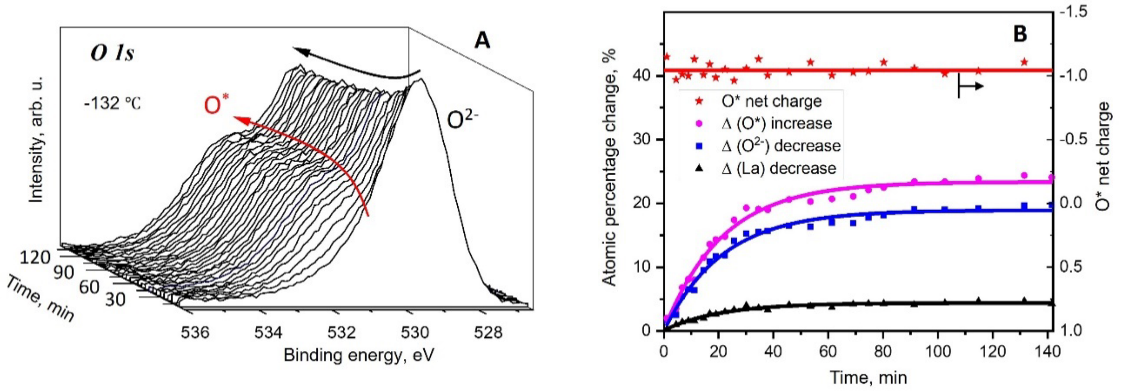

Fig. 1. Panel A) time dependent O 1s spectra taken after Ar^+ etching of clean La_2O_3 surface at -132°C. Panel B) the net concentration changes of O, O^{2-}, La and atomic net charge of the O* species for the experiment presented in panel A.*

To confirm the proposed model of the stable peroxide centers density functional theory (DFT) calculations were performed. The surface peroxide model DFT calculations have shown that the surface peroxide is unstable, as the potential energy of this structure is even higher than gas phase oxygen. Motivated by high stability of the observed O* species, we propose a new model of *subsurface peroxide* structure which is thermodynamically favored with significantly lower potential energy. According to computational results the new *subsurface peroxide* structure also provides a reasonable explanation for the poisoning effect induced by carbonates, the observed products from the transient experimental studies and the spectroscopic measurements of the *in situ* prepared catalysts.

Acknowledgement: This work was supported by the National Natural Science Foundation of China, grants No. 22072107, No. 22072092, No. 92045301, No.22172188. The authors would also like to acknowledge Shell Global Solutions International B.V., Netherlands for the provided funding (WO CW373032).

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OP-I-05

Mechanistic Study of Selective Oxidation of Methanol over Monolayer V_2O_5/CeO_2 Catalyst

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An *operando* FTIRS study of the oxidation of methanol over a monolayer V_2O_5/CeO_2 catalyst was carried out at atmospheric pressure in a temperature range of 150-300°C. It was found that the oxidation starts at 200°C, when the main products — methyl formate and dimethoxymethane — are formed with a selectivity of 62% and 38%, respectively. An increase in the reaction temperature initiates the formation of formaldehyde, CO, and CO_2, and at 300°C CO becomes the main reaction product. The main reaction intermediates are methoxy groups, formates, dioxymethylene species, and adsorbed formaldehyde. According to X-ray photoelectron spectroscopy studies, the reaction involves a reversible reduction of V^{5+} and Ce^{4+} cations, indicating that both vanadia and ceria are involved in the oxidation of methanol [1]. In fact, cerium oxide decreases the reducibility of the supported vanadium oxide and thereby affects the catalytic properties. As a result, the V_2O_5/CeO_2 catalyst shows less activity in the low-temperature oxidation of methanol then V_2O_5/TiO_2 catalyst, in which the support is not reduced under the reaction conditions [2,3].

A reaction mechanism of the oxidation of methanol over supported vanadium oxide catalysts is discussed.

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental assignment for Boreskov Institute of Catalysis (project FWUR-2024-0032).

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OP-I-06

Mechanism of Catalysis by Solid Acids in an Aqueous Medium. Cellulose Hydrolysis at the Molecular Level

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Cellulose can be hydrolyzed into soluble sugars, and the latter can be used as a feedstock for producing a multitude of chemicals: fuels like bioethanol or biobutanol, biodegradable polymer precursors like levulinic acid, platform chemicals (5-hydroxymethyl furfural), etc. [1]

Catalysis of cellulose hydrolysis by strong mineral acids is well known and efficient, but isolation of the catalyst from the reaction products is complicated. The clear benefit of the solid acid catalysts (sulfonated or oxidized carbons, ion exchange resins, zeolites, acidic oxide catalysts) is the ease of their separation from the reaction medium: this can be made trivial by embedding magnetic particles inside catalyst grains. Solid catalysts of cellulose conversion are actively developed in the direction of bifunctionality and one-pot processes combining hydrolysis and hydrogenation. Despite continued research into hydrolysis of cellulose using solid acid catalysts over the last decade, the mechanism of the interaction between the two solid substances remains largely unclear.

In this work [2], on theoretical level, we make the first attempt to describe the interaction of cellulose and solid acid catalysts of hydrolysis from the electrical double layer point of view. Specifically, we will focus on proton concentrations that are attained near the cellulose surface, and electrostatic interaction energies.

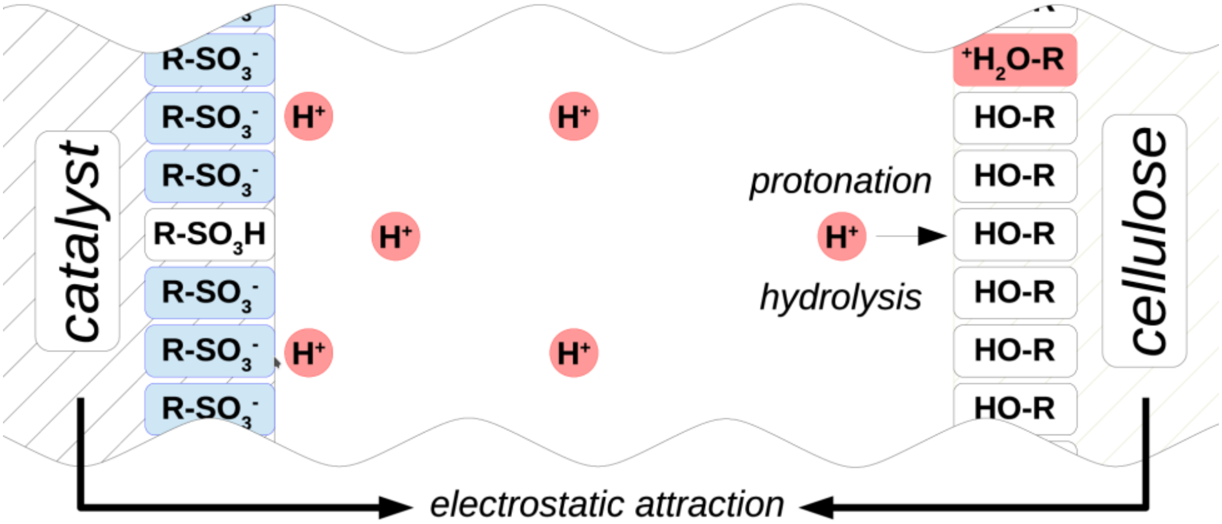

Fig. 1. Schematic representation of the proposed electric double layer model for interaction of cellulose with solid acid catalysts.

As the result, a variety of experimental data from literature can be adequately explained at least on qualitative level. Protonation of cellulose by the diffuse proton layer of solid catalysts with strong (sulfonic) acid groups causes electrostatic attraction of the solid carbohydrate to the catalyst. This ensures that close contact between the two solids is constantly maintained. So, cellulose is constantly immersed in thin but concentrated diffuse proton layer where hydrolysis takes place. This electrostatic attraction also facilitates establishing chemisorption with catalysts that bear organic (carboxylic and phenolic) acid groups. Organic acid groups are too weak to create a concentrated proton layer and to cause appreciable attraction; but once chemisorption is established (by mechanical collision or by attraction due to sulfonic groups), they exhibit higher hydrolytic activity than sulfonic groups. The influence of electrostatic attraction between the catalyst and the cellulose is believed to decrease when temperature increases and/or solid particles become smaller.

In second paper [2], we continue working on our theory of electrical double layers resulting exclusively from dissociation of a solid electrolyte. These address the role of the inner volume of a solid electrolyte particle. Specifically, we perform theoretical modeling to analyze formation of a diffuse electrical layer in two systems: inside an infinitely long cylindrical pore, and near a flat surface of a gel electrolyte. The importance of analyzing the situation inside pores arises from the fact that high catalyst porosity and surface area are preferable for reactions with soluble substrates in order to maintain high reaction rate. Gel electrolytes are interesting because many ion exchange resins have gelular structure and they are frequently used as catalysts in aqueous media.

Our last work is aimed an experimental study of cellulose hydrolysis over strong (sulfonic ion exchange resin) or weak (oxidized carbons) solid acid catalysts. We monitored the structural changes of the polysaccharide. The original cellulose and the cellulose isolated from the reaction were characterized by a set of physicochemical methods: X-ray diffraction (the degree of polymerization), IR spectroscopy, SEM (particle morphology). It has been established that the hydrolysis of cellulose in an aqueous medium on solid catalysts with strong and weak acid groups differs in mechanisms. The results are interpreted in terms of the formation of an electrical double layer on the surface of solid acid particles.

We believe that the reported findings represent an important piece in the puzzle of systematic fundamental understanding of the interaction between cellulose and solid acid catalysts of hydrolysis. Having such understanding would allow designing more effective hydrolysis processes based on such catalysts.

Acknowledgement: This work was supported by the Russian Science Foundation (project 21-73-20269) and budget project for ICCT SB RAS (FWES-2021-0012).

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OP-I-07

Mechanism of C_3-C_4 Alkane Activation and Transformation on In-Modified Zeolite BEA Studied by ^1H and ^{13}C MAS NMR Spectroscopy

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In-modified zeolites demonstrate superior activity and selectivity for the conversion of light alkanes to a mixture of aromatic hydrocarbons (benzene, toluene, xylenes) [1].However, a deactivation of the catalyst was observed due to the reduction of cationic or oxide-like indium species to metallic indium [2, 3]. For development of active and selective catalysts for alkane aromatization and overcome the problems with the catalyst deactivation, an understanding of the mechanism of alkane activation and clarifying the pathways of alkane transformation are neccessary.

In this work, the mechanisms of C_3-C_4 alkane activation and transformation on In-modified zeolite BEA were investigated using solid-state NMR spectroscopy. ^1H MAS (MAS=Magic Angle Spinning) NMR was applied for in situ monitoring the kinetics of the H/D exchange between BAS (BAS= Brønsted Acid Site) of the zeolite and the C_3-C_4 alkane molecule with the aim of establishing the effect of indium species loaded in zeolite on alkane C-H bonds activation by BAS [4, 5]. ^{13}C MAS NMR was used for monitoring the intermediates and the products formed in the course of the reaction.

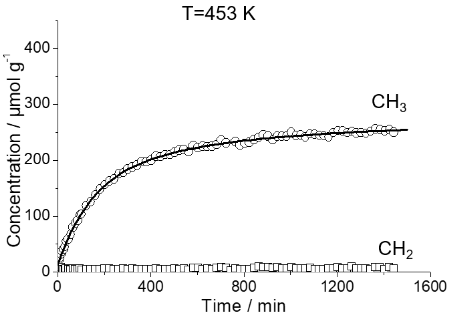

Fig. 1. Kinetics of regioselective H/D exchange (in the methyl group) of propane-d_8 with BAS on InO^+/H-BEA zeolite, T= 453K.

Analysis of the kinetics has shown a dramatic increase of the rate, a decrease of activation energy and appearance of the regioselectivity of the H/D exchange in the methyl groups of propane and butanes upon indium species loading on zeolite (Fig. 1). This implies primary activation by BAS of alkane methyl groups with assistance of indium species preceding further chemical transformation of alkane. Two-exponential kinetics of the regioselective exchange was rationalized in terms of two different mechanisms providing the regioselectivity and acceleration of the exchange compared to H-form zeolite. According to the first mechanism (the mechanism of direct exchange with assistance of In species), the adsorption complex is formed by the interaction of InO^+ species with the methyl group of alkane. Thus activated methyl group of the alkane is further involved in the exchange with BAS of the zeolite. The second mechanism (the mechanism of indirect exchange) contributes to the H/D exchange after accumulation of alkene formed in small quantities at alkane dehydrogenation.

Deuterated alkene is protonated by BAS to form a carbenium ion with protium label in the methyl group. The cation abstracts further hydride (deuteride) ion from the incoming deuterated alkane, affording finally an alkane with a protium label in the methyl group.

^{13}C MAS NMR revealed the formation of the intermediates, including indium-alkyl species and alkene on InO^+/H-BEA zeolite.The reaction products were represented by aromatic hydrocarbons (toluene) and carboxylic acids (mainly acetic and propionic acids). The reaction products were also identified by GC−MS as toluene and carboxylic acids [6, 7].

Thus, two parallel pathways of alkane transformation were identified: dehydrogenation followed by the alkene aromatization and the alkane oxidation to C_2−C_3 carboxylic acids (Fig.2) [6, 7].

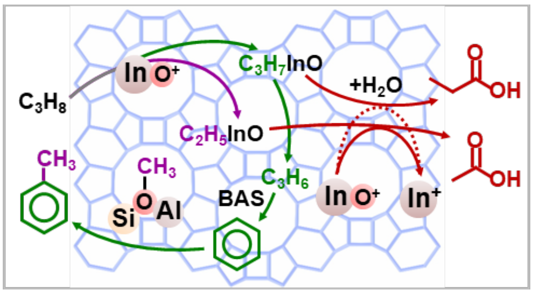

Fig. 2. The pathways of propane transformation on InO^+/H-BEA zeolite, revealed by ^{13}C MAS NMR.

The mechanism of alkane transformation to the detected oxygenates was suggested and discussed. Three pathways of C_3-C_4 alkane activation by the alkane dissociative adsorption on InO^+ sites via either C−H or C−C bond cleavage were suggested. In case of propane transformation, it is inferred that acetic acid may be formed following the dissociation of the initial alkane C−C bond, whereas propionic acid is formed after the dissociation of the alkane C−H bond.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 22-13-00029.

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OP-I-08

The Nature and Role of the Monovalent and Divalent Nickel Species in the Ni(II)-α-Diimine Based Ethylene Polymerization Catalyst Systems

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Branched polyethylene is a highly-demanded product of the modern polymer industry. It is produced in two different ways: radical ethylene polymerization [1] and ethylene/α-olefin copolymerization using of Ziegler-type or metallocene catalysts [2]. Synthesis of branched polyethylene via catalytic ethylene homopolymerization is seems to be more convenient way both from economic and technological points of view.

In 1995, Brookhart and co-workers discovered a family of novel divalent nickel complexes with N,N-bidentate α-diimine ligands (Fig. 1) that were capable to catalyse the formation of branched polyethylene from sole ethylene as a feedstock [3]. This discovery inspired the numerous investigations devoted to the search of the active and thermally stable nickel catalysts for producing of branched polyethylene with a desired molecular structure. To date, Ni(II) α-diimines remain the most studied among post-metallocenes [4].

For the rational search of the catalyst it is necessary to achieve the clear understanding of the polymerization mechanism. In the pioneering works of Brookhart and co. it was established that polymer chain growing and branching in the ***model*** catalytic system $[LNi^{II}Me(OEt_2)]^+[BAr_4]^-/C_2H_4$ (L = α-diimine ligand) occurs on the cationic species containing nickel(II)-alkyl moiety (e.g. $[LNi^{II}R(C_2H_4)]^+$, where R = alkyl group) [5]. The key role of the cationic Ni(II) complexes as the true polymerization active sites was generally recognized soon. Nevertheless, the questions about the nature of the active sites in the ***real*** catalytic systems (e.g. $LNi^{II}Br_2$/activator) and the structure and role of the monovalent nickel species formed during the catalytic process, remained unsolved for a long time.

In present report we summarize the results of our recent studies of the nature and role of the Ni(II) and Ni(I) compounds formed upon activation of $LNi^{II}Br_2$ with various co-catalysts – methylalumoxanes, aluminium trialkyls, and alkyl aluminium chlorides.

Using NMR spectroscopy *in situ* it was established that diamagnetic Ni(II) complexes of the type $[LNi^{II}(\mu{-}Me)_2AlMe_2]^+[MeMAO]^-$ and $[LNi^{II}{-}{}^tBu]^+[MeMMAO]^-$ predominate in $LNiBr_2$/MAO and $LNiBr_2$/MMAO systems, correspondingly. On contrary, paramagnetic Ni(II) species with proposed structure of $[LNi^{II}(\mu{-}R)(\mu{-}Cl)AlRCl]^+[AlR_2Cl_2]^-$ were found upon $LNiBr_2$ activation with $Al_2R_3Cl_3$ (R = Me, Et). All of these Ni(II) compounds contain cationic Ni^{II}-alkyl moieties and, according to the Brookhart results, can act as the direct precursors of the true ethylene polymerization active sites.

However, Ni(II)-alkyls observed were stable in reaction solution only at low temperatures ($T < -20$ °C) and rapidly reduced into to the Ni(I) species upon the samples heating. Using of

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NMR and EPR spectroscopy *in situ* it was established that two types of the paramagnetic Ni(I) complexes are formed in the catalytic systems studied: (1) dialkyl-bridged heterobinuclear complexes of the type $LNi^{I}(\mu-R)_2AlR_2$ and (2) alkyl-halide bridged $LNi^{I}(\mu-R)(\mu-X)AlR_2$ species (R = Me, Et, ^{i}Bu; X = Cl, Br). The predominance of one or another complex in the reaction mixture is strongly depends on the ligand structure and co-catalyst nature and excess.

To elucidate the role of the Ni(I) species observed in the polymerization process the catalytic experiments were performed. It was found that preliminary activation of $LNi^{II}Br_2$ with an appropriate co-catalyst (to achieve a complete Ni(II)→Ni(I) reduction) slightly changes the catalytic activity but has no effect on the molecular structure of the polymer obtained. This result clearly witnesses the identity of the active species operating the ethylene polymerization both in $LNi^{II}Br_2$/co-catalyst (1) and «pre-activated $LNi^{II}Br_2$»/co-catalyst systems. In contrast, the rate profiles of the ethylene consumption for the systems (1) and (2) were significantly differ. In the first case, the kinetic curve was typical for the most of homogeneous polymerization catalysts: high initial activity followed by gradual activity decay. In the second one 3 sections of the kinetic curve were distinguished: slow activity growing (inducing period, I), constant activity value (II), and gradual activity decrease (III). Very probably, during the inducing period (I) monovalent nickel species convert into Ni(II) counterparts – true ethylene polymerization active sites. The mechanism of Ni(I) re-involving into the catalytic cycle is still uncertain, probably disproportionation Ni(I) → 1/2Ni(II) + 1/2Ni(0) takes place. Nevertheless, it is reasonable to conclude that Ni(I) species formed in the systems studied are not the products of the catalyst deactivation and play role of the catalyst dormant state.

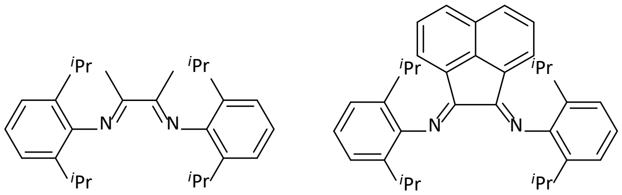

Fig. 1. Structures of α-diimine ligands used by Brookhart in [3]

Acknowledgement: This work was supported by the Russian Science Foundation, grant 24-23-00033.

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OP-I-09

Dimerization and Oligomerization of Alkenes under the Action of Metallocenes: New Catalytic Systems and Reaction Mechanisms

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Development of novel Ziegler-Natta type homogeneous catalytic processes requires a deep understanding of reaction mechanisms. Modern models suggest the involvement of bimetallic structures of catalytically active centers formed by the reaction between transition metal complexes and cocatalysts, as well as accounting for the dynamics of intermediates [1].

To investigate the role of metal hydride intermediates in Ziegler-Natta processes, we studied the reactions of titanium subgroup metal complexes with organoaluminum compounds (OAC) and activators (MAO, $[CPh_3][B(C_6F_5)_4]$, $B(C_6F_5)_3$) using NMR spectroscopy and high-resolution mass spectrometry. Formation of intermediate Zr,Zr- and Zr,Al-hydride complexes was observed in systems based on metallocene chlorides and hydrides L_2MCl_2 – $XAlBu^i_2$ (M= Zr, Hf; X=H, Bu^i), $[L_2MH_2]_2$ – $ClAlR_2$ (R= Me, Et, Bu^i) in the presence of activators. For the first time, it was experimentally demonstrated that alkene dimerization and oligomerization proceed via different types of active species: high molecular weight aggregates of bis-zirconium hydride complexes with activators were found to be key intermediates in alkene dimerization, while cationic Zr,Al-hydrides led to the formation of oligomers [2,3].

A quantum-chemical study of the reactions of complexes Cp_2ZrH_2, Cp_2ZrHCl, Cp_2ZrMe_2, $Cp_2ZrMeCl$ and $Cp_2ZrCH_2CH_2$ (zirconacyclopropane) with linear and cluster models of methylaluminoxane (MAO) was carried out. It was shown that MAO clusters form weak associates with zirconium complexes, while linear structures contribute to the formation of thermodynamically stable adducts. The thermodynamic stability of the complexes decreases in the series [Cp_2ZrH_2-MAO-chain]> [Cp_2ZrHCl-MAO-chain]> [Cp_2ZrMe_2-MAO-chain]> [$Cp_2ZrMeCl$-MAO- chain]> [$Cp_2ZrCH_2CH_2$- MAO- chain]. A thermodynamically favorable transfer of a chlorine atom from Cp_2ZrHCl and $Cp_2ZrMeCl$ complexes to an aluminum atom in the chain model of MAO has been shown. It was found that the insertion of propylene to form precursors of active centers $Cp_2Zr(Alk)$-O(MAO) with a highly polarizable Zr-O bond is possible only for complexes Cp_2ZrHCl, Cp_2ZrMe_2 and $Cp_2ZrMeCl$ with chain MAO structures. For intermediates formed by MAO clusters, reactions are accompanied by high activation energies mainly due to steric hindrances.

The influence of the OAC and activator structure on the chemo- and stereoselectivity of terminal alkene oligomerization has been studied [5]. The reaction of alkenes with AlR_3 (R=Me, Et, Bu^i) in the presence of enantiomerically pure *ansa*-complex Zr dichloro[(*R,R*)-

ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium and activators (MAO, $[CPh_3][B(C_6F_5)_4]$) provides functionalized oligomerization products with high chemo-, dia- (99%*de*), and enantioselectivity (up to 93%*ee*). It has been shown that the enantioselectivity of oligomerization in the studied systems is achieved both through control at the alkene coordination site and growing chain control.

Quantum chemical modeling of the mechanism of asymmetric induction during the coordination of alkenes (propene, 1-hexene) with stereoisomeric complexes $Cp_2ZrMe(Cl)$-methylaluminoxane has been carried out [6]. Significant influence of the relative configuration of chiral centers at the aluminum atoms in the activator on the energy parameters of the reaction of alkene insertion into Zr-C bonds in the complexes has been demonstrated.

The obtained results contribute to the development of highly selective methods for the construction of C-C, C-H, and metal-C bonds, while understanding the nature and principles of action of active centers in homogeneous catalytic systems of Ziegler-Natta type provides the foundation for further advancement and the development of efficient processes and technologies for hydrocarbon feedstock processing.

Acknowledgement: The studies were carried out in accordance with the Federal Program No. FMRS-2022-0081.

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OP-I-10

Radical Mechanism of *trans*-Borylation of *α*-Olefins with Dichloro(Diizopropylamino)Borane Catalyzed by Cp_2TiCl_2: Combination of DFT Calculations and EPR Measurements

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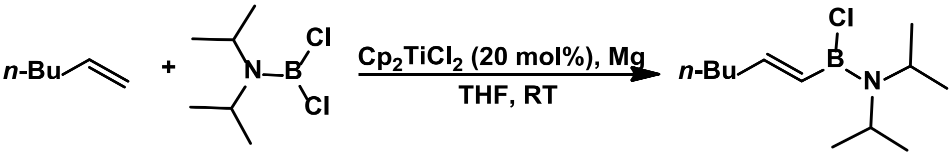
One of the ways of formation of B-C bond is the borylation reaction, which is a simple, efficient, but still a poorly studied synthetic route to 1-alkenylboranes [1]. 1-Alkenylborane derivatives are the major building blocks for the synthesis of π-conjugated organic photophysical and electronic devices [2] and are used for the preparation of many natural and biologically active products [3]. Despite the practical interest in the borylation products, the reaction mechanism still remains unclear. The literature reports a reaction involving catalysts based on transition metal (Rh, Ru, Ir, Pd) complexes, however data on the use of titanium-based catalysts in the borylation reactions are scarce. A few publications of D.H. Motry describes borylation of olefins with benzo-1,3,2-diazaborolane catalyzed by $(Cp^*)_2Ti(CH_2)_2$ [4,5]. Recently we obtained new experimental data on the Cp_2TiCl_2-catalyzed synthesis of 1-alkenylboranes [6]. The reaction of *α*-olefins with dichloro(diizopropylamino)borane (*i*-Pr_2NBCl_2) in the presence of Mg metal and the Cp_2TiCl_2 catalyst selectively affords *trans*-borylation products, *trans*-1-alkenyl(chlorodiisopropylamino)boranes, in up to 95% yields (Scheme). It was unexpected because replacement of the boron reagent *i*-Pr_2NBCl_2 in this reaction by boron halides ($BF_3 \cdot THF$ and $BCl_3 \cdot SMe_2$) or by alkyl-, or aryl(dichloro)boranes ($RBCl_2$) changes the reaction pathway and, instead of borylation, cycloboration of *α*-olefins takes place to give boriranes [7-9].



Scheme. Selective Cp_2TiCl_2-catalyzed borylation of α-olefins with i-Pr_2NBCl_2

The mechanism of cycloboration of *α*-olefins was studied by quantum chemical methods in relation to the reaction of propene with BCl_3 [10]. Obviously, reaction route switching is due a different catalytically active complex. Thus, the purpose of this study was to elucidate the mechanism of the Cp_2TiCl_2-catalyzed borylation of hex-1-ene with *i*-Pr_2NBCl_2 using both theoretical (DFT level) and experimental (NMR, EPR) approaches. Comprehensive analysis of the results would help to develop a detailed and experimentally substantiated mechanistic scheme for this borylation reaction. All calculations were carried out at the DFT level in the Priroda 9 [11] program using the PBE/3ζ method [12].

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A theoretically substantiated free radical mechanism was proposed, including three steps: (i) the complex [$Cp_2Ti(Cl)$-$B(Cl)N(i$-$Pr)_2$] formation *via* "Cp_2Ti" with the aminoborane interaction (ii) dissociation of the complex into radicals $Pr_2N(Cl)B^\bullet$ и $Cp_2TiCl^\bullet$ due to polarization of the Ti-B bond, (iii) the reaction of the radicals with the olefin, and (iv) β-hydride transfer in the formed *in situ* 1,4-diheterosubstituted key intermediate $Cp_2Ti(Cl)$-$CH(Et)$-CH_2-$B(Cl)N(i$-$Pr)_2$. The selectivity of the *trans* isomer formation is determined by the most energetically favorable conformational state of key intermediate, in which the C-H activation is accompanied by the kinetic advantage of the formation of the *trans*-isomer.

By analysis of the CW EPR and pulsed ENDOR data, it was confirmed that *α*-olefin borylation proceeds via free radical formation. The integral intensities of the four observed signals were calculated as a function of the reaction time, DFT calculations of the geometry and isotropic HFC constants of the complexes proposed on the basis of quantum chemical modeling were carried out, and EPR signals were assigned from a complex analysis of the experimental (multinuclear ^{11}B NMR spectroscopy) and theoretical experiments. The accumulation of titanium hydride complexes during the reaction was established which causes the formation of by-products.

Acknowledgement: The structural studied were carried out in the framework of the State Assignment (FMRS-2022-0081) Organoboron and organoaluminium compounds were synthesized in the framework of the State Assignment (FMRS-2022-0075) in the Regional Center for Collective. The authors thank Dr R.B. Zaripov from Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center of RAS for EPR study.

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OP-I-11

Alkene π-Complexes with Metal Cations in Zeolites: Spectroscopic Characteristics, Thermodynamic Stability, and Bonding Mechanism

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Zeolites modified with metal cations (Zn^{2+}, Ag^{+}, Cu^{2+}, etc.) are considered to be perspective catalysts for light alkene conversion to valuable chemicals such as higher alkenes and simple aromatic compounds. The first step of alkene transformation on cation-exchanged zeolites is the formation of a π-complex of an alkene with a metal cationic site [1-2]. The formed π-complexes differ in stability and reactivity, which is reflected in the temperature required for further alkene transformation and the reaction mechanism. Namely, very stable metal-alkene π-complexes can survive on the zeolite surface at temperatures up to 573 K and prevent alkene transformation on zeolite Brønsted acid sites [1].

Alkene π-complexes with metal cations have been detected by ^{13}C MAS NMR and FTIR spectroscopy to form from C_2–C_4 alkenes on various metal-modified zeolites [1-4]. In FTIR spectra, a π-complex formation is manifested in a redshift of the $\nu_{C=C}$ frequency by 10–100 cm^{-1} compared to gaseous alkene. While in ^{13}C MAS NMR spectra, alkene π-complexes with metal cations are observed by the shift of the signals of the C=C fragment of an alkene molecule. Interestingly, such a shift can be upfield or downfield and significantly vary in magnitude for the signals of different positions in the molecule.

The differences in ^{13}C MAS NMR and FTIR characteristics may be the indications of the metal-alkene π-complex stability or the nuances of its structure. For instance, for CO adsorbed on metal oxides and metal-modified zeolites, a linear correlation was established between the ν_{CO} shift and the CO adsorption heat on metal cationic sites [5]. The question arises if similar correlations exist for light alkenes on metal-modified zeolites.

As for the structure of metal-alkene π-complexes, conventionally, two possible contributions to the bonding are discussed. First, electrons can be donated from the bonding π-orbital of an alkene to a vacant outermost orbital of a cation (σ-bonding). Second, there can be the back-donation of the electrons from the occupied d-orbitals of a cation to the alkene antibonding π*-orbital (π-bonding). However, the contributions of σ- and π-bonding in metal-alkene complexes on zeolites and their interrelations with stability and reactivity are unknown.

In this work, propene π-complexes with a series of metal cations (Na^{+}, Ca^{2+}, Ag^{+}, Zn^{2+}, Cu^{2+}, Co^{2+}) in ZSM-5 zeolites were studied by DFT calculations. The model systems were chosen due to the availability of experimental data, FTIR and calorimetry. The preferable sites for propene adsorption were analyzed. The enthalpy of π-complex formation (ΔH_{ads}) was calculated. The interrelationship between ΔH_{ads} values and a set of parameters (e.g., $\nu_{C=C}$ shift, metal cation ionic radius, and metal-carbon distance in a π-complex) was examined. The bonding mechanism in the studied π-complexes, i.e. the contributions of σ- and π-bonding were investigated by the natural bond orbital (NBO) analysis (Fig. 1).

It was obtained that the relations between ΔH_{ads} and metal cation charge or $\nu_{C=C}$ shift were complex, indicating these parameters could not be used as simple descriptors of π-complex stability. Subsequently, NBO calculations revealed that the bonding in metal-alkene π-complexes was governed by several factors besides generally accepted σ- and π-contributions. Therefore, previously adopted models turned out to be oversimplified and, thus, unreliable. Other contributions included electrostatic polarization of an alkene molecule, the metal cation orbital shell structure, and the geometrical compatibility between metal cation and alkene interacting orbitals.

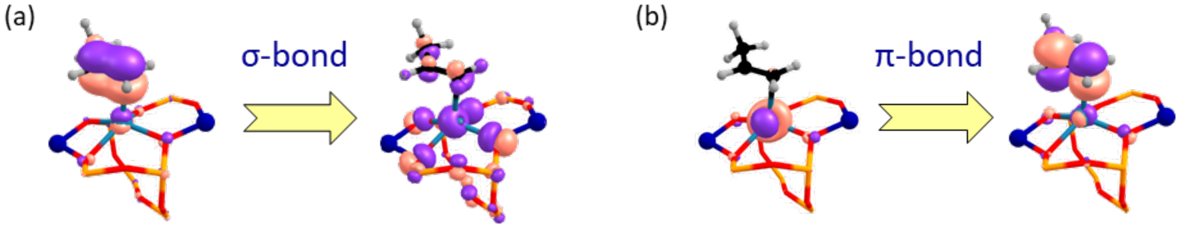

Fig. 1. The orbitals involved in the bonding in propene complex with Zn^{2+} cation: via σ-bonding (a) and π-bonding (b)

The results of the study provide a deeper understanding of the properties of solid acid catalysts in terms of guest-host interactions and the reaction mechanisms.

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OP-I-12

Boosting the Activity of PdAg Bimetallic Catalysts towards the Selective Acetylene Hydrogenation by Means of CO-Induced Segregation: a Combined NAP XPS and Mass-Spectrometry Study

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Selective hydrogenation (or semi-hydrogenation) of acetylene into ethylene is an important industrial process. Polyethylene being the most demanded polymer is typically produced via the polymerization of ethylene. It is the selective hydrogenation of acetylene over specially selected catalyst that is widely adopted as the most cost-efficient approach. The catalyst should be able to catalyze the hydrogenation of triple bonds in an excessive presence of ethylene with a very high selectivity since the hydrogenation to ethane is also economically harmful. Palladium is a prototypical hydrogenation catalyst, but its activity is usually too high to provide sufficient ethylene selectivity with respect to the total hydrogenation. The use of bimetallic Pd-derived catalysts with the second component being appreciably less active is another versatile and highly potent approach. PdAg system is among most promising catalysts especially for the low-temperature mode of the selective acetylene hydrogenation [1–2]. Although fundamental reasons for synergistic effects in bimetallic catalysts remain largely a subject of debate, there is consensus among researchers that the surface composition of catalytic nanoparticles should be studied directly during the reaction in order to learn the exact role played by the second component of a Pd-derived bimetallic catalyst. The chemical composition and structure of active sites in bimetallic systems are certainly determined by the ratio of metals in the synthesis load, but not to a full extent. The surface structure of a bimetallic nanoparticle can undergo spontaneous changes under the action of a reactive atmosphere at the course of a catalytic reaction [3]. Furthermore, it can be deliberately tuned by specific treatments of a catalyst in a specially adjusted gas atmosphere [4]. This spectacular phenomenon referred to as adsorption-induced segregation may be used as a surface engineering tool to tune the surface composition and morphology and deliberately introduce specific types of active sites in bimetallic catalysts. The combination of model systems, where the bimetallic nanoparticles deposited on the planar support, with *in situ/operando* techniques may top up reliability and informativity concerning the surface composition of the active component and its chemical state therein.

In this study we have used a combination of *in situ/operando* techniques (NAP XPS, DRIFTS CO and mass-spectrometry) in order to study two different kinds of systems. Model bimetallic

PdAg/HOPG catalysts (active nanoparticle deposited on planar support) in order to study the CO-induced segregation of palladium. Real bimetallic PdAg/Al_2O_3 catalysts in order to learn regularities governing the CO-induced segregation and elaborate practical procedures for tuning the surface structure of Pd-Ag nanoparticles to improve on their catalytic performance towards the selective hydrogenation of acetylene to ethylene.

Model catalyst based on Pd-Ag nanoparticles supported on HOPG has been thoroughly studied by NAP XPS and MS techniques under conditions of the CO oxidation in the stoichiometric reaction mixture at a total pressure of 0.25 mbar in a range of temperatures from RT – to 300°C. It was found that the Pd segregation on the surface takes place under reaction conditions at room temperature. It escalates at increasing temperature to 150°C.

NAP XPS was applied to monitor CO adsorption-induced segregation effects on supported $PdAg_2/Al_2O_3$ catalysts. A treatment of the catalyst in a CO flow induces a substantial segregation of Pd atoms to the surface of bimetallic particles already at room temperature. In sum, this leads to a nearly 25% increase of the Pd/Ag surface atomic ratio as measured by XPS. The surface enrichment with Pd further increases (to ca. 31%) if the treatment temperature is increased up to 250°C. This specific configuration with a redistributed Pd/Ag surface atomic ratio is appreciably stable and self-sustained even at the absence of CO at moderately elevated temperatures. Nevertheless, a reductive treatment in hydrogen at 450°C reverts the nanoparticle surface structure to the pristine state.

Catalytic properties of this peculiar CO-induced configuration of $PdAg_2/Al_2O_3$ towards the selective acetylene hydrogenation were investigated using a combination of NAP XPS and MS techniques. The $PdAg_2/Al_2O_3$ catalyst with the surface enriched with Pd due to the CO-induced segregation manifests improved activity with 100% selectivity under the conditions used. Importantly, this state is preserved in the acetylene hydrogenation reaction mixture even at moderately elevated temperatures. These results clearly demonstrate that CO adsorption-induced segregation is indeed a powerful tool that can be used to optimize the surface composition and catalytic performance of bimetallic nanoparticles.

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for SRF SKIF Boreskov Institute of Catalysis (FOUR-2024-0042).

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OP-I-13

Adjusting Pt/TiO$_2$ Activity in Low-Temperature Ammonia Oxidation

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NH_3 is one of the most important reagents in the chemical industry; however, it is also a toxic air pollutant and therefore its emission into the environment must be strictly regulated. The operation of current diesel vehicles inevitably leads to the slip of ammonia into the atmosphere. As a result, catalysts for ammonia oxidation are an essential component of exhaust aftertreatment systems. Pt-based catalysts have long been recognized as efficient components for the low-temperature oxidation of NH_3. However, their main drawback is their low selectivity towards environmentally friendly molecular nitrogen. In this study, we focused on analyzing Pt/TiO$_2$ catalysts in order to understand fundamental aspects of their operation in the ammonia oxidation reaction and improve their selectivity towards N_2.

The Pt/TiO$_2$ catalysts were prepared by impregnating titanium oxide (P25, Degussa) with platinum nitrate, followed by calcination at 400°C. To enhance the low-temperature activity and N_2 selectivity, the surface of the samples was modified with potassium, chlorine, and tungsten oxide. The former two were introduced by impregnating the Pt/TiO$_2$ sample with the corresponding precursor solutions, while the latter was deposited on the titania support before the platinum deposition. The resulting catalysts were studied using various physicochemical techniques, including in situ/ex situ XPS and IR methods. The catalysts' activity was evaluated using temperature-programmed reaction NH_3+O_2.

The modification of Pt/TiO$_2$ samples with potassium and tungsten oxide led to the preferential stabilization of the metallic platinum state, in contrast to the initial Pt/TiO$_2$ catalysts where oxidized platinum species were predominant. However, the K^+-modified catalysts did not show significant changes in catalytic activity, while the introduction of WO_x species on the surface resulted in a 20°C decrease in the onset temperature of NH_3 conversion. The temperature required for 50% NH_3 conversion decreased from 180 to 160°C. TPD-NH_3 data revealed differences in the acidic properties of the K^+- and WO_x-modified samples. The introduction of chlorine to the Pt/TiO$_2$ sample increased the number of oxidized platinum species, but did not affect the operating temperature range of the catalysts. However, it significantly improved the selectivity towards N_2 at low temperatures (up to 95%).

Overall, the experiments conducted in this study emphasize the important role of the platinum oxidation state and surface acidity in the selective low-temperature oxidation of ammonia.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-23-00322.

OP-I-14

In situ XAS Investigation of the Rh/NR_3 Catalytic Systems Active in the Reductive Hydroformylation

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Reductive hydroformylation is a simple way to produce primary alcohols from olefins through a one-step process (fig. 1). For now, only cobalt-based systems are used in industry for one-stage production of the primary alcohols from olefins. At the same time, Rh catalysts are known to be more active in hydroformylation [1]. Several types of Rh-based systems active in the reductive hydroformylation were reported [2].

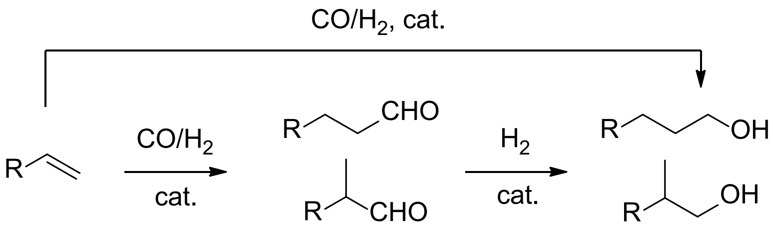

Fig. 1. Reductive hydroformylation of olefins

Among them, one of the most promising is Rh/NR_3. Despite being known for over 50 years for now [3], reductive hydroformylation in Rh/NR_3 systems still has several unclear aspects concerning its mechanism and the structure of the active Rh species. Rh clusters were previously detected under the syngas pressure by IR- and NMR-methods [4,5]. In this study, we investigated Rh/NR_3 catalytic system under the reductive hydroformylation conditions by X-ray absorption spectroscopy to clarify their role in the catalytic process and the effect of the N-ligand structure on their formation. In parallel, we performed the catalytic experiments with different N-ligands, their various concentrations, concentrations of Rh, etc, to establish the effect of these parameters separately on the two stages of the reductive hydroformylation process.

The analysis of the spectral data (Fig. 2 and Tab. 1) showed that the addition of triisobutylamine ($i\mathrm{Bu_3N}$) provides significantly less change in the Rh coordination sphere compared to the amine-free system than two other tested amines, NEt_3 and N-methylpirrolidine (NMP-dine), both under ambient and under the reaction conditions. Under the reaction conditions, in all cases Rh-Rh bonds emerged, but the addition of the N-ligands reduced their number to various extent: it was 2.7 with no ligand, 1.6 with $i\mathrm{Bu_3N}$ and ≤ 1 with the two others. $i\mathrm{Bu_3N}$ also has the minimal effect on the catalysis of three: contrasted to Rh/NEt_3 and Rh/NMP-dine systems, $Rh/i\mathrm{Bu_3N}$ one has insignificant activity in aldehyde hydrogenation.

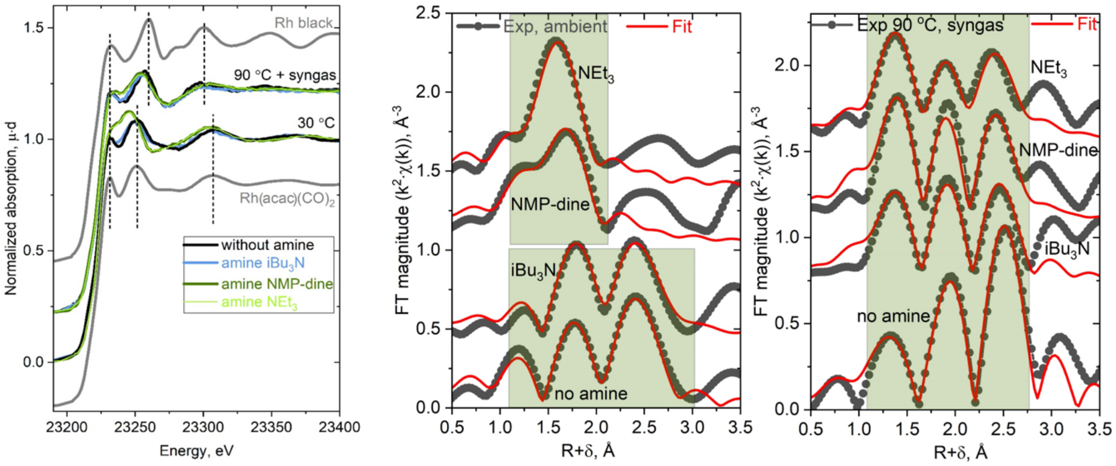

Fig. 2 In situ XAS and EXAFS of Rh/NR$_3$ systems under ambient and reaction conditions

These data can be explained by the inhibition of Rh clusterization resulted from the addition of amines, especially of less sterically hindered ones. Also, presumably Rh clusters are less active in the aldehyde hydrogenation, the second step of the tandem process.

Table 1. Structural parameters obtained from EXAFS fit for the catalytic systems under reaction conditions.

Sample	Coordination sphere	Coordination number	Distance	R factor
Rh(acac)(CO)$_2$	C(CO)	2.0	1.90	0.02
	C/O	1.0	2.09	
	Rh	2.7	2.74	
Rh(acac)(CO)$_2$, NMP-dine	C(CO)	0.9	1.90	0.04
	C/O/N	2	1.96	
	C/O/N	1.6	2.14	
	Rh	1.0	2.70	
Rh(acac)(CO)$_2$, NEt$_3$	C(CO)	1.2	1.88	0.01
	C/O/N	1.3	1.95	
	C/O/N	1.1	2.17	
	Rh	0.7	2.70	
Rh(acac)(CO)$_2$ *i*Bu$_3$N	C(CO)	1.0	1.89	0.02
	C/O/N	1.3	1.97	
	C/O/N	1.2	2.14	
	Rh	1.6	2.74	

Acknowledgement: This research was funded by the Ministry of Science and Higher Education of the Russian Federation, agreement No. 075-15-2021-1363.

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OP-I-15

Co and Ce Oxides Embedded into Nanosilicas as Catalysts for the CO-PROX: SiO_2 Morphology and Activity Relationship

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Nanosilica particles with a three-dimensional amorphous structure are attractive for catalytic application due to the tunable specific surface area, porous structure and presence of highly reactive surface silanol groups for direct binding of the metal precursor. Among them macroporous 3D-systems with well-ordered periodicity based on artificial opals are of special interest in the rational design of heterogeneous catalysts. It becomes possible to control the morphology of embedded oxides and obtain, for example nanoparticles within the pores or coatings on the surface of opal building blocks. It was found recently [1] that Co_3O_4 embedded in the opal matrix had the best catalytic performance in the CO oxidation compared with micro- and mesoporous silica also decorated with cobalt oxide. In this work Co and Ce oxides were embedded in the synthetic opal grown from non-porous silica nanoparticles. The impact of nanosilica morphology on the structure and catalytic behavior of Co-Ce/SiO_2 in the CO-PROX process was studied. To find the best conditions for catalyst synthesis the order of oxide introduction and their ratio was varied among with the silica nature. Two types of nanosilicas of different pore structures were used.

Meso–microporous spherical silica particles (Si_{mm}) having specific surface area and pore volume of up to 1400 m2/g and 0.8 cm3/g, respectively, were synthesized by the basic hydrolysis of silicon-containing precursors (tetraethyl orthosilicate (TEOS), diethoxy(3-glycidyloxypropyl)methylsilane (DEGPMS), 3-(methacryloyloxy)propyltrimethoxysilane (MPTMOS)) in an NH3–H2O–C2H5OH mixture containing CTAB (cetyltrimethylammonium bromide) according to [2]. Macroporous three-dimensionally ordered structures (artificial opal - Si_{op}) consisting of close-packed submicron spherical SiO_2 particles (≈800 nm) with following characteristics of 11m2/g and 0.2 cm3/g were grown from an aqueous suspension of amorphous SiO_2 particles by sedimentation as described in [1]. The resulting sediment was dried at a temperature of 100°C and annealed at 800°C in air. Both nanosilicas were decorated with cobalt and cerium oxides via impregnation with water solutions of $Co(NO_3)_2$ and $Ce(CH_3COO)_3$ (2-15 wt.%) followed by heat treatment at 400°C. The synthesized materials tested as catalysts for the selective oxidation of CO (CO-PROX) in excess H_2 (1 CO, 1 O_2, 49 H_2, 49 He, vol.%).

The synergistic action of Co and Ce oxides embedded into nanosilicas in CO-PROX was found previously [3]. As can be seen from Fig. 1 the sample (a) on the opal-like face-centered cubic structure Si_{op} is much higher active in the CO-PROX reaction in comparison with one (b) on micro-mesoporous silica Si_{mm}. In addition, their activity strongly depends on the order of introduction of the active components. Typical TEM images (Fig. 2) of Si_{op} samples show that when Co oxide was firstly embedded (a,b) large aggregates (20-30nm) are mostly formed in the voids between SiO_2 spheres. In another case, when cerium oxide was introduced first (Fig. 2c), highly dispersed crystallites of both oxides were closely located on the silica surface. This resulted in the formation of new Co–O–Ce active sites responsible for the high efficiency of Co/Ce/Si_{op} catalysts. They provide almost complete conversion of CO at 150°C. The structure - catalytic behavior relationship is discussed based on XPS and FTIR spectroscopy data. The main difference in the structure and properties of samples based on nanosilica with different porosity is determined by the specific interactions of the oxides with each other and with the silica surface. The use of synthetic opal seems to be very promising in the design of new materials with improved catalytic properties for the removal of CO in the hydrogen rich mixture.

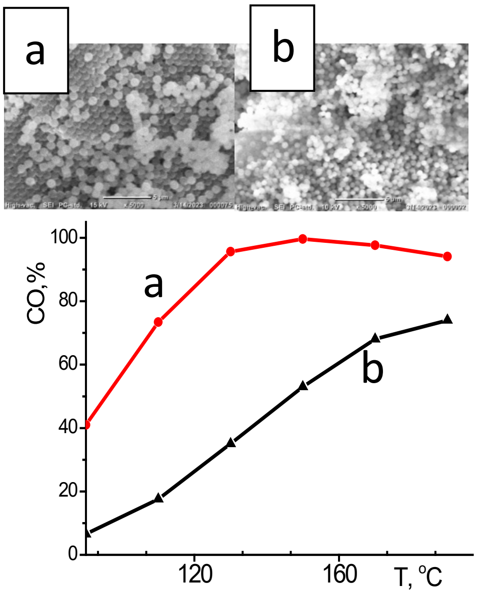

Fig.1. SEM images and temperature dependencies of the CO conversion for Co-Ce on Si_{op} (a) and Si_{mm} (b)

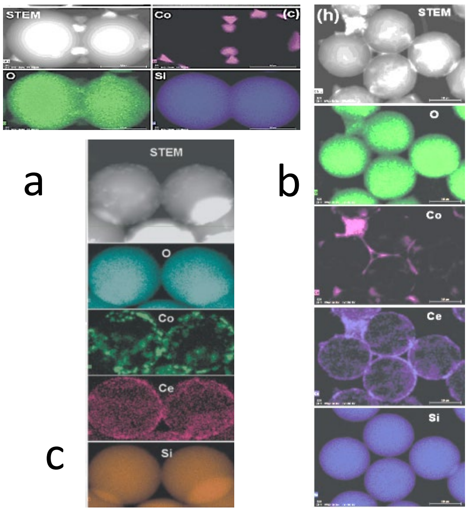

Fig.2. TEM images of Co (a), Ce/Co (b) and Co/Ce samples on Si_{op}

Acknowledgement: This work was performed within the framework of the state budget agreements (FFUG-2024-0017; AAAA-A21-121011590090-7; 122040500058-1) and MSU Development Program.

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OP-I-16

Birds of a Feather – Asymmetric Organocatalysis Meets Asymmetric Transition Metal Catalysis

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Results of the recent studies of the mechanism of stereoinduction in asymmetric hydrogenation catalyzed by complexes of various transition metals [1-4] suggest that hydrogen activation by metal atom and generation of enantioselectivity by organic ligand proceed independently. Hence, these reactions can be considered as a variant of a cooperative organocatalytic reaction. This conclusion opens a broader view on the rational catalysts design suggesting that the structural ideas from different fields can be exploited reciprocally. [5]

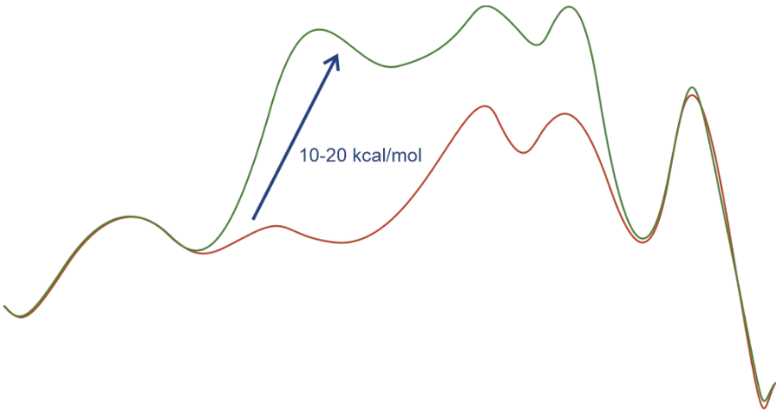

Fig. 1. Representative profiles of Gibbs free energies for the pathways with coordinated (green) and non-coordinated (red) double bond in the case of electron-rich diphosphine ligands.

Authors are requested to send their abstracts as a Microsoft Word file via the conference website**.** Abstracts will be peer reviewed following a standard procedure.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 24-43-00011.

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OP-I-17

Method of High Temperature IR Diffuse Reflectance Spectroscopy In Situ in Studying the Mechanism of Catalytic Reactions

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The method of high temperature IR in situ diffuse reflectance spectroscopy (IRDRS) allows for continuous recording of IR spectra of the catalyst surface in the temperature range of 25-450 °C in a flow of any gas or steam. Registration of I IRDRS spectra directly in the flow of the substrate under conditions close to the conditions of the catalytic experiment makes it possible to monitor the content of starting substances and products of the catalytic reaction on the surface of the catalyst, as well as to record intermediates of the process, i.e. allows us to come closest to understanding the mechanism of the catalytic process.

Zeolite catalysts of the MFI structure, active in the process of alkylation of toluene with decene -1, were studied using the IRDRS method. Using the method we developed, we calculated the relative content of BAS of different strengths, including hydronium ions. Analysis of the composition of BAS of various strengths allowed us to conclude that the activity of the zeolite catalyst for the alkylation of toluene depends on the ratio of weak and strong BAS on its surface. The process occurs simultaneously on both weak and strong acid sites, but the centers perform different functions - weak centers are responsible for the stabilizing function, which leads to secondary alkylation products, and strong acid sites are responsible for the protonating function, leading to side processes of olefin isomerization. Super-acidic centers (H_3O^+), on the contrary, inhibit the process.

When studying the alkylation of toluene with decene-1, it was possible to detect in the IR spectra the intermediates of the process, namely, the conjugated delocalized double bond of decene-1, which arises during the protonation of decene, as well as 4-decyl-toluene formed during alkylation [1].

The process of catalytic hydrogenation of guaiacol and diphenyl ether on zeolite catalysts of the MFI structure modified with Ru was also studied using the IRDRS method. In the case of guaiacol, the target product cyclohexane with the “chair” and “boat” conformations, as well as process intermediates: methane, pyrocatechol, phenol, cyclohexanone, were identified. For the SBA-15 catalyst, cyclohexanol and the skeletal isomerization product of guaiacol were registered, while no spectral signatures of cyclohexane were detected. The process intermediates, benzene and phenol, and the target product, cyclohexane, were identified for diphenyl ether [2].

The next stage of the work was the study of the hydrogenation of guaiacol on catalysts of different morphologies containing oxidized and reduced forms of Ru [3]. For a sample with lower acidity, the maximum differences in the formation of products for the oxidized and reduced forms of ruthenium are shown. The target reaction products were registered -

cyclohexanol and cyclohexane, as well as intermediates of various routes of the hydrogenation reaction of the initial substrate (Fig 1).

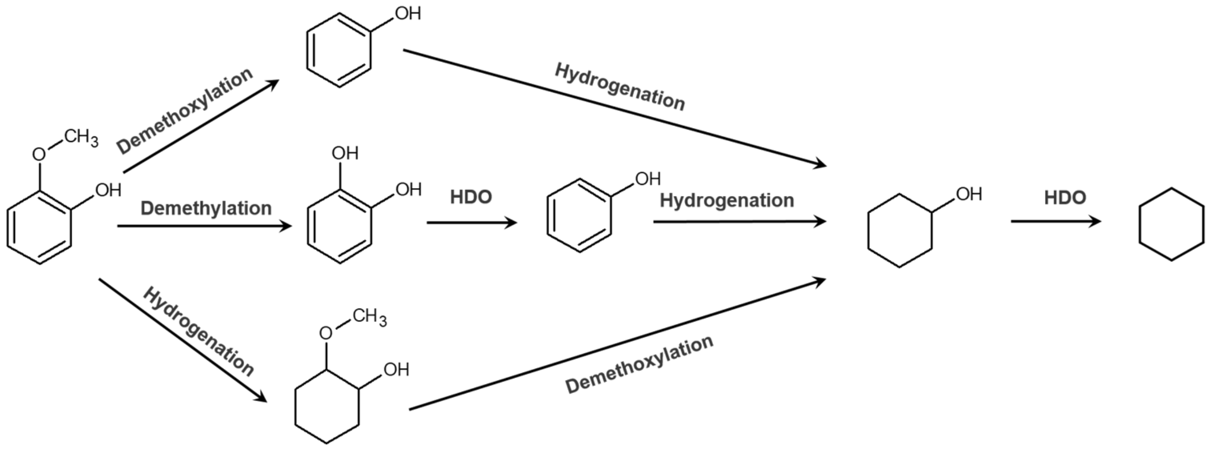

Fig. 1. General reaction pathways of guaiacol hydrogenation.

Acknowledgement: This work was carried out with the financial support of the Ministry of Science and Higher Education of Russia. Project 13.2251.21.0206 (project ID RF----2251.61323X0071). Agreement 075-15-2023-583

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OP-I-18

Degradation Pathways for Molecular Pd/NHC Catalysts and Stabilization of Active Centers with Anionic NHC Ligands

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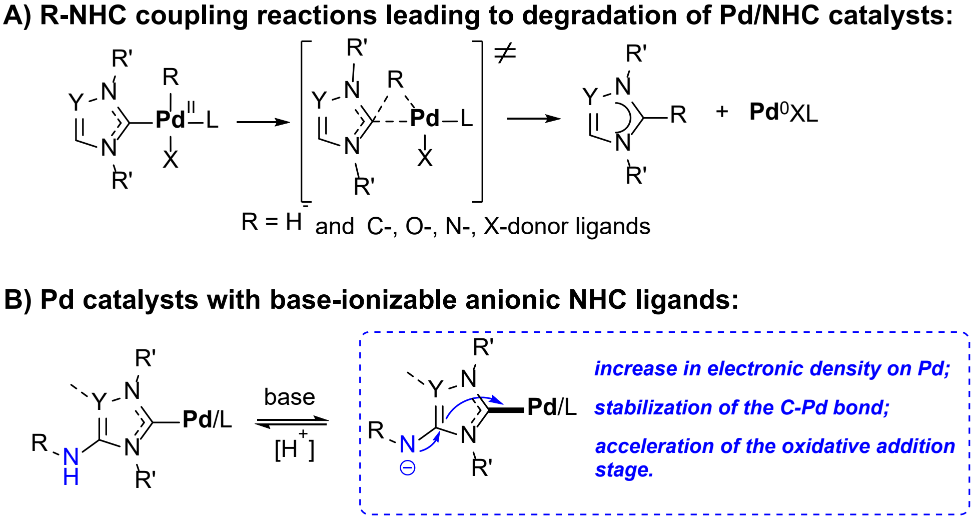
N-Heterocyclic carbene (NHC) ligands are widely used in homogeneous palladium catalysis. Despite their typically high thermodynamic stability, molecular Pd/NHC complexes often undergo degradation during catalysis, with cleavage of the Pd-NHC bond leading to the formation of nanoparticulate Pd species [1]. The degradation of molecular Pd/NHC complexes can switch the mechanism of catalysis from a truly homogeneous to a nanoparticulate mode or cause catalyst deactivation [2].


A) R-NHC coupling reactions leading to degradation of Pd/NHC catalysts:

R = H⁻ and C-, O-, N-, X-donor ligands

B) Pd catalysts with base-ionizable anionic NHC ligands:

increase in electronic density on Pd;
stabilization of the C-Pd bond;
acceleration of the oxidative addition stage.

Scheme. 1. R-NHC coupling reactions (A) and novel base-ionizable NHC ligands

The main mechanisms of Pd-C(NHC) bond cleavage during catalysis and their relative impact on the evolution of molecular Pd/NHC systems to nanoparticulate systems will be discussed. Recently disclosed NHC reductive elimination reactions (R-NHC couplings) such as O-NHC [3], N-NHC [4] and other R-RNC couplings will be considered in detail (Scheme 1) and possible solutions to the problem of Pd-C(NHC) bond cleavage will be examined. The main focus will be on the recently developed approach based on the use of novel base-ionizable anionic NHC ligands [5, 6]. These ligands can be deprotonated under basic conditions due to their NH-acidic aryl(alkyl)amino groups (Scheme 1, A). The deprotonation of these NHCs facilitates electron donation to the metal center, thereby increasing the stability of the Pd-C(NHC) bond and accelerating the oxidative addition step (Scheme 1, B). In catalytic application, the ligands and their corresponding Pd/NHC complexes showed remarkable variations in Suzuki-Miyaura (SM), Buchwald-Hartwig (BH) and ketone α-arylation reactions using unactivated aryl chlorides. The catalyst performance depended on two distinct facets related to the NHC structure: (i) the steric environment around the Pd atom, which is mainly provided by the neighboring N-aryl(alkyl) groups, and (ii) the ligand's capacity for NH deprotonation under basic conditions.

Strategies for further development of anionic NHC ligand designs and their applications in metal-catalyzed reactions will also be discussed.

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation, project FENN-2024-0002.

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OP-I-19

Stereoelectronic Effect in Phosphonium Enolates and its Application in Phosphine Organocatalysis

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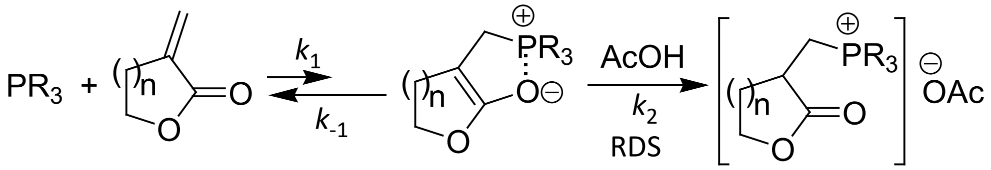
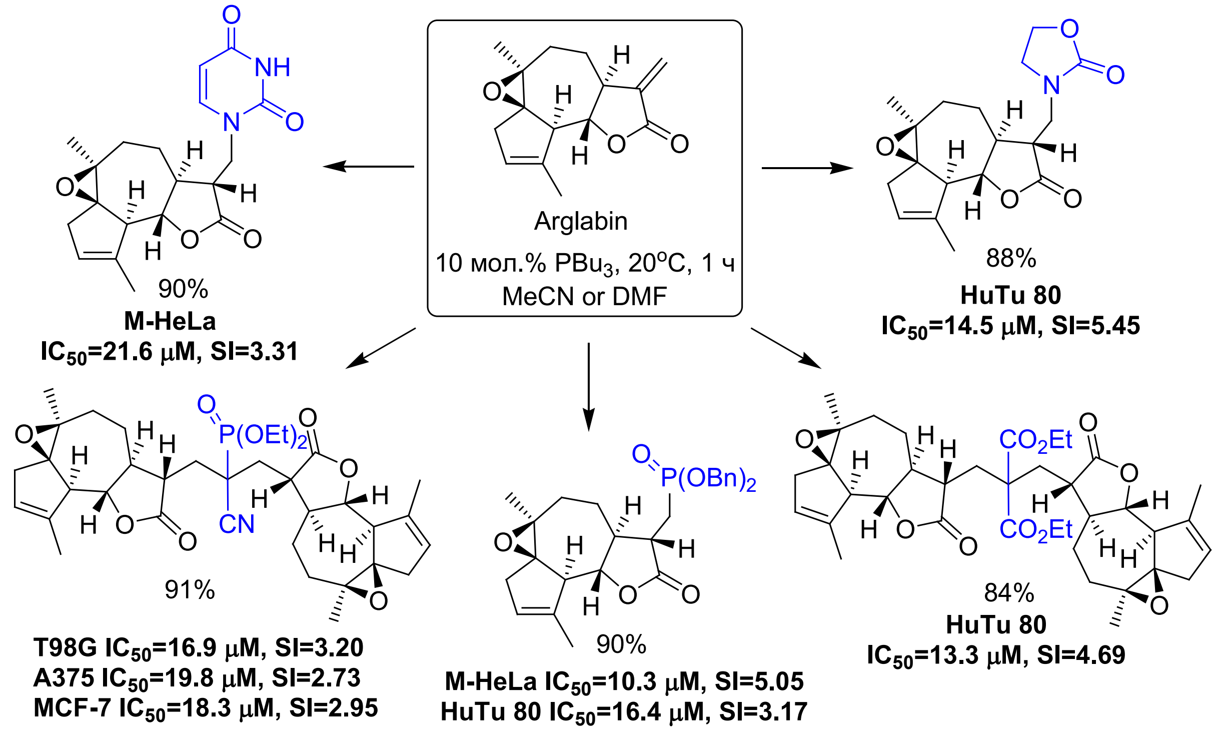
Our kinetic studies show that α-methylene lactones are much more reactive than their acyclic analogs in the reaction with tertiary phosphine nucleophiles, and the observed acceleration increases going from five-membered α-methylene-γ-butyrolactone to six-membered α-methylene-δ-valerolactone [1-3].



RDS=rate-determining step

At the same time, the reactivity of α-methylene-γ-butyrolactam used as a nitrogen-containing counterpart of lactones is very low and resembles that of acyclic analog – methacrylamide. The reactivity of α,β-unsaturated lactones and lactams was analyzed by DFT calculations at the RwB97XD/6-31+G(d,p) level of theory, which indicated that the formation of intermediate phosphonium enolate is strongly dependent on the structure of the heterocycle. The formation of these intermediates is enhanced by an intramolecular interaction between phosphonium and enolate oxygen centers predetermined by the locked s-*cis*-geometry of the Michael acceptors. However, to enable this interaction to occur, the heterocycle has to undergo distortion in the initial geometry leading to stabilizing stereoelectronic effect for lactone cycles and destabilizing effect for the lactam cycle. The geometry of lactone cycles is slightly changed upon the addition of phosphine, and a more flexible six-membered cycle allows for a stronger P···O interaction than it does the corresponding five-membered cycle. The addition of phosphine to α-methylene-γ-butyrolactam induces rehybridization of the nitrogen atom and is strongly disfavored due to the caused deformation of the lactam cycle.

Based on the stereoelectronic effect, a practical and mild method for the conjugate addition of phosphorus-, nitrogen-, and carbon-centered pronucleophiles to α-methylene-γ-butyrolactone and α-methylene-δ-valerolactone employing *n*-Bu_3P organocatalyst has been developed. This strategy was used for the design of phosphine-catalyzed reactions with the related sesquiterpene α-methylene-γ-butyrolactones of pharmaceutical significance, such as arglabin and parthenolide. 2-Oxazolidinone, uracil, diethyl malonate, dibenzyl phosphonate, and diethyl cyanomethylphosphonate derivatives of arglabin exhibited more potent antiproliferative activity towards several cancer cell lines and lower cytotoxicity towards normal cell lines in comparison to the parent arglabin, indicating the feasibility of the developed methodology for the design of novel anticancer drugs with better therapeutic potential.



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OP-I-20

Chiral NNO-Type Cu(II) and Ni(II) Complexes as Catalysts in Asymmetric Reactions

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Chiral copper(II) and nickel(II) complexes represent an important class of enantioselective homogeneous catalysts [1]. Herein, we report the synthesis and characterization of chiral Cu(II) and Ni(II) complexes based on the Schiff base of (*S*)-2-aminomethylpyrrolidine and 3,5-di-*tert*-butylsalicylaldehyde containing both Lewis and Brønsted acid/basic functionalities (Figure 1) [2]. Further, their application as asymmetric catalysts in the Henry reaction and in the kinetic resolution of epoxides with CO_2 was detailed (Figure) [3,4]. It was shown that the water molecules play a crucial role in the reactivity of the Cu(II) complex in the Henry reaction with up to 82% *ee*. The mechanism of the reaction was kinetically investigated. The bridging OAc-ion acted as a basic group deprotonating nitromethane molecule. It was shown that the presence of water can become a crucial feature of the catalysis by copper(II) complexes [3].

In the kinetic resolution of epoxides, the Ni(II) complex with iodide anion in combination with a co-ligand provided the desired carbonates with the selectivity factor up to 11.5 (the best result for styrene oxide was achieved) [4].

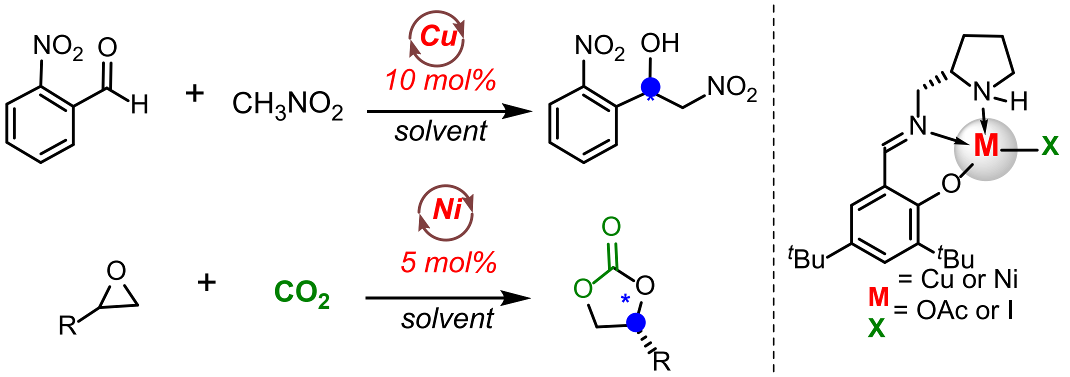

Fig. 1. Cu(II) and Ni(II) complexes in asymmetric reactions

Acknowledgement: This work was supported by the Russian Science Foundation, grant 20-13-00155.

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OP-I-21

The Role of Different Active Sites in Cascade Transformation of Glycerol over Pt-Based Nanoparticles Immobilized in UiO-66

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Since biodiesel is considered an alternative to fossil fuels, the main by-product of its production, glycerol, became highly available and relatively cheap. One of the most promising products of glycerol valorization is lactic acid (LA), which was included in the list of chemicals considered potential building blocks for the future [1]. However, in the absence of a base this transformation is multistep and requires different active sites in the catalyst (Fig. 1). A rapid conversion of the main intermediates, i.e., dihydroxyacetone (DHA) and methylglyoxal (MGO), on the right pathway is a key to high LA selectivity.

Recently, our group has shown that Zr-based metal-organic framework (MOF) UiO-66 is a suitable catalytically active support for bimetallic nanoparticles (NPs) in selective transformation of glycerol into LA in the absence of any base [2]. In the present work, we investigate the importance of different kinds of active sites on the main stages of the process over hybrid catalyst with Bi- and Sb-doped Pt NPs immobilized in Zr-UiO-66. The understanding of the effects of amount, strength and spatial arrangement can help to modify the catalyst structure in order to direct the reaction in the desired pathway and enhance the selectivity.

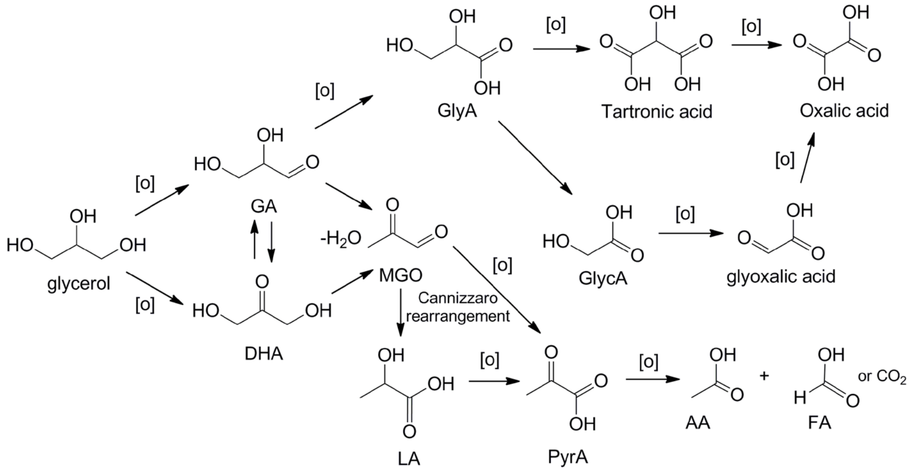

Fig. 1. Tentative reaction pathways of glycerol conversion under oxidative conditions in the presence of base or acidic sites.

Modification of Pt NPs by Sb and Bi helps to oxidize glycerol under base-free conditions predominantly in the secondary hydroxyl group with the formation of preferable intermediate, i.e., DHA. The DHA conversion increases with a decrease in electron density on Zr active sites caused by the presence of substituent in organic linker in the MOF structure (in a row NH_2-UiO-66 > UiO-66 > NO_2-UiO-66 [3]). However, acidity of the initial suspension of the reaction mixture decreases in the same row (Table 1, column 2). At the same time, the

DHA dehydration to MGO proceeds in the presence of both homogeneous Brønsted acids and the sites on the UiO-66 surface (entries 4-6), but at similar pH value the DHA conversion in the absence of MOF is significantly lower (entries 2 and 5).

Higher amounts of linker defects connected with higher amount of coordinatively unsaturated Zr sites improves both DHA conversion and LA selectivity (entries 2 and 4). Coupled with higher LA/MGO ratio in the case of higher amount of defects, it strongly supports the importance of Lewis acid sites in the MGO rearrangement steps into LA, which was further confirmed in the experiments with MGO as a substrate. However, their strength should be medium according to the obtained LA/MGO ratio in the presence of UiO-66 with different substituents.

Table 1. Catalytic properties of Zr-MOFs with UiO-66 structure

№	**Catalyst**	**$pH_{initial}$**	**l.d.***	**DHA conversion**	**Selectivity, %**			
					MGO	**LA**	**PyrA**	**AA**
1	NH_2-UiO-66	3.35	3.3	47	48	44	2	7
2	UiO-66	3.06	3.1	55	42	50	1	7
3	NO_2-UiO-66	2.74	3.3	58	48	44	1	7
4	UiO-66-hi	3.11	2.6	46	44	46	1	9
5	H_2SO_4	3.02	-	14	94	1	1	~0
6	no catalyst	3.85	-	10	98	1	~0	~0

* - amount of linker defects per one Zr-oxo-cluster;

Reaction conditions: 3 mmol DHA, 100 mg of catalyst, 100 °C, 4 h

In the absence of Lewis acid sites under acidic conditions, MGO can be oxidized to pyruvic acid, which undergoes the C–C bond cleavage with the formation of acetic acid, while in the presence of UiO-66 the rate of the MGO rearrangement is significantly higher and leads to LA as the main product. The latter is highly stable under the same conditions, excluding the possibility of acetic acid formation through its acid-catalysed C–C cleavage.

The influence of the nature of different active sites on the side reactions of DHA isomerisation to glyceraldehyde and its subsequent oxidation to glyceric acid as well as the ways to suppress these processes will be also discussed.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 19-73-30026.

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OP-I-22

New Photocatalysts for Hydrogen Generation under Visible Light Based on Layered Perovskite-Like Titanate $H_2La_2Ti_3O_{10}$ Grafted by Aromatic Molecules

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Photocatalytic water splitting and dehydrogenation of bioalcohols and other plant biomass components is a promising environmentally friendly way of hydrogen production alternative to the conventional energy-consuming methods. In view of this, one of the topical areas of materials science is the design of new photocatalysts effectively using not only ultraviolet, but also visible radiation. Layered perovskite-like oxides represent a promising class of heterogeneous photocatalysts for hydrogen production, their activity may be significantly improved via intercalation of water and substrate molecules into the interlayer space [1-3] and exfoliation with the formation of nanosheets [4, 5]. We continue the development the way to design new photocatalysts on the base of organically modified layered perovskite-like titanates $H_2La_2Ti_3O_{10}$ that have proven to be highly active photocatalysts of hydrogen evolution from aqueous solutions of methanol, glucose and xylose [2,3]. However, the derivatives with n-alkylamines and n-alkoxy groups tested earlier did not allow utilizing visible light, despite the impressing activity achieved under UV-irradiation.

In the current study, the titanate has been successfully modified with a series of aromatic compounds capable of conjugating their electron density with the perovskite matrix, which lead to the photosensitization of the initially colourless sample and the bandgap energy decrease from 3.5 eV to 2.45 eV. Samples of 25 mg decorated by 1% of Pt demonstrated enhanced hydrogen evolution activity from 1 mol. % aqueous methanol under simulated solar light (up to 38 μmol/h, apparent quantum efficiency up to 5.2%) and pure visible irradiation (up to 21 μmol/h), while the initial titanate $H_2La_2Ti_3O_{10}$ is known to function only in the ultraviolet range. Moreover, the most active organic-inorganic hybrids were shown to be stable towards photodegradation under operating conditions.

As a result, the inserted aromatic components not only provide photosensitization but also facilitate the entrance of the reactants (methanol and water) into the interlayer space which can be considered as additional reaction zone responsible for the improved performance of the inorganic-organic photocatalysts.

Acknowledgement: This work was supported by the Russian Science Foundation, grants 19-13-00184 and 22-73-10110.

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OP-I-23

Deliberate Control of the Structure-Specific Active Sites in PdIn Bimetallic Catalysts Using Adsorbate Induced Segregation Effects

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Currently, bimetallic catalysts have attracted considerable attention from many researches due to their ability to enhance catalytic properties towards numerous industrially relevant reactions. Despite thorough attempts to rationalize synergistic effects which occur upon introducing a second metal into a monometallic catalyst, their fundamental reasons and regularities still remain a subject of debate. Nevertheless, it is well established that the addition of a second metal results in the emergence of bimetallic active sites with a specific geometry on the nanoparticles surface and a change in their electronic properties. Due to this reason, most researchers believe that detailed study of their surface plays a key role for the comprehension of such effects. The chemical composition and structure of active sites are determined at the preparation step. However, it can be deliberately modified by specific treatment of the surface sample in the reactive gas atmosphere for fine surface composition tuning and consequent optimization of catalytic properties in low temperature reactions [1, 2]. It should be mentioned, that the adsorbate induced segregation effects have been reported mostly for substitutional solid solutions as PdCu, PdAu, and PdAg, while for intermetallic catalysts on the basis of compounds such as PdGa, PdZn or PdIn, these effects are not typical due to their high thermodynamic stability. However, the surface structure and catalytic performance of the intermetallic catalysts can be tuned by an alternative method, which consists in the selective oxidation of one of the components of an intermetallic nanoparticle. The combination of model systems, where nanoparticles of active metals are deposited onto an atomically smooth planar support, together with *in situ/operando* techniques may increase reliability and information content concerning the chemical and surface composition of the active component therein. One of the planar supports, which can be successfully used in such investigations, is highly oriented pyrolytic graphite (HOPG) [3, 4].

In this work, two kinds of Pd-In bimetallic catalysts have been investigated in terms of O_2-induced surface segregation: model Pd-In/HOPG and "real" Pd-In/Al_2O_3. Model bimetallic Pd-In/HOPG catalysts with size-selected particles and different metal atomic ratios have been prepared using the successive thermal vacuum metal deposition. Intermetallic Pd-In nanoparticles formation and their post-synthesis transformation upon oxidative treatments have been investigated by the combination of synchrotron radiation-based X-ray photoelectron spectroscopy and scanning tunneling microscopy. It was shown that the reversible RedOx transformation $PdIn_{intermet} \leftrightarrow Pd^0 + InO_x$ can be efficiently used to deliberately tune the nanoparticles surface composition/structure and respective catalytic characteristics.

A “real” Pd-In/Al_2O_3 catalyst was prepared and subjected to a series of oxidative/reductive pretreatments followed by studying the surface structure of PdIn nanoparticles by *in situ* NAP-XPS and diffuse reflectance infrared Fourier transform spectroscopy of adsorbed CO (DRIFTS CO). In parallel, the impact of the oxidative/reductive treatments on catalytic characteristics of Pd-In/Al_2O_3 catalyst in liquid-phase hydrogenation of diphenylacetylene (DPA) was investigated. It was shown that an oxidative treatment of the catalyst induces preferential oxidative leaching of the indium component from the intermetallic compound, modifying the catalyst active sites structure to the state with a high hydrogenation activity but poor stilbene selectivity. The changes upon the redox treatments are essentially reversible and reproducible (Figure 1). This effect can be intentionally used to get an optimum balance between activity and selectivity of the catalyst.

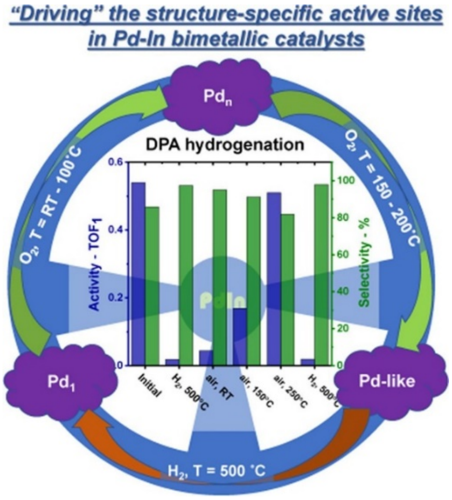

Fig. 1. A scheme of transformation of active sites in Pd-In/Al_2O_3 catalyst during oxidative-reductive treatments

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for SRF SKIF Boreskov Institute of Catalysis (FWUR-2024-0042).

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OP-I-24

The Application of Aromatic Polymers Including the Sulfonated Ones in Selective Hydrogenation of Levulinic Acid to Gamma-Valerolactone: the Role of Polymer Functionalities

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Last decades, the development of novel polymeric supports for different catalytic applications is a promising approach. In contrast to inorganic supports, polymers allow fine tuning of their properties, such as hydrophobicity, swelling ability, porosity and functionality, which directly influences the morphology of catalytically active phase and the performance of resulting catalytic system. Moreover, the distribution of metal-catalyst in the support strongly depends on the precursor nature and chosen polymer.

Different polymers were reported for the immobilization of metal-containing nanoparticles (NPs) for the reaction of levulinic acid (LA) hydrogenation to gamma-valerolactone (GVL) [1-3], among which the polymers containing acidic functional groups (-SO_3H) are promising [1, 3, 4]. For example, Yao et al. [1] developed a bifunctional catalyst based on Ru NPs of about 3 nm in diameter immobilized in cross-linked sulfonated polyestersulfone for selective hydrogenation of LA to GVL. The combination of acid and metal centers allowed for high reactivity since the mechanism of this reaction involves the dehydration step. It is noteworthy that the LA conversion achieved in 2 h at 70°C and 3.0 MPa increased from 87.9% up to 92.1% after the first hydrogenation and then up to 97.2% during the fourth catalytic cycle.

It is noteworthy that LA is a platform chemical produced from lignocellulose biomass, which is applied for the synthesis of a variety of important compounds. At present, bifunctional catalysts based on inorganic supports containing Lewis and Brønsted acid sites are the most widespread in the reaction of selective hydrogenation of LA to GVL. Despite the obvious advantages of such catalysts, there is an issue caused by high acidity of the surface – the formation of coke resulting in the catalyst deactivation [5-7]. Moreover, agglomeration and leaching of metal-catalyst can occur [8].

We have shown that hyper-cross-linked polystyrene (HPS) can be successfully used as a support for the synthesis of Ru [9, 10] and Ru-Co [11] catalysts of LA hydrogenation in aqueous medium. It was shown that the use of HPS allows formation of highly active NPs mainly consisting of RuO_2. It is important to emphasize that the HPS functionalized with tertiary amino groups allowed formation of tiny Ru-containing NPs (1-2 nm), which allowed 100% yield of GVL at 100°C and 2.0 MPa for 100 min. For comparison, the non-functionalized HPS containing NPs with diameter of about 4 nm allowed only 83% of GVL yield. It is noteworthy that in the case of non-functionalized HPS, Ru-containing NPs tended to form grape-like aggregates located closer to the outer surface of the polymer [9]. The reaction mechanism was proposed to follow the L-H kinetics, were hydrogen was adsorbed on metallic ruthenium sites, while the adsorption of LA as well as the dehydration step occurred over ruthenium (IV) oxide possessing its own Lewis acidity.

In the framework of this study, for the first time the amorphous aromatic polymeric network was synthesized by the direct knitting method [12] using phenanthrene (PHE) as a monomer. The polymer was obtained via the Friedel-Crafts reaction using $FeCl_3$ as a polymerization catalyst and methylal as a cross-linking agent. The resulting polymer possessed high specific surface area (660 m^2/g) with predominant microporosity. Moreover, PHE-based polymer was sulfonated via conventional procedure, which allowed formation of both sulfite and sulfate groups (designated as SPHE). Both PHE and SPHE polymers were used as supports for the impregnation of Ru-containing precursor. As a result, single Ru atoms as well as small sub-nanometer ruthenium clusters consisting of both metallic Ru and mixed ruthenium oxide phase were formed.

Synthesized polymeric catalysts containing 1 wt.% of Ru were tested in hydrogenation of LA to GVL in aqueous medium at variation of temperature (80-140°C) and hydrogen partial pressure (1.0-4.0 MPa). The activity of the SPHE-based catalyst was in about three times higher as compared to the catalyst based on non-functionalized PHE polymer and allowed more than 90% of LA conversion for 2 h at 120°C and 2.0 MPa. Higher activity of Ru/SPHE was attributed to the presence of $-SO_3H$ groups, which likely accelerated the dehydration step. Stability of Ru/SPHE catalyst was studied in repeated cycles. It was shown that after the second run the catalyst composition and morphology responsible to catalytic activity was stabilized. It was proposed that small ruthenium atoms and clusters are likely serve as a source of NPs formed *in situ* and remained relatively stable under reaction conditions.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-79-00009.

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OP-I-25

The Investigation of the Gd-Fe-Co Complex Oxides Catalysts in Processes Involving Greenhouse Gases

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The efficient utilisation of the two main greenhouse gases (CO_2 and CH_4) for the synthesis gas production and its further use in the Fischer-Tropsch process can be one of the solutions to the problem of finding alternative fuels due to limited oil resources [1,2].

This work focuses on the study of the physicochemical and catalytic properties of complex oxide systems with perovskite structure $GdCo_xFe_{1-x}O_3$ (x = 0, 0.2, 0.5, 0.8, 1) in dry reforming of methane (DRM) and in the carbon oxides hydrogenation. The samples were prepared by sol-gel technology using citrate-nitrate technique at atmospheric pressure. The catalysts were characterised by several modern physical and chemical methods: XRD, BET, DSC, TGA, SEM/EDX and XPS. All samples have an orthorhombic lattice, similar surface morphology and porous structure. From the XPS results, the metals in the complex oxides were found to be in the heterovalent Fe^{2+}/Fe^{3+} and Co^{2+}/Co^{3+} states, compensated by oxygen vacancies.

A reliable correlation between the amount and state of metals in the B-position of the oxides, the fraction of surface and lattice oxygen and the activity of the perovskite in the processes of DRM and CO/CO_2 hydrogenation was established when studying the catalytic properties of the obtained complex oxide systems. The partial substitution of Fe by Co in the perovskite structure led to an increase in the catalytic activity of the ferrite under DRM conditions, and high conversions of methane and carbon dioxide (~ 96-100%) were observed for all the oxides studied, and the synthesis gas ratio was close to stoichiometric. In the CO and H_2 interaction process, increasing the cobalt fraction also increased the CO conversion, and the most selective for ethylene was the sample with cobalt fraction x = 0.2, where the ratio $Co^{2+}/\sum Co^{p+}$ is maximal and $Fe^{2+}/\sum Fe^{n+}$ minimal. It is shown that Co^{3+} and Fe^{3+} are active centres in the Gd-O-Me composition, and the presence of Co^{2+} somewhat inhibits the hydrogenation process, shifting it towards olefin formation. It has been found that variation in the composition of the complex oxides $GdCo_xFe_{1-x}O_3$ results in changes in the oxygen-metal bonding energy in Gd-O-Me, the ratio of metals in different degrees of oxidation, the amount of surface and lattice oxygen, which is reflected in the adsorption and catalytic properties of the complex oxides.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 24-29-00341, https://rscf.ru/project/24-29-00341

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OP-I-26

C-C Coupling Catalyzed by Platinum Iodo Complexes: a Journey from Electrophilic to Nucleophilic Reactivity

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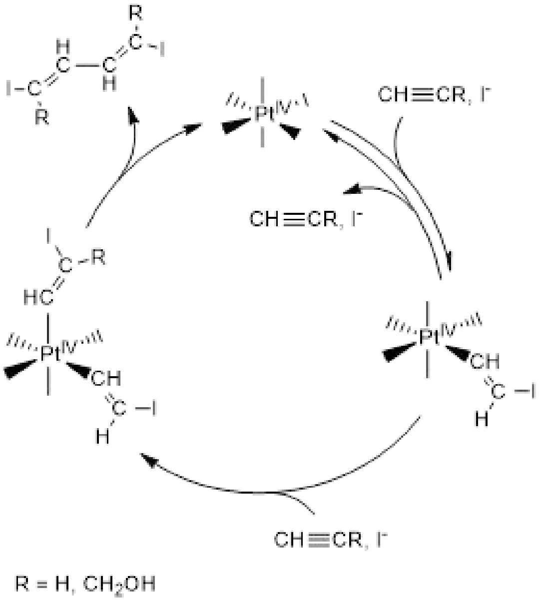
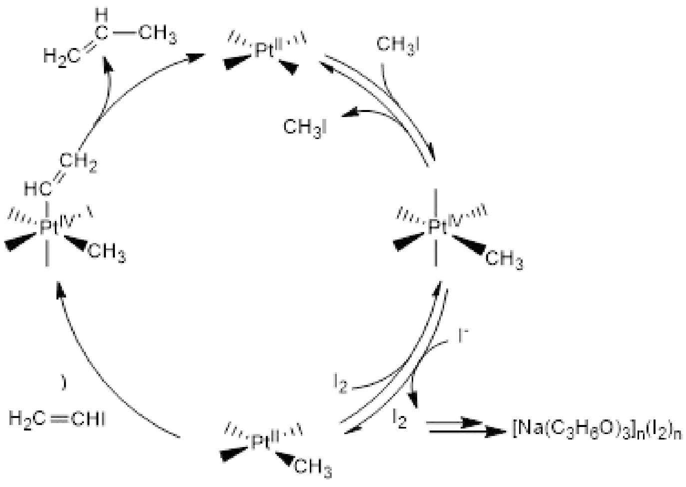
The C-C coupling reactions catalyzed by transition metal complexes have been widely used in fine organic synthesis to produce drugs, biologically active compounds, agrochemicals, functional materials, etc. [1-7]. The key intermediates of these reactions are usually metal complexes containing two organyl ligands in a mutual cis-position in the coordination sphere. There are several ways to generate such complexes. In conventional C-C coupling [8-11], bis-organyl metal derivatives are mostly generated by oxidative addition of an organic electrophile to a metal in a low oxidation state followed by transmetalation of the resulting organometallic intermediate with an organoelement nucleophile.

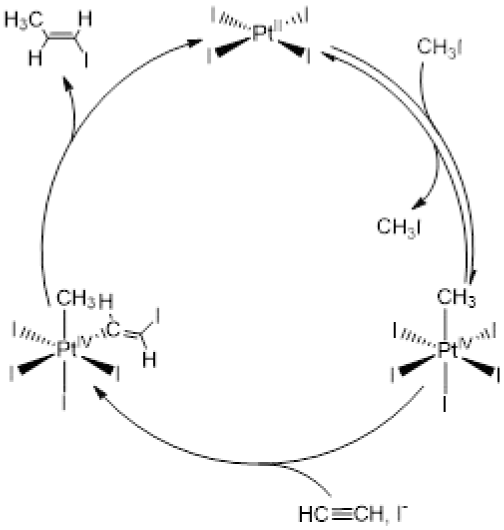
Platinum bis-organyl complexes can be generated by taking advantage of the electrophilic or nucleophilic properties of the metal complexes in its different oxidation states. So, Pt(IV) iodo complexes that show electrophilic properties are able to activate the triple bond of alkynes followed by their iodoplatination. As a result, bis-iodovinyl derivatives of Pt(IV) are generated [12], further decomposition of the latter by reductive elimination of vinyl ligands yields the C(sp^2)-C(sp^2) coupling products, 1,4-diiodo-1,3-dienes (E,E-RIC=CH-CH=CRI, R = H, CH$_2$OH).





Exploiting the solely nucleophilic properties of Pt(II) iodo complexes allowed the sequential oxidative addition of two organic electrophiles, methyl iodide and vinyl iodide, to form a methylvinyl derivative of Pt(IV) [13]. The cross-electrophile C(sp^2)-C(sp^3) coupling product, propylene, is released from the resulting intermediate by reductive elimination of methyl and vinyl ligands.

OP-I-26



Finally, it was possible to generate a methyliodinyl complex of Pt(IV) through a sequence of steps involving the oxidative addition of methyl iodide to Pt(II) iodo complexes and subsequent iodoplatination of the acetylene triple bond by the resulting methyl derivative of Pt(IV). This was achieved through the combination of the nucleophilic properties of Pt(II) in the oxidative addition of C-electrophile with the electrophilic properties of the resulting organometallic derivative Pt(IV) in activating the triple C-C bond [14]. The Pt(IV) methyliodinyl complex decomposes via reductive elimination of its methyl and vinyl ligands, resulting in the formation of iodopropene, a C(sp^2)-C(sp^3) coupling product.

The detailed reaction mechanisms of the considered C-C coupling reactions will be highlighted, and their theoretical justification will be given in the report.

Acknowledgement: This work was supported by the State Assignment "Catalytic transformations of hydrocarbons and their derivatives under homogeneous and heterogeneous conditions to form new C-C, S-O, and C-element bonds" (Grant No. FRES-2023-0005).

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OP-II-01

Kinetic Peculiarities of Ethylene, Propylene and Hexene-1 Polymerization over the Stereospecific Supported Titanium-Magnesium Catalysts According to the Data on the Molecular Weight Distribution of Polymers Produced

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It is well known the presence of different internal donors (ID) in the composition of titanium-magnesium catalysts (TMC) determines the high stereospecifity of these catalysts and affects greatly as well on the molecular weight distribution (polydispersity) of polypropylene produced.

We have obtained in our work new experimental data on the effect of different internal donors in the composition of TMC (di-n-butyl phthalate (DBP), diethyl 2,3-di-isobutyl succinate (DIBS), isopropyl-isopentyl-dimetoxypropane (IPIPDMP)) on the molecular weight distribution of polyethylene (PE), polypropylene (PP) and polyhexene (PH) produced over these catalysts at polymerization in the absence and presence of hydrogen. It was shown that polydispersity (Mw/Mn values) of PE is practically the same for different ID (fig 1). On the contrary for propylene and hexene-1 polymerization the structure of internal donors and presence of H_2 affect Mw/Mn values (fig 2). These data allowed to propose the explanation of the effect of internal donor composition on the polydispersity (Mw/Mn values) of polypropylene and polyhexene produced over these catalysts and the absence of this effect in case of polyethylene produced with the same catalysts.

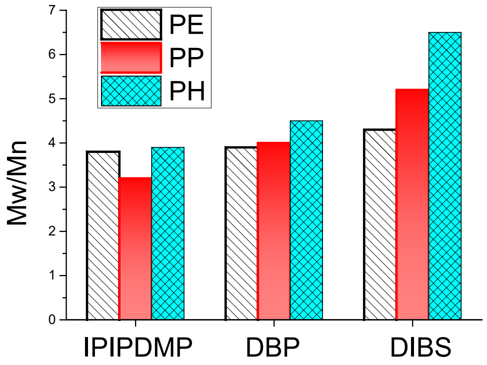

Fig. 1. Mw/Mn values of PE, PP and PH, produced over the TMC with different ID in the presence of H_2.

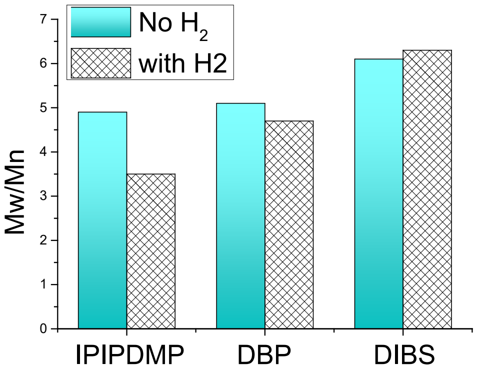

Fig. 2. Mw/Mn values of PH, produced over the TMC with different ID in the absence or presence of H_2.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-90-01001.

OP-II-02

The Process Mechanism View to Design Catalysts. Conversion of Ethylene to Propylene over $NiO-MoO_3/Al_2O_3$ Catalyst

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Propylene is one of the highly-demanded raw materials for the petrochemical industry. To reduce the existing gap between the demand for propylene and its production from the traditional sources, new efficient technologies are being developed (propane dehydrogenation, methanol conversion, metathesis, etc.). One of the most exciting methods is the conversion of ethylene to propylene, but today it is a step by step industrial process with different catalysts on the each stage. To make this process more profitable, one effective catalyst is proposed to use for the conversion of ethylene to propylene by one stage.

This process can be carried out by the sequential reactions of ethylene dimerization, isomerization of the obtained 1-butene to 2-butenes, and their metathesis with ethylene. From the thermodynamic point of view all these required stages of the conversion of ethylene to propylene are possible at temperatures up to 200°C. Therefore, it makes sense to carry out these sequential reactions over one catalyst, characterized by the simultaneous presence of different active sites.

We have designed the $NiO-MoO_3/Al_2O_3$ polyfunctional catalyst, in accordance with the process mechanism view. The active components of the proposed catalyst were selected based on the data that Ni-containing catalysts are typical catalysts for the dimerization and oligomerization of ethylene. The isomerization of 1-butene to cis-/trans-butene catalyze by the acidic sites. Finally, typical metathesis catalysts are based on W, Mo and Re oxides.

Direct conversion of ethylene to propene catalytic activity experiments were carried out in a fixed bed flow reactor at 100-250°C, atmospheric pressure and weight hourly space velocity of 0.25-2 h^{-1}. The catalytic activity increased with an increase in reaction temperature, reaching a maximum at 150-250°C. At the same time, with increasing temperature the propylene selectivity decreased, while the selectivity of butenes and C_{6+} hydrocarbons increased. The catalyst $NiO-MoO_3/Al_2O_3$ showed the maximum propylene yield of 57 wt.% with ethylene conversion of 90% at 150°C and 0.25 h^{-1}.

The kinetic model for the process has been proposed, based on the experimental data, which adequately described the formation of the main reaction products. All of the main reactions such as ethylene dimerization, isomerization of butenes, metathesis of butenes-2 and ethylene, metathesis of butenes, and oligomerization of ethylene, propylene, butenes, etc. were considered in the kinetic model. To reduce the complexity of the kinetic model and increase its clarity, a combination of genetic algorithm and L1 regularization was used.

The rate-limiting step for the process for conversion of ethylene to propylene was established to be the reaction of ethylene dimerization. The most significant reactions for the product formation are the ethylene dimerization, the isomerization of butene-1 to butenes-2, and the metathesis of butenes-2 and ethylene. The kinetic study of catalysts deactivation showed that the three main reactions rates decreased over time. Moreover, the fastest deactivation was observed for the metathesis active sites as evidenced by a significant decrease in the rate constant of this reaction. The contribution of oligomerization and isomerization reactions to the formation of products increased accordingly.

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov lnstitute of Catalysis (project FWUR-2024-0039).

OP-II-03

Applying Isotope-Labeled Reagents to Gain Insight into the Mechanisms of Acetylene Catalytic Hydrochlorination

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Polyvinyl chloride (PVC) is the third most produced synthetic polymer in the world after polyethylene and polypropylene. The global PVC market size exceeded USD 40 billion in 2022 and is expected to grow at a rate of over 4% in the next five years. Depending on the raw stock, different technologies have been developed to produce the only monomer, vinyl chloride. The first commercial process was based on acetylene hydrochlorination and, having been launched in the 1920s, remains the main production technology in China until today due to abundant coal resources. Meanwhile, a balanced process combining chlorination and oxychlorination of ethylene was developed in the 1950s and is now the predominant technology in Europe and the United States. Nonetheless, acetylene hydrochlorination remains important as about half of the world's PVC production is still manufactured in China by this method. This reaction is getting more and more attention, becoming a hot topic after the signing of the Minamata Convention on Mercury in 2013 [1]. A strong driver for this is the use of traditional mercury-containing catalysts, which sublimate under process conditions, reducing process efficiency and posing serious concerns for human health and environmental pollution. To reduce mercury emissions, the development of alternative mercury-free catalysts for acetylene hydrochlorination is urged.

The targeted design of new catalytic systems is not feasible without a clear insight into the mechanism of catalytic action. However, the generation of clear ideas on the catalytic transformation mechanisms is usually complicated, since most reactions proceed in a sequence of a fairly large set of elementary steps. One of the important targets on the way to solving this problem is to identify the rate-limiting step as playing a crucial role in the reaction mechanism. Another challenge is to define the selectivity of the reaction, since tuning the process parameters could shift the selectivity of the reaction due to changes in its mechanism. The gaining of mechanistic insight becomes more challenging when the target product is the only one, as in the case of catalytic acetylene hydrochlorination. In this case, the stereoselectivity of the reaction can provide a piece of data regarding its mechanism.

Addressing both questions is facilitated when the reaction is carried out using isotope-labeled reagents, since this approach provides information on both the rate-limiting step (and transition state structure) and the stereoselectivity of the reaction. The use of deuterochloride in systems with mechanically pre-activated salts K_2PtCl_6 and K_2MCl_4 (M = Pt, Pd) allowed us to reveal [2-5] two isotope effects differing in magnitude, the kinetic isotope effect (KIE) and the product isotope effect (PIE) [6]. These indicate the rupture of the H-Cl bond in at least two steps of the reaction, in the rate-limiting chlorometallation step of the π-coordinated acetylene and the rapid protonolyses of the formed chlorovinyl metal derivative. Besides, the use of H(D)Cl allowed us to determine the stereoselectivity of the reactions in the above systems, where exclusively the product of the *anti*-coupling of chlorine and deuterium atoms to the acetylene triple bond was formed.

In contrast to systems with bulk mechanically pre-activated catalysts, for $PdCl_2$ supported on activated carbon, $PdCl_2/C$, products of both *anti*- and *syn*-addition of D and Cl atoms to the acetylene triple bond were found during acetylene hydrochlorination in HCl/DCl atmosphere [7]. Two different in magnitude isotope effects, KIE and PIE, were also found here, indicating the involvement of the hydrochloride molecule in the two steps of the catalytic reaction. In $PdCl_2/C$ systems, the yield ratio of *trans*-HDC=CHCl and *cis*-HDC=CHCl stereoisomers was calculated [7] assuming that the PIE value for both routes is the same. However, kinetic isotope effects of HCl/DCl could distort the indicated ratio, so to obtain reliable information about the stereoselectivity of the reaction, it is necessary to exclude their possible contribution. This could be achieved by using deuterated acetylene C_2D_2 and HCl in the reaction. We used this approach to clarify the stereoselectivity of the catalytic acetylene hydrochlorination in a system with a $PdCl_2$ catalyst supported on activated carbon.

The results of a mechanistic study using isotope-labeled reagents of the vapor-phase acetylene hydrochlorination over bulk and supported heterogeneous catalysts will be reported.

Acknowledgement: This work was supported by the State Assignment "Catalytic transformations of hydrocarbons and their derivatives under homogeneous and heterogeneous conditions to form new C-C, S-O, and C-element bonds" (Grant No. FRES-2023-0005).

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OP-II-04

Hydrogen Adsorption as a Limiting Stage for Hydrogenation of Unsaturated Hydrocarbons

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In a number of works [1-4] it was suggested that in the case of hydrogenation of unsaturated hydrocarbons, the limiting stage is hydrogen adsorption. Thus, the heat of hydrogen adsorption should determine the rate of hydrogenation. However, such a relationship has not been found in explicit quantitative form in the literature.

Two catalysts were chosen for the study. The first is the skeletal nickel catalyst, which has a long history and is very well described and studied [5]. The second is nickel deposited on silica gel via the mechanochemical method (Ni/SiO_2) [6]. Sodium maleate was chosen as a model reactant, the kinetics of which hydrogenation has been well studied [6-8]. This choice of the reactant and catalysts was made to avoid the influence of side processes as much as possible. To increase the variability of the system (increase the number of measured points), each catalyst was modified with a small quantity of deactivating agent. This made it possible to change the number of active centers in a given way. The well-known [6,7,9] catalytic poison sodium sulfide was chosen as a deactivating agent. Aqueous solutions both without additives and with the addition of alkalis and simple monohydric alcohols were used as solvents.

To study the activity of catalysts, a static method was used under unsteady conditions, using a sealed liquid reactor of periodic action, providing such mixing of the reaction mass, which made it possible to eliminate the influence of external mass transfer [6]. To experimentally measure the heat of hydrogen adsorption over the surface of catalysts under conditions identical to those described above, a liquid reaction calorimeter with an isothermal shell was used [6]. As a result of the studies described above, for each catalytic system (catalyst-solvent-deactivating agent), the activities (A), the maximum distribution of the heat of hydrogen adsorption on the catalyst ($\Delta_a H_{meas}^{peak}(H_2)$), and the quantity of catalyst deactivating agent (n(CDA)) were established. These data are presented in Fig. 1 (red balls).

An equation of the plane was derived that well describes the experimental data obtained (see the coincidence of the plane and balls in Fig. 1):

$$A_{calc} = A_{max}\left(1 - \frac{\Delta_a H_{meas}^{peak}(H_2)}{\Delta_a H_{max}^{peak}(H_2)} - \frac{N_A \cdot K_{S-Ni}}{N_{as}^{norm}} \cdot n(CDA)\right) \qquad \text{(eq.1)}$$

Based on the data obtained, the equation for TOF can be derived:

$$TOF_{calc} = TOF_{max}\left(1 - \frac{N_{as}^{norm} \cdot 60}{K_{S-Ni} \cdot n(CDA)}\right)\left(1 - \frac{\Delta_a H_{meas}^{peak}(H_2)}{\Delta_a H_{max}^{peak}(H_2)} - \frac{N_A \cdot K_{S-Ni}}{N_{as}^{norm}} \cdot n(CDA)\right) \qquad \text{(eq.2)}$$

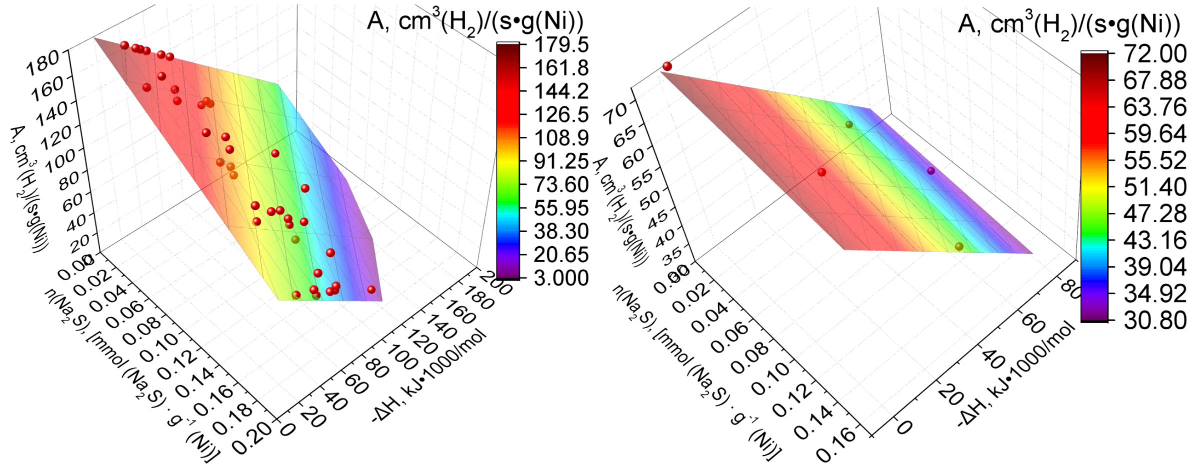

Fig. 1. Linear relationship of the activity of the catalyst and hydrogen adsorption enthalpy

Table 1. Constants for Equations 1 and 2

	Skeletal nickel catalyst	Ni/SiO$_2$	
$\Delta_a H_{max}^{peak}$=	-242	-155	Maximum on the hydrogen distribution graph on the heat of adsorption over the catalyst, kJ·mol−1
A_{max}=	196	72.5	The maximum possible activity of 1 gram of catalyst (measured from calorimetric experiment), cm^3·s^{-1}·g^{-1}
N_{as}^{norm}=	1.85·10^{21}·[10]^{a}	4.79·10^{19} ^{a,b}	The number of active centers per one gram of a catalyst, g^{-1}
K_{S-Ni}=	8	0.03	Coordinating number for catalytic poison in relation to the active metal of the catalyst

[a] The surface area is determined using low -temperature adsorption of nitrogen according via the BET method;

[b] To determine the number of surface atoms of reduced nickel on the surface of a catalyst, a combination of EDX, XPS was used.

Thus, it is thermodynamically confirmed that hydrogen adsorption is the limiting stage.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 24-23-00362, https://rscf.ru/en/project/24-23-00362/ .

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OP-II-05

Mechanism of Isomerization-Disproportionation Conversion of Straight-Run Gasoline on a Composite Catalyst

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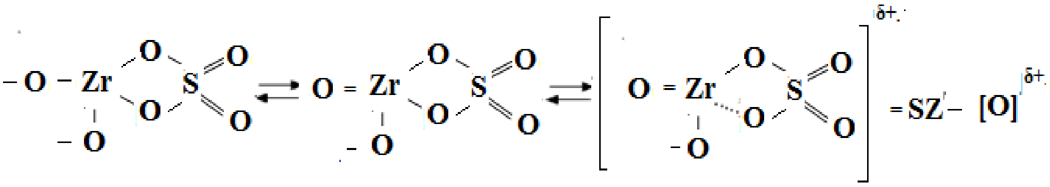
The conversion of straight-run gasoline (SRG) on a composite catalyst consisting of sulfated zirconium dioxide (SZ) and Co-modified zeolite HZSM-5 was studied. The process was carried out at atmospheric pressure, at a temperature of 140-200^{0}C, in a flow-through laboratory installation in the presence of hydrogen. Optimal process conditions (180^{0}C; H2/CH=3; WHSV = 2.5 h^{-1}) was established, under which the conversion of C_{7+} hydrocarbons of SRG is 77.3%, and the sum of high-octane gasoline components C_5–C_6 alkanes increases from 11% to 61%. It has been established that the C_{7+} components of SRG are capable of transformation, both monomolecularly with the formation of C_{4-} products, and in parallel with their involvement in the formation of [C_{4-}+C_{7+}] bibimolecular intermediate and their hydrocleavage. The presence of water vapor in the reaction zone within 5% has a complete deactivating effect on the conversion of straight-run gasoline with the participation of a composite catalyst. To elucidate the effect of water vapor on the active centers of the individual components of the used catalyst with their participation, we studied the acid-base reaction of the conversion of ethanol into diethyl ether and ethylene, which proceeds with the release of water molecules. From the results obtained (table) it follows that SZ turned out to be practically inactive in the process of C_2H_5OH conversion under the conditions of SRG conversion. In contrast to SZ, Co/HZSM-5 exhibits sufficient activity and stability both in the individual conversion of C_2H_5OH and in mixtures with SRG. Therefore, the formation of water molecules has an inhibitory effect on the centers located on the SZ. At the same time, it follows from the results obtained (table) that the primary activation of the C_{7+} components of SRG proceeds with the participation of active sites that do not exhibit acid-base properties located on the SZ. Such centers can be electrophilic oxygen atoms that are part of the modifying SO_4^{2-} anion. As a result of the interaction of water molecules, the resulting SZ, such

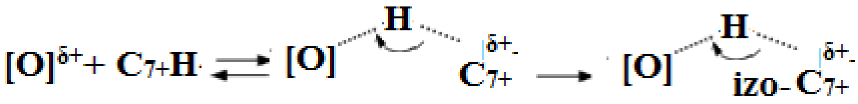
Table.Conversion of ethanol and a mixture of SRG:C_2H_5OH (4:1 mol) on CC and its components. T=180^{0}C, WSHV=2.5 h^{-1}, $\upsilon_{H2} \geq 40$ ml·min^{-1}, τ=60 min.

Catalyst sample	Conversion of C_2H_5OH, %	Conversion of SRG : C_2H_5OH, %	
		SRG	C_2H_5OH
SZ	traces	-	-
Co/HZSM-5	12.0	-	9.5
Co/HZSM-5-SZ	12.2	-	8.8

centers either lose their electrophilicity or are blocked for interaction by C_{7+} hydrocarbons. At the same time, the centers located on Co/HZSM-5 are independent of the action of water molecules and retain their activity in the acid-base type reaction, which includes the hydrocracking of C_{7+} type alkanes on SZ, there is an equilibri-um of the type (1) with the participation of which the initial activation and isomerization of natural gas paraffins occurs (2)

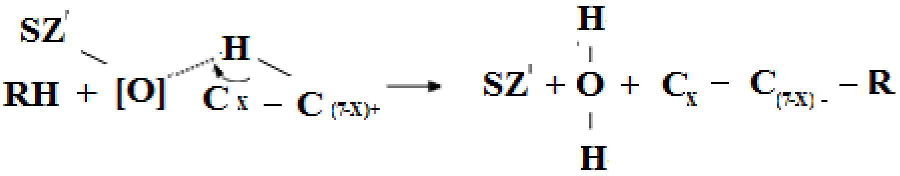


(1)



(2)

Stabilization of (2) proceeds on SZ' with the participation of RH molecules contained in the reaction medium (where R=H, or the alkyl group of C_{4-}).



(3)

Stabilized alkanes in the case of $RH=H_2$ and process conditions can be isolated as isomerization products or undergo hydrocracking with the participation of the zeolite component. In the case of low activity of the cracking component, the accumulation of intermediate products will contribute to the deactivation of the composite catalyst.

Inactivated as a result of reduction (2), SZ is reactivated again by oxidation:

$$SZ' + H_2O \rightleftarrows SZ + H_2$$

OP-II-06

The Active Centers in Pt/CeO$_2$ Catalysts for CO Oxidation. Experimental Study and Kinetic Simulations

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Catalysts based on the ceria and platinum demonstrate high activity in carbon monoxide oxidation reaction, which is the most popular and informative reaction used for the investigation of reaction mechanisms. The main factors determining the catalysts' activity are the size, microstructure of active species and the oxidation state of platinum atoms in their composition. All these factors can be important in CO oxidation when the catalyst performance is realized in different temperature ranges. As a consequence, the influence of these factors is reflected in the corresponding temperature dependencies of CO conversion which can be located in different temperature ranges and exhibit specific kinetic features. To describe the kinetic behavior in CO oxidation, only one type of active centers is usually considered, and only one mechanism is usually applied: Langmuir-Hinshelwood (LH) or Mars-van Krevelen (MvK) mechanism. Such an approach does not allow describing the reaction kinetics in a wide temperature range properly.

In this work, for the first time, a complex modeling of the kinetics of the CO oxidation reaction using the full set of active centers on the surface of Pt/CeO$_2$ catalysts was carried out in a wide temperature range of -50-450 ^{o}C. The experiments give evidence to the formation of Pt-containing active species in metallic and oxidized states, the latter including the isolated Pt^{2+} ions (Pt^{2+}-single atoms, Pt^{2+}-SA-centers) and oxidized PtO$_x$ clusters [1]. The relative content of these centers is determined by the method of preparation, redox pretreatment and loading of platinum in the catalysts [2]. Considering the concepts of the MvK mechanism, the modeling of the CO conversion on temperature was satisfactorily carried out in the temperature range of 100-450 °C on the base of Pt^{2+}-SA centers formed in the Pt/CeO$_2$ catalysts with a low content of platinum. It was established that, however, the kinetic description at lower temperatures using only Pt^{2+}-SA-centers was unsuccessful [3].

To extend the reaction simulation range towards low temperatures, it is necessary to consider other active centers, which are formed at an increased content of platinum. The complex of experimental methods (XRD, XPS, HRTEM, Raman, TPR-CO) allowed us to establish the formation of small PtO$_x$ (Pt$_n$O$_m$, where n is 3-10) clusters with high oxygen reactivity towards CO. Modeling using MvK mechanism on PtO$_x$ clusters made it possible to describe the experimental data in the temperature range of 50-100 °C, but it was not possible to describe the experimental data at lower temperatures under any theoretical assumptions and stage parameters.

It has been established that the low-temperature range below 50 °C is modeled by a reaction route based on the associative (concerted) trimolecular mechanism proposed earlier in the literature [4,5] for a number of catalytic systems. The introduction of stages providing the implementation of both the MvK mechanism and the associative (concerted) Low-T mechanism at PtO_x centers into the full kinetic model made it possible to simulate a complete description of the experimental data over the entire temperature range of the reaction from -50 °C to 450 °C (Fig.1).

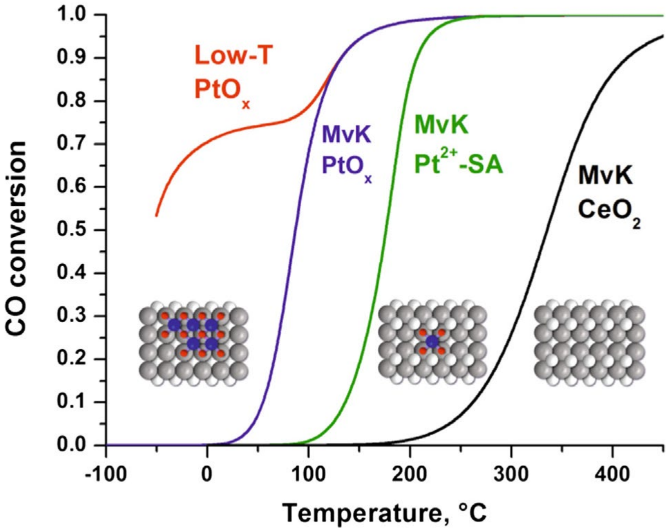

Fig. 1. Results of the simulations of CO oxidation over CeO_2 and Pt/CeO_2 catalysts

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental assignment for Boreskov Institute of Catalysis (project FWUR-2024-OO32).

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OP-II-07

Control of Polycarbonate Degradation Reactions Using Catalysis and Photocatalysis by Nanoparticles Differing in Chemical Nature, Shape and Size

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The kinetics of thermal degradation of polycarbonate films containing Ag, Au, Pt, Pd, Ni and TiO_2 nanoparticles was studied in vacuum using automatic vacuum thermobalances [1]. It has been shown that the rate of destruction of polycarbonate nanocomposites (NC) depends not only on the chemical nature, size and shape of nanoparticles, but also on preliminary UV irradiation.

Polymer samples containing spherical Ag nanoparticles with a size of <40 nm in the volume of the samples decompose at the highest rate; deposition of Pt, Ni, and Ag nanowires onto polycarbonate films by laser ablation [2] also leads to an increase in the rate of NC degradation.

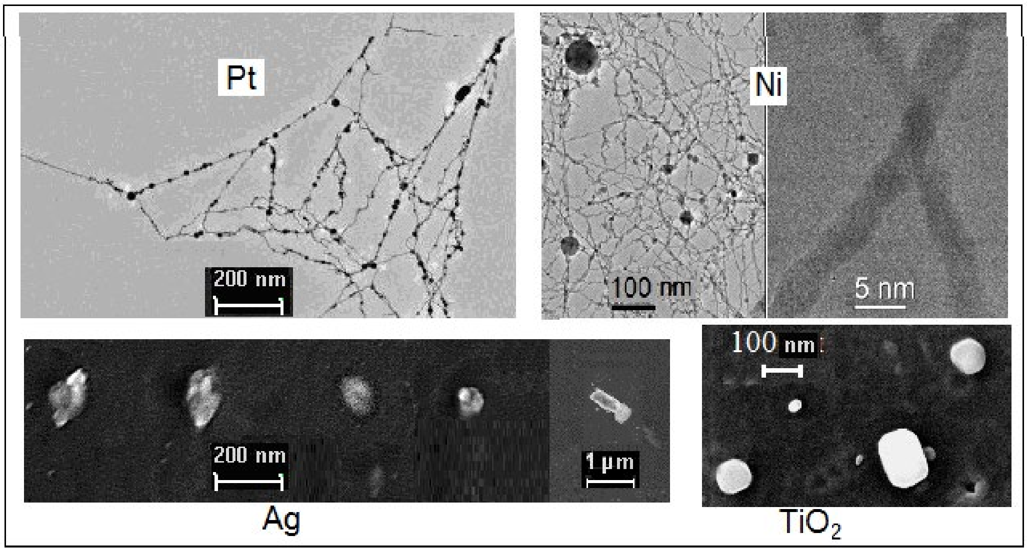

Fig. 1. TEM images of Pt and Ni nanowires and SEM images of Ag and TiO2 nanoparticles in polycarbonate films.

The kinetics of thermal degradation of polycarbonate films containing TiO_2 nanoparticles deposited on polymer films by electron-beam evaporation of TiO_2 powder in vacuum has been studied. The weighted average thickness of the deposited layer was 5–30 Å, which corresponded to ~0.003–0.020 wt. %. TiO_2 nanoparticles in the polymer. The rate of degradation of polycarbonate films increases with increasing concentration of TiO2 nanoparticles deposited on film samples. However, it is important to note that after UV irradiation of polymer films containing TiO_2 nanoparticles (the polymer films of 80-100 μm in thickness were irradiated with a DRT-400 mercury lamp with wavelength λ < 390 nm for 6 hour.) the rate of degradation of polycarbonate NC decreases as the concentration of nanoparticles increases.

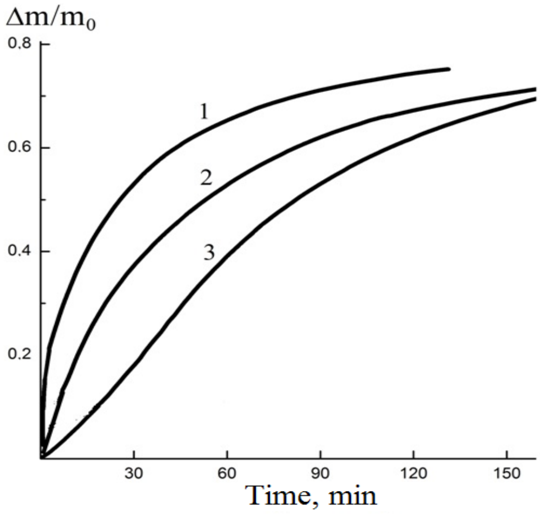

Fig. 2. Kinetic curves of relative mass reduction during the thermal degradation of the *original polycarbonate (2); non-irradiated (1) and irradiated (3) polycarbonate films containing 0.01 wt. % TiO2 nanoparticles; T=420°C.*

The addition of solid decomposition products of non-irradiated NC containing TiO_2 particles to a fresh polymer also leads to an increase in the rate of degradation of polycarbonate, which suggests that the thermal decomposition of the latter is catalyzed by non-irradiated TiO_2 particles. The slowdown in the rate of mass loss during the decomposition of irradiated NC is apparently caused by photocatalysis of competing reactions of crosslinking of polymer chains by irradiated TiO_2 nanoparticles.

Thus, by changing the size, shape and concentration of nanoparticles, as well as irradiation conditions, it is possible to control the rate of competing decomposition and cross-linking reactions during thermal transformations of polycarbonate nanocomposites.

Acknowledgement: This work has been performed in accordance with the state tasks, state registration N 124013100856-9 and 124013000757-0 using equipment of the Center for Collective Use FRC PCP MC RAS.

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OP-II-08

Insight into Mechanism of 5-HMF Aerobic Oxidation over PdAu Supported Catalysts under Mild Conditions

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FDCA is an attractive alternative to terephthalic acid for polymer industry, with the aerobic oxidation of 5-hydroxymethylfurfural (HMF) over noble metals (Au, Pd, Pt, Ru) catalysts being the most promising way of its production (Fig. 1) [1-3]. Over the past two decades, the 5-HMF oxidation to FDCA was extensively studied, and different reaction mechanisms were proposed for different catalysts [4]. The mechanism of the cascade HMF oxidation through a gemdiol formation in a strongly alkaline medium (pH > 12, NaOH) over the monometallic Au, Pd, Pt catalysts is the most studied one. Nevertheless, there is no detailed understanding of the reaction mechanism for other catalysts and/or conditions. The present study is focused on the kinetic and mechanistic study of the HMF oxidation to FDCA under mild conditions (pH = 8, using $NaHCO_3$ instead of NaOH) over alloyed AuPd catalyst.

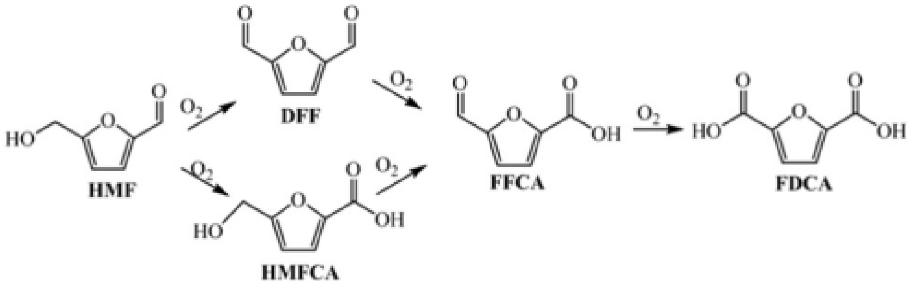

Fig. 1. The scheme of 5-HMF transformations.

Metal 1-xAuxPd nanoparticles (NPs) with different Au:Pd ratio were obtained via pulsed laser ablation (PLA) [5]. $Ce_{1-y}Zr_yO_2$-supported mono- and bimetallic catalysts were prepared by impregnation-reduction technique using H_2PdCl_4 and $HAuCl_4$ as metal precursors and $NaBH_4$ as a reducing agent. The samples were characterized by XRD, UV-vis spectroscopy, XRF, XPS, CO or O_2 chemisorption, temperature-programmed reduction with hydrogen (TPR-H_2), and TEM. The HMF oxidation was carried out in the Parr 5500 HR reactor, with the reaction mixture being analysed by HPLC.

The results obtained indicate that both colloidal and supported bimetallic samples characterized by the formation of alloyed $Au_{1-x}Pd_x$ NPs with x=0.35-0.55 show superior catalytic performance towards the HMF oxidation to FDCA due to the synergistic effect. Kinetic curves of the 5-HMF oxidation show that the reaction mixture composition differs significantly for monometallic and bimetallic alloy catalysts (Fig. 2). The primary intermediate of the 5-HMF oxidation for alloyed catalyst is FFCA, while for monometallic samples, HMFCA is the main product.

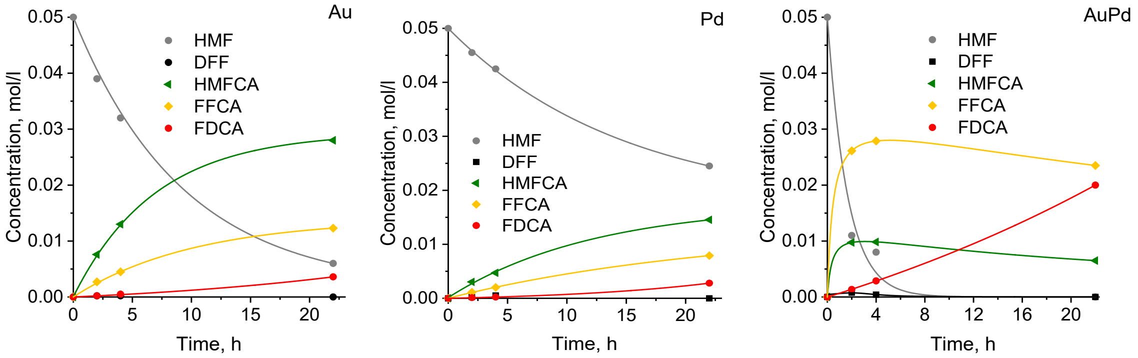

Fig. 2. Kinetic curves for HMF oxidation over colloidal Au, Pd, and 60Au40Pd catalysts. Experimental conditions: HMF/metal/$NaHCO_3$ molar ratios of 1/0.01/4, 5 atm O_2, 80 °C.

The detailed kinetic studies, including those for intermediate compounds (DFF, HMFCA, FFCA), showed that the synergistic effect observed for bimetallic alloy particles was accompanied by a change in the reaction pathway of the HMF oxidation under low-base conditions. In contrast to the dead-end pathway via the aldehyde group oxidation to form HMFCA over the monometallic Au and Pd catalysts, its oxidation over bimetallic alloy NPs proceeded via the hydroxyl group oxidation to form DFF followed by its further consecutive oxidation to FFCA and FDCA, with the FFCA oxidation to FDCA being the rate-limiting stage. For the AuPd/$Ce_{1-y}Zr_yO_2$ catalyst, the lattice oxygen of the $Ce_{1-y}Zr_yO_2$ support was shown to be directly involved in the cascade HMF oxidation promoting more efficient oxidation of FFCA to FDCA.

The roles of oxygen activation, substrate adsorption, base presence, and support redox properties were considered to clarify the reaction mechanism of the HMF oxidation under mild conditions.

Acknowledgement: This work was supported by the Russian Science Foundation, grant №19-73-30026.

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OP-II-09

Influence of the Composition of $LaFe_{1-x}Co_xO_3$ Perovskites on the Activity in the Decomposition Reaction of Nitrous Oxide

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Greenhouse gas emissions have approximately quadrupled over the past 20 years. Among greenhouse gases, nitrous oxide has a significant global warming factor, about 320 times higher than that for CO_2, so withlower N_2O emissions is an urgent task. One of the main sources of nitrous oxide entering the atmosphere is the production of nitric acid (global emission of nitrous oxide in nitric acid production is about 300–400 kt/ year), in which nitrous oxide is formed in the process of non-selective oxidation of ammonia on platinum catalyst gauzes, as well as in the interaction of the main product - nitric oxide - with ammonia (that has slipped through gauzes) in the space after the gauzes.

One of the ways to reduce nitrous oxide emissions is the high-temperature decomposition of nitrous oxide on a secondary catalyst, which is located after the catalyst package (along the gas course) in the ammonia oxidation reactor [1]. In this case, the catalyst must be active and stable in the reaction environment, not decompose the reaction product – nitric oxide, reduce the amount of ammonia slip, and also be characterized by low hydrodynamic resistance.

Due to their physical and chemical properties, ABO_3 perovskites are of interest as catalysts for various high-temperature processes involving oxygen oxide, including catalysts for the decomposition of nitrous oxide. $LaFeO_3$, $LaCoO_3$, $LaMnO_3$ and $LaNiO_3$ perovskites are known to be active in the reaction of high-temperature decomposition of nitrous oxide. Well-known industrial catalysts for high-temperature decomposition of nitrous oxide are, for example, a granulated four-hole catalyst based on La-Ce-Co-O perovskite, as well as a honeycomb catalyst based on La-Ce-Fe-O perovskite, which provide an 80-90% degree of decomposition of nitrous oxide under industrial conditions. The properties of ABO_3 perovskites can vary considerably, not only depending on the nature of the A and B cations, but also when their stoichiometric ratio is changed or when substitute cations are introduced into the A and/or B sublattices. It has been shown, for example, that the substitution of iron for manganese results in an increase in activity of 10-15% relative to lanthanum ferrite and a maximum conversion at 900 °C demonstrated samples of $LaFe_{1-x}Mn_xO_3$ with x=0.2-0.6 [2]. Another factor influencing the activity of perovskites is the method of preparation, which determines not only the specific surface area values but also the features of the microstructure of oxides [3].

The object of this study is the perovskites $LaFe_{1-x}Co_xO_3$ (x=0–1), which were studied in the reaction of high-temperature decomposition of nitrous oxide. The physicochemical properties of oxides are characterized by the methods of XRD, BET, EM, XPS, and H_2-TPR. $LaFe_{1-x}Co_xO_3$ catalysts were prepared by the Pechini method from a mixture of nitric acid salts taken in a stoichiometric ratio and with the addition of citric acid and ethylene glycol. After evaporation of the solution, the formed polymer-salt precursor was burned and then calcined at 900 °C. The catalytic activity in the nitrous oxide decomposition reaction was determined in a flow reactor in the temperature range of 750-900 °C for the catalyst particles of 0.25-0.5 mm at a contact time of 0.001 s using a reaction mixture of 0.15% N_2O + 3% O_2 + 3% H_2O in helium. It was preliminarily established that there was no homogeneous process in the reactor under these conditions and reaction proceed without internal and external diffusion limitations.

It is shown that all prepared samples are single-phase perovskites with a specific surface area of 6.1-9.7 m^2/g. At $x \le 0.4$ samples are orthorhombic perovskites, at $x \ge 0.6$ –

rhombohedral, which indicates the presence of a morphotropic phase transition in the region x = 0.4-0.6. The introduction of cobalt leads to a decrease in the parameters of the perovskite cell and the reduced volume due to the formation of homogeneous solid solutions in the system $LaFe_{1-x}Co_xO_3$ under study because the size of Co^{3+} cations in the octahedral environment (0.75Å) is smaller than that of Fe^{3+} cations (0.79Å). The X-ray particle size varies at a minimum for samples from the morphotropic phase transition region (Table).

Table. X-ray data for $LaFe_{1-x}Co_xO_3$

Compound	Sim. Group	a, Å	b, Å	c, Å	V, Å^3	X-ray size, Å
$LaFeO_3$	Pmna	5.561(3)	7.854(3)	5.545(2)	60.5515	632.0
$LaFe_{0.8}Co_{0.2}O_3$	Pmna	5.491(5)	7.786(7)	5.497(9)	58.76	539
$LaFe_{0.6}Co_{0.4}O_3$	Pmna	5.487(7)	7.756(5)	5.470(8)	58.19	301.6
$LaFe_{0.4}Co_{0.6}O_3$	R-3mn	5.471(2)	5.471(2)	13.202(8)	57.04	483.5
$LaFe_{0.2}Co_{0.8}O_3$	R-3m	5.449(3)	5.449(3)	13.139(8)	56.31	580.9
$LaCoO_3$	R-3m	5.4377	-	13.0789	55.8192	1200

a *b*

***Figure**. Dependence of conversion (a) and rate of decomposition reaction (b) of nitrous oxide on the composition for perovskites $LaFe_{1-x}Co_xO_3$.*

It has been established that activity of $LaCoO_3$ is higher than activity of $LaMnO_3$ and that the introduction of cobalt in $LaFe_{1-x}Co_xO_3$ oxides and an increase in the test temperature lead to an increase in the conversion of nitrous oxide, which is more significant as compared with the introduction of manganese in $LaFe_{1-x}Mn_xO_3$ oxides [2]. The maximum conversion (94.1-94.5% at 900 °C) was demonstrated by samples x=0.8 and x=1 (Figure, a). The introduction of cobalt lead to an improvement in the reduction of oxides according to H_2-TPR data as well. There is a linear correlation between the reaction rate at temperatures <850 °C and the amount of hydrogen absorbed (samples reducibility), which is consistent with the proposed reaction mechanism of N_2O decomposition in which the oxygen desorption stage is the limiting step. At higher test temperatures (>850°C), the rate of decomposition of nitrous oxide for x=1 decreased (Figure, b), which may be due to the instability of the surface layer of $LaCoO_3$ in the reaction medium.

Acknowledgments: The work was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation within the framework of the state assignment of the Institute of Catalysis SB RAS (project FWUR-2024-0038).

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OP-II-10

1-xPdxCu@UiO-66-NH_2 and 1-xPdxCu@UiO-67(bipy) Catalysts for Selective 5-Hydroxymethylfurfural Reduction

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Biomass represents a viable alternative to crude oil and natural gas to produce numerous valuable products in a more ecofriendly way [1]. Among the various biomass-derived products, 5-hydroxymethylfurfural (HMF) is considered one of the most promising raw materials and the most important platform molecules considered as the basis to synthesize a wide range of valuable products [2-4].

The present work is focused on an approach to regulate the properties of mono- and bimetallic 1-xPdxCu catalysts for the reductive HMF conversion via the interaction with the functional groups of the Zr-based metal-organic frameworks (Zr-MOFs) modified with NH_2 groups (UiO-66-NH_2-Y, Y is a fraction of amino terephthalate linkers) or pyridine nitrogen atoms (UiO-67(bipy)-Y, Y is a fraction of biphenyldicarboxylic linkers).

(100-x)PdxCu@UiO-66-NH2-Y and (100-x)PdxCu@UiO-67(bipy)-Y catalysts with 2 wt.% of metal and different fractions of Pd and Cu (100-x and x, respectively) were prepared considering the adsorption properties of the Zr-MOFs towards Pd and Cu precursors, which allows the formation of metal particles mainly in the porous space of the Zr-MOF. The obtained samples were studied using a complex of methods, including XRD, low-temperature nitrogen adsorption, CO pulsed chemisorption, UV-visible spectroscopy, Raman spectroscopy, and IR spectroscopy.

The catalytic properties of the materials were studied in cascade reactions of reductive conversion of HMF using the Parr 4560 reactor (Parr, USA) at 140-160 °C, 15 atm of hydrogen, HMF concentration of 0.05 mol/l, and HMF/metal molar ratio of 100. Specifically, the influence of the Pd:Cu ratio in bimetallic systems was studied using a series of samples, namely, (100-x)PdxCu@UiO-66-NH_2-50 and (100-x)PdxCu@UiO-67(bipy)-50. For a series of monometallic Pd and Cu samples based on UiO-66-NH_2-Y and UiO-67(bipy)-Y Zr-MOFs with different NH_2 and bipy content, the effects of various nitrogen sites of the Zr-MOF on the catalytic properties of the catalysts were studied.

The results obtained show that the used approach to regulate the properties of 1-xPdxCu catalysts through the formation of heteroatomic bonds with the functional groups of the Zr-MOFs provides prospects for purposeful design of new catalytic materials for the selective HMF hydrogenation into valuable products. Specifically, for the catalysts based on UiO-66-NH_2-Y, the preferential formation of the metal particles/clusters in the porous space of the support was established, which was due to the stabilization of the metal precursor in the porous space of the Zr-MOF. The results of catalytic studies of the Pd-containing samples based on the UiO-66-NH_2-Y with different NH_2 contents indicate their high catalytic activity due to the high dispersion of the metal particles. At the same time, monometallic samples containing Cu as an active component, especially systems based on the UiO-66-NH_2-50 and UiO-66-NH_2-100, show low catalytic activity. A characteristic feature of the catalysts based on UiO-66-NH_2-Y, regardless of the presence of amino groups in the MOF and the composition of the active component, was the formation of the 2,5-dihydroxymethylfuran (DHMF) and 2,5-dihydroxymethyltetrahydrofuran (DHMTHF) as the main products. This can be due to the steric effects during the HMF hydrogenation reaction in the porous space of the UiO-66. The Pd:Cu ratio in the catalyst additionally allows controlling the depth of the HMF reduction.

The results on the HMF reduction over (100-x)PdxCu@UiO-66-NH2-Y and (100-x)PdxCu@UiO-67(bipy)-Y catalysts will be presented, with the effect of the functional groups of the Zr-MOFs on the catalyst performance and insight into the reaction pathways of the HMF reduction over the catalysts studied being discussed.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-23-00173.

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OP-II-11

Catalytic Reforming of Dimethoxymethane to Hydrogen-Rich Gas

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Growing worldwide concerns about the increase in greenhouse gas emission and local environmental pollution have stimulated active research and development in fuel cell technology in the past decades. There is no doubt that fuel cells will play an important role in the global restructuring of energy supply, because they have several advantages over conventional power units such as high efficiency, noiseless operation, simple and modular design and environmental friendliness. Generally, fuel cells are fed by hydrogen or hydrogen-containing gas produced by the catalytic conversion of hydrocarbons and oxygenated organic compounds.

Similarly to methanol and dimethyl ether, dimethoxymethane (DMM) is an easy to synthesize (from natural gas) oxygenated compound of C1 chemistry. It is worth noting that DMM synthesis based on CO_2 produced from biogas and hydrogen supplied by water electrolysis is under development now. Successful implementation of methods for DMM synthesis from renewable raw materials minimizes or completely neutralizes the "carbon footprint" in the production of hydrogen from DMM. DMM is a corrosion-inert nontoxic liquid, which is easily stored and transported. It has attracted a growing interest as an ecologically benign raw material with a wide scope of applications. in particular, as a hydrogen source for fuel cell feeding. Recently, we demonstrated the feasibility of H_2/syngas production by DMM catalytic steam reforming (SR) and partial oxidation (PO) using the $CuO\text{-}CeO_2(ZnO)/Al_2O_3$ [1,2] and the $Pt/CeO_2\text{-}ZrO_2$ [3,4] catalysts, respectively. Table 1 summarizes the data for DMM catalytic reforming:

- the bifunctional $CuO\text{-}CeO_2(ZnO)/Al_2O_3$ catalyst containing on its surface both acidic and copper-based sites is active and selective for DMM SR to hydrogen-rich gas. In particular, the catalyst provides 100% DMM conversion (X_{DMM}) with high selectivity and hydrogen production rate at 300 °C and GHSV=10000 h^{-1}. The produced hydrogen-rich gas mixture with low (< 1 vol.%) CO content can be used for direct feeding of high temperature polymer electrolyte membrane (PEM) fuel cell without any further CO removal;

- the $Pt/CeO_2\text{-}ZrO_2$ catalyst containing surface metal particles of sizes in the range of 1-2 nm shows good performance in DMM PO reaction. The catalyst at atmospheric pressure, temperature ~400 ^oC, GHSV=10000 h^{-1} and reaction mixture DMM:air = 2:5 provides complete DMM conversion and syngas (H_2 + CO) concentration above 60 vol.%, and can be considered as efficient DMM PO catalyst with high promises for the development of a compact fuel processor generating syngas for solid oxide fuel cell (SOFC) feeding applications.

Table 1. Catalytic properties of $CuO–CeO_2/\gamma\text{-}Al_2O_3$ and $Pt/CeO_2\text{-}ZrO_2$ in DMM reforming reactions as compared with thermodynamic values calculated by minimizing of the Gibbs free energy.

Catalyst	T, °C	Inlet mixture, vol.%	X_{DMM}, %	Outlet concentration, vol. %				Y_C, %
				H_2	CO_2	CO	CH_4	
$CuO\text{-}CeO_2/\gamma\text{-}Al_2O_3$ (Equilibrium)	300	DMM:H_2O:N_2 14:70:16	100 (~100)	60 (3.4)	20 (11.6)	0.5 (0.02)	- (20.6)	- (-)
$Pt/CeO_2\text{-}ZrO_2$ (Equilibrium)	400	DMM:O_2:N_2 28.6:14.3:57	97 (~100)	36 (9.7)	6.5 (10.7)	26 (0.29)	3 (14.6)	- (50.6)

The experimental results (DMM SR and DMM PO) were compared with respective equilibrium data (Table 1). It turned out that the catalytic reactions are more efficient in terms of hydrogen production than it is predicted by thermodynamic analysis [5]. This observation is associated with that the proposed catalysts selectively promoted the hydrogen production reactions and kinetically hindered the side reactions producing methane and carbon. Reactions mechanism is discussed based on the obtained catalytic and in situ FTIR results.

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (project FWUR-2024-0033).

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OP-II-12

Kinetics of Catalytic Oxidation of Cellobiose to Gluconic and Glucaric Acids

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The products of glucose oxidation (gluconic and glucaric acids) are in-demand substances. In particular, gluconic acid is widely used in the food, pharmaceutical, metallurgical, and textile industries [1]. Glucaric acid is a product of a deeper oxidation of glucose. It can be used for the production of detergents [12] and polymers [14].

In this study, an assessment was made of the possibility of using heterogeneous catalysts based on a polymer matrix of hypercrosslinked polystyrene containing noble metals (Pt, Pd, Au, Ru) in the hydrolytic oxidation of cellobiose to gluconic and glucaric acids. The use of Pt-containing catalytic systems in this reaction was shown to be promising. The optimal process conditions were determined as follows; at a temperature of 145 °C, an O_2 pressure of 5 bar, and a substrate/catalyst mass ratio of 4/1, the yields of gluconic and glucaric acids reached 21.6 and 63.4%, respectively, at 100% cellobiose conversion.

In the process of optimizing the conditions for the hydrolytic oxidation of cellobiose, the obtained results of a qualitative and quantitative nature were analyzed. A reaction scheme for the conversion of cellobiose to gluconic and glucaric acids in the presence of 3% Pt/HPS MN270 was suggested (Fig. 1).

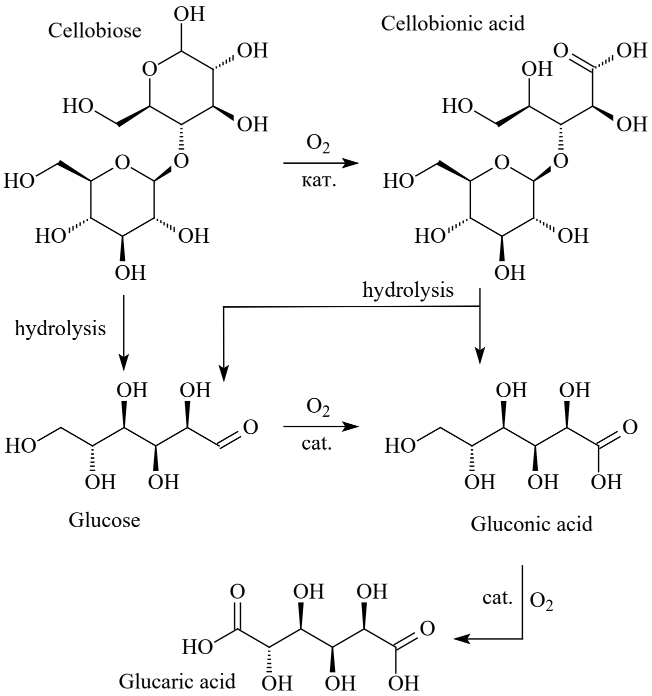

Fig. 1. Proposed scheme for the conversion of cellobiose into gluconic and glucaric acids in the presence of a catalyst, 3% Pt/HPS MN270.

The formal description of the kinetics of cellobiose hydrolytic oxidation was obtained. The mathematic model of cellobiose conversion to gluconic and glucaric acids in the presence of

3% Pt/HPS MN270 was proposed. The kinetic parameter estimation was performed according to the model developed. The data calculated according to the model were compared with those obtained in the experiments. The value of the root mean square (RMS) deviation was used to choose the mathematic model fitting the experimental data (Fig. 2).

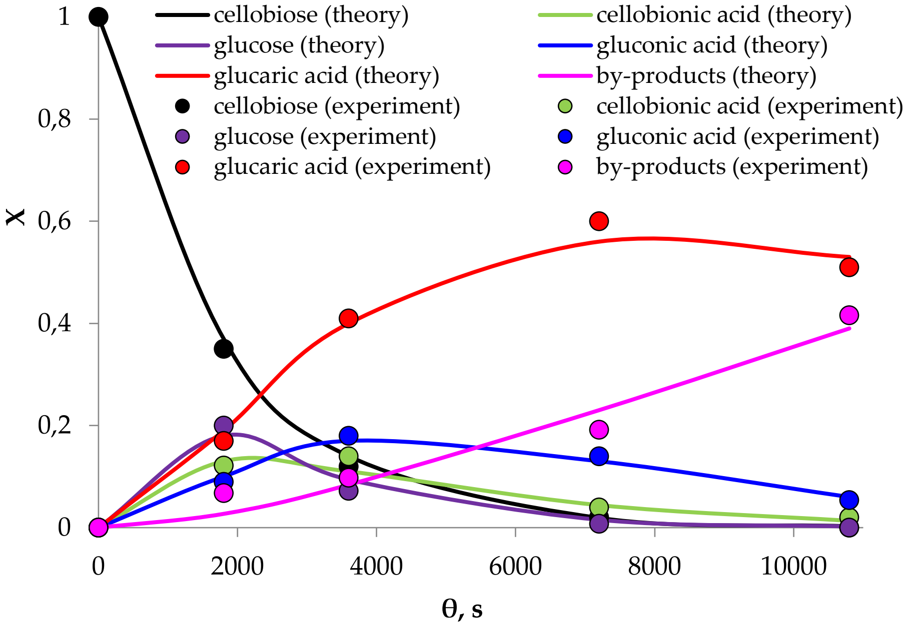

Fig. 2. X~ϑ dependence for cellobiose hydrolytic oxidation using 3% Pt/HPS MN270.

The results obtained can be further used to create a technology for the catalytic conversion of plant polysaccharides, primarily cellulose, into aldonic and aldaric acids, which are widely used in the chemical, food, pharmaceutical, and other industries.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-79-00009.

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OP-II-13

Kinetic Investigation and Optimization of an Environmentally Safe Process of Peroxide Delignification of Wood in the Presence of Dissolved Catalysts

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In recent years, there has been a sharp increase in interest in obtaining new environmentally friendly cellulose materials: microcrystalline, microfibrillated, nanocrystalline celluloses, which are increasingly used in the food, pharmaceutical, chemical industries, constraction and in other fields [1]. To produce these cellulose materials, more environmentally friendly than traditional methods of delignification of wood are being developed based on the use of non-toxic delignifying agents (hydrogen peroxide, oxygen, ozone) and organic solvents.

We have developed an ecology safe method of producing microcrystalline, microfibrillated and nanocrystalline cellulose based on peroxide delignification in mild conditions different types of hardwood and softwood in the medium “hydrogen peroxide-acetic acid-water” in the presence of suspended solid catalyst TiO_2 [2]. The advantages of using dissolved catalysts in delignification process are the creation of more effecient contact of the catalyst with the solid substrate and the ease of separating the catalyst from the cellulose product.

In this work we tested the activity of various dissolved catalysts based on transition metals in the process of peroxide delignification of larch wood which is of the main forest-forming species of Siberia. The delignification conditions have been selected based on previous studies [3].

The content of residual lignin in the cellulose product was used to evaluate the catalyst activity. The delignifying activity of the catalysts increase in the following order: $CuSO_4 \sim FeSO_4 < ZnSO_4 < MnSO_4 < (NH_4)_6Mo_7O_{24}$.

The process of wood peroxide delignification is described by the first order equation. Depending on the nature of the dissolved catalyst, the effective rate constants of the delignification process at 100 °C vary from $0.59 \cdot 10^{-4}$ to $1.92 \cdot 10^{-4}$. For experimental and mathematical optimization of the process of peroxide delignification of larch wood, an affordable and inexpensive catalyst $MnSO_4$ was selected.

At optimal conditions of the process (temperature 100 °C, concentration of hydrogen peroxide 6 mas. %, acetic acid 30 mas. %, hydromodule 15, time 4 h) the cellulose product was obtained with an yield of 44.3 mas. % and following characteristics: content of cellulose 92.7 mas. % residual lignin 0.6 mas. %, hemicellulose 5.7 mas. %, degree of polymerization 700, cristallinity index 0.7, crystallites size 3 nm.

OP-II-13

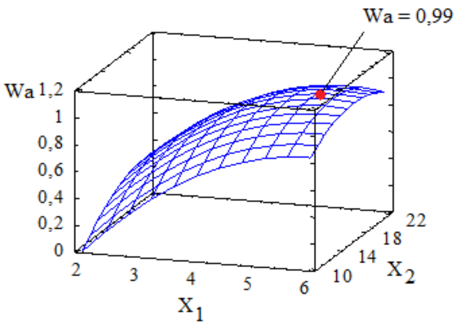

Fig. 1. The response surface of the generalized parameter for optimizing the process of peroxide delignification of larch wood in the presence of soluble catalyst $MnSO_4$

According to these characteristics, the obtained cellulose product corresponds to the commercial microcrystalline cellulose (MCC). By hydrolysis of MCC from larch wood with 55 % H_2SO_4 at 25 °C during 1 h. and following ultrasonic treatment during 0.5 h the microfibrillated cellulose (MFC) and nanofibrillated cellulose (NFC) were obtained with an yield 18.2 mas. % and 8.9 mas. % (from cellulose content in the wood), respectively. Degree of polymerization and crystallinity index are 178 and 0.78 and for MFC, 109 and 0.69 for NCC.

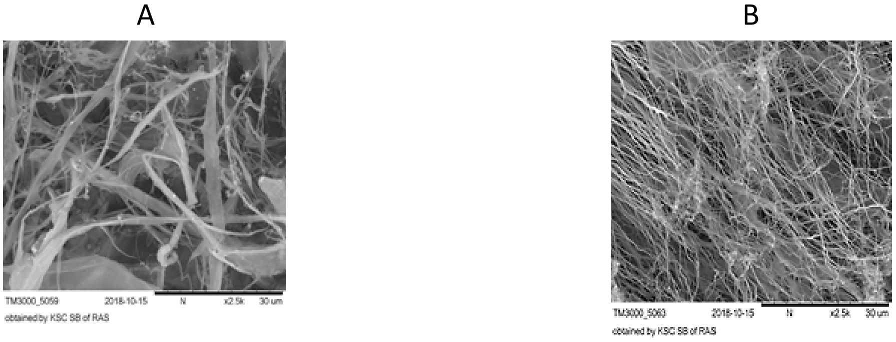

Fig. 2. SEM-images of the samples MFC (A) and NCC (B) obtained from larch wood. (magnification 2000 times)

The possible mechanisms of wood lignin degradation in the process of peroxide delignification in the presence of dissolved catalysts on the based of transition metals were discussed.

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OP-II-14

Comparison of Triglycerides, Methyl, and Ethyl Esters HDO over Ni-Phosphide Catalysts

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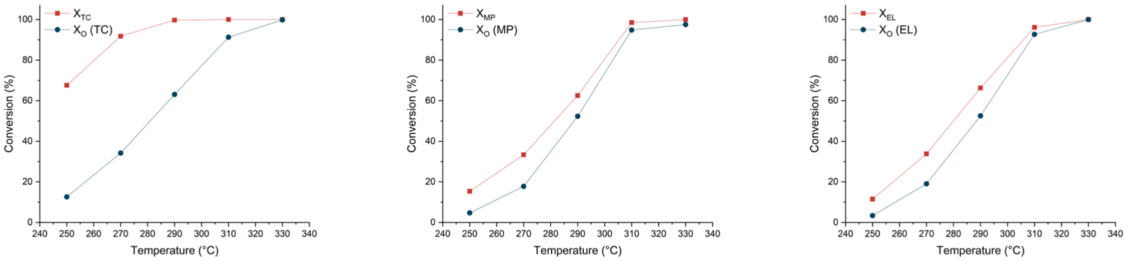
Hydrodeoxygenation (HDO) reaction of nonedible vegetable oils and animal fats attracts much attention as a way to produce renewable fuels. Long-chained n-alkanes (C15–C18) are formed in this process. Industrial HDO is carried out over hydrotreating Ni(Co)Mo sulfide catalysts. Other active components are tested in HDO in search of the ways to avoid sulfur addition and to increase activity. Ni phosphides are perspective catalysts for HDO showing high activity. Development of HDO catalysts led researches to the question about influence of acid sites on the activity [1]. There are several reports about synergetic effect of acid and metal sites in HDO [2]. However, most studies are only focused on the reactions of single model compound (fatty acid methyl or ethyl ester – FAME or FAEE, free fatty acid, pure triglyceride – TG) or complex mixtures like vegetable oils and fats. There is still little known about the relative HDO rates of FAMEs, FAEEs, and TGs.

The aim of this work is to compare TG (tricaprylin), FAME (methyl palmitate, methyl octanoate), and FAEE (ethyl laurate) HDO over Ni_2P catalysts on supports with different acidity (SiO_2, SBA-15, and Al_2O_3) based on the experiments and reaction pathways.

The catalysts were prepared by impregnation of a support with aqueous solution of $Ni(OH)_2$ and H_3PO_3 (Ni/P = 0.33, Ni content 7–9 wt%) followed by drying (80 °C, 24 h) and reduction in hydrogen flow in catalytic reactor at 600 °C for 1 h. The catalysts were characterized by ICP-AES chemical analysis, low-temperature N_2 adsorption, NH_3-TPD, XRD, and TEM. HDO of FAME (10 wt% methyl palmitate in n-dodecne, 5.8 wt% methyl octanoate in n-tetradecane), FAEE (8.7 wt% ethyl laurate in n-decane), and TG (5.5 wt% tricaprylin in n-tetradecane) was conducted in a continuous-flow fixed bed reactor at 250–330 °C, 3 MPa, LHSV = 90 or 45 h^{-1}, H_2/feed = 600 Ncm^3/cm^3, concentration of O in the initial feeds was 0.564 mol/L. The products were analyzed by GC/MS and GC/FID. O content was determined by Vario el cube elemental analyzer.

The content of Ni in the catalysts was similar, but amount of P after reduction was different. For SiO_2 and SBA-15 supports P content decreases and Ni/P ratio is lower than in the impregnation solution due to formation of volatile P-containing compounds during reduction. Al_2O_3-supportd sample have Ni/P ratio that is close to the ratio in the impregnation solution. XRD analysis confirmed formation of Ni_2P phase in all the catalysts with sizes of 3.8–7.0 nm. S_{BET} after supporting Ni_2P decreases in all the samples, and acidity changes in the following order: Ni_2P/SBA-15 140 µmol/g < Ni_2P/SiO_2 163 µmol/g < Ni_2P/Al_2O_3 354 µmol/g.

Over the sample with high acidity (Ni_2P/Al_2O_3) the rates of FAME and FAEE HDO at 250–330 °C were shown to be very similar, but the values of TG conversion at the same temperatures were higher (Fig. 1). The difference of FAEE and TG conversion suggests that β-elimination (Fig. 2) may not be crucial for higher initial rate of TG HDO.



a) *b)* *c)*

Fig. 1. a) Tricaprylin (TG), b) methyl palmitate (FAME), c) ethyl laurate conversion and O conversion vs temperature over Ni_2P/Al_2O_3. P = 3 MPa, LHSV = 90 h^{-1}, H_2/feed = 600 Ncm^3/cm^3

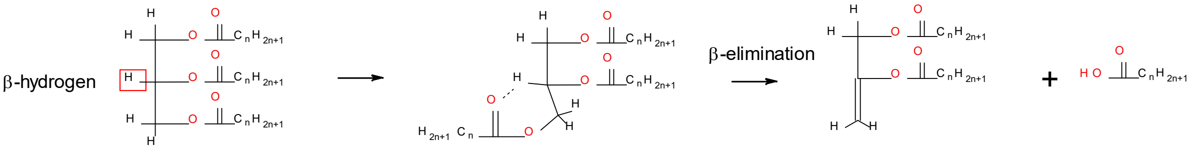


Fig. 2. β-elimination in TGs. For tricaprylin n = 7

The rate of TG HDO initial step is high and tricaprylin HDO experiments over the catalysts with different acidity (Ni_2P/Al_2O_3, Ni_2P/SiO_2, and Ni_2P/SBA-15) showed the similar conversion of the initial compound and O. Thus, the synergy between metal and acid active sites does not play any role in TG HDO. In absence of significant amount of acid sites (Ni_2P/SiO_2) both conversion of initial FAME, FAEE, and intermediate fatty acid and alcohol are significantly lower than the same parameters for TG. Therefore, it was concluded that TG HDO rate is not limited by the rate of fatty acid conversion.

This work shows that the choice of model compounds is a very important decision in HDO catalysts study. FAMEs and FAEEs can be useful to obtain similar product distributions and O conversion. But comparison of the initial compounds reaction rates may lead to incorrect conclusions.

Acknowledgement: This work was supported by the Russian Science Foundation (grant no. 22-13-00371).

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OP-II-15

The Effect of Nickel Content and Preparation Method on the Catalytic Properties of Ni/CeO₂-SnO₂ Systems in Dry Reforming of Methane

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Dry reforming of methane (DRM) to syngas is a promising way for methane conversion to chemicals, fuels and reduction of greenhouse gas (e.g., CO_2 and CH_4) emission [1]. Nickel based systems have exhibited relatively high catalytic activity in DRM comparable to noble metal catalysts. However, Ni is prone to rapid deactivation due to coking and sintering under DRM conditions. Application of different active metal addition methods is a possible way to influence activity and stability of catalysts through tuning the strength of interaction between metal and support [2, 3]. In addition to preparation method, metal loading also influences particle size and dispersion. The aim of this work is to elucidate the effect of nickel content and preparation method on the catalytic properties of Ni/CeO_2-SnO_2 in DRM.

Ceria-tin (CeSn) oxide catalytic systems were synthesized using Pluronic 123 (P123) as organic template and aqueous solutions of $Ce(NO_3)_3·6H_2O$ and $SnCl_2·2H_2O$ as precursors. Ni (3 and 9wt.%) was applied on oxide support using wet impregnation (WI) and deposition-precipitation (DP) methods from aqueous solution of $Ni(NO_3)_3·6H_2O$. We also synthesized nickel-ceria-tin systems (3 and 9wt.%Ni) from salts aqueous solutions using co-precipitation (CP) method. All systems were calcined at 800°C. All catalysts (0.1 g) were reduced in 10 vol.% H_2/N_2 for 1 h at 750°C before catalytic tests. The catalysts were tested in DRM at 800 °C using a reaction mixture $CH_4/CO_2/N_2$ = 1/1/2 (F_0 = 30 ml/min). The reaction products and unconverted reagents were analyzed by online gas chromatography Chromatec-Crystal 5000.2 (“Chromatec”, Russia) with Carboxen-1010 PLOT column (“Supelco”, USA).

All systems were active in DRM but significantly different in catalytic properties. System prepared by impregnation showed the highest stationary conversion of both methane ($X(CH_4)$ = 32% and carbon dioxide ($X(CO_2)$ = 51%) compared to 9Ni/CeSn-CP ($X(CH_4)$ = 26%, $X(CO_2)$ = 45%) and 9Ni/CeSn-DP ($X(CH_4)$ = 18%, $X(CO_2)$ = 36%) (fig.1).

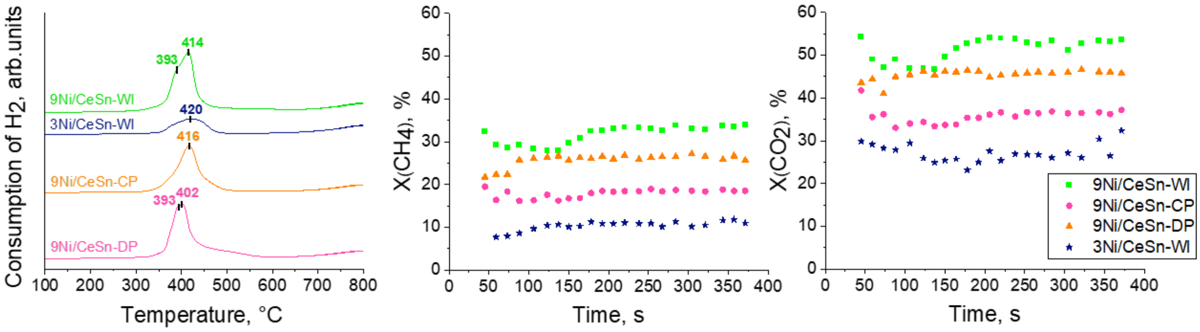

Figure 1. TPR-H_2 and catalytic results (conversion (X) of CH_4 and CO_2 vs. time) for 9Ni/CeSn-WI, 9Ni/CeSn-CP, 9Ni/CeSn-DP and 3Ni/CeSn-WI catalysts tested in DRM

Increase of Ni content also led to rise both methane and carbon dioxide conversion for all systems due to increase the amount of active metal sites. For example, 9Ni/CeSn-WI catalyst exhibited about three times higher stationary methane and carbon dioxide conversion compared to 3Ni/CeSn-WI (X(CH_4) = 11%, X(CO_2) = 29%) (fig.1). It's worth mentioning the increase in active metal content from 3 to 9 wt.% doesn't affect the stability of studied systems.

According to ex situ XPS 9Ni/CeSn-WI and 9Ni/CeSn-DP have similar Ce/Ni ratio equal to 0.46 and 0.51 respectively. For 9Ni/CeSn-CP sample this value is significantly higher (Ce/Ni = 2.75) indicating Ni(II) species concentrate in volume. According to H_2-TPR (fig.1) reduction maxima for 9Ni/CeSn-WI and 9Ni/CeSn-CP are shifted to a higher value compared to 9Ni/CeSn-DP. For these samples Ni-support interaction is stronger. Weak interaction in 9Ni/CeSn-DP sample is also confirmed by appearance of high-temperature component (460–560˚C). This maximum is associated with the presence of CeSnOx species don't interact with NiO particles, the spillover effect is absent. Weak metal-support interaction causes a tendency towards sintering of active sites under DRM conditions. The presence of such Ni species results in slightly lower catalytic activity for this catalyst. The use of co-precipitation method led to strong interaction between the components and the formation of mixed nickel-cerium-tin oxide phase. Such strong metal-support interaction results in lower catalytic activity, but improved stability and resistance towards deactivation. In the case of 9Ni/CeSn-WI, the optimal size and dispersion of Ni particles lead to higher catalytic activity in DRM.

Additionally, detailed studies using TEM, EPR, SEM-EDX, Raman and low-temperature nitrogen adsorption-desorption methods revealed the influence of state of Ni particles on the surface, as well as the textural and morphological characteristics of the resulting systems, on their activity and stability in the DRM reaction.

Strong interaction between catalyst components, optimal content, size and dispersion of Ni particles provide good catalytic properties in DRM of Ni/CeSn catalyst prepared by impregnation of cerium-tin oxide systems with Ni, opening the way of simultaneous activation of two main greenhouse gases — methane and CO_2.

Acknowledgement: The work was carried out using scientific equipment purchased under Lomonosov Moscow State University development programme.

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OP-II-16

Revealing the Mechanisms for Nucleation and Growth of Graphene via the Boudouard Reaction

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Following the game-changing HiPCO process that established the first facile route toward largescale production of single-walled carbon nanotubes, we propose CO synthesis of cm-sized graphene crystals of ultra-high purity grown during tens of minutes [1]. The Boudouard reaction serves for the first time to produce individual monolayer structures on the surface of a metal catalyst, thereby providing a chemical vapor deposition technique free from molecular and atomic hydrogen as well as vacuum conditions. This approach facilitated inhibition of the graphene nucleation from the CO/CO_2 mixture and maintained a high growth rate of graphene seeds reaching largescale monocrystals. Unique features of the Boudouard reaction coupled with CO-driven catalyst engineering ensured not only suppression of the second layer growth but also provided a simple and reliable technique for surface cleaning. The kinetic data (SEM, AFM, THz spectroscopy) obtained in combination with modeling based on the DFT method allowed us to highlight the rate-limiting processes and propose new models of graphene nucleation and growth (Figure 1). Moreover, carbon monoxide ensures peculiar modification of catalyst and in general opens avenues for graphene-catalyst composite production.

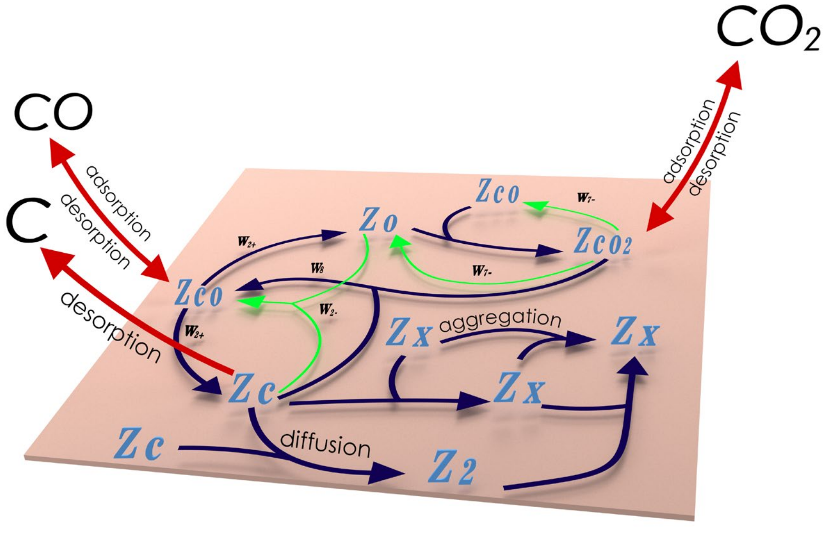

Fig. 1. Scheme for the propose chemical reactions during the graphene nucleation

Acknowledgement: The authors acknowledge valuable contribution of prof. K. Laasonen (Aalto University, Finland) and Russian Science Foundation grant No. 21-72-20050 (THz-FIR spectroscopy).

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OP-III-01

State of Palladium in the Active Centers of the Catalyst $Pd/\gamma\text{-}Al_2O_3$ Low Temperature Oxidation of Carbon Monoxide

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The oxidation reaction of carbon(II) monoxide with oxygen is of fundamental and practical interest. The reaction can be used as a model to elucidate the general principles of oxidation processes involving molecular oxygen. Practical interest in studying this reaction is associated with the use of such catalysts in devices that protect people from carbon monoxide. Among the catalysts for this reaction, a group of contacts is distinguished that are active at temperatures below 100°C (low-temperature oxidation catalysts). Low-temperature heterogeneous catalysts are divided into oxide, metal, and supported metal complex catalysts [1, 2].

A large number of publications have been devoted to their development and study, but the detailed mechanism of action of supported metal catalysts has not yet been elucidated.

Previously, we studied the kinetic patterns of this reaction and the mechanism of action of the supported metal complex catalyst $PdCl_2–CuCl_2/\gamma\text{-}Al_2O_3$, the active centers of which under the process conditions contain, according to IR spectroscopy, carbonyl complexes of palladium(I) and palladium(II) [3–5].

The next goal of our work is to study the mechanism of action of the supported metal catalyst $Pd/\gamma\text{-}Al_2O_3$. There are various methods for producing palladium nanoparticles on the surface of supports [6], and the activity of a catalyst of a certain composition strongly depends on the method of its preparation. We used various options for preparing this catalyst.

Our group studied the $Pd/\gamma\text{-}Al_2O_3$ catalyst, which was obtained by depositing palladium(II) acetate on $\gamma\text{-}Al_2O_3$ with subsequent reduction [7]. According to XPS data, the material obtained by depositing $Pd_3(OAc)_6$ on $\gamma\text{-}Al_2O_3$, before contact with CO, contains palladium compounds in oxidation states I and 0. Based on the correlation between catalytic activity and the content of Pd(I) and Pd(0) compounds, using the data received by XPS method, the specific catalytic activity of palladium compounds in different oxidation states was assessed. The data obtained indicate a higher specific activity (2–3 times) of Pd(I) compounds compared to Pd(0). This catalyst is unstable in operation under the conditions of the carbon monoxide oxidation process, but can be regenerated as a result of contact with atmospheric oxygen [7].

A more stable and active $Pd/\gamma\text{-}Al2O3$ catalyst was obtained by applying palladium polyhydroxide complexes to aluminum oxide with their subsequent reduction [8, 9]. The catalyst prepared using this method compares favorably with the previous sample by being more active and stable. It provides a CO conversion rate of at least 90% in the temperature range of 20 – 75 °C with a volumetric air flow rate in the range of 12000 – 36000 h^{-1}, CO content in the air from 100 to 300 mg/m^3 and moisture content in the purified air up to 20 g/m^3. Stable during long-term storage. This catalyst will be used to study the kinetics and mechanism of low-temperature oxidation of carbon monoxide.

Acknowledgement: The authors thank Elena Aleksandrovna Skryleva, research fellow at the Center for Collective Use “Materials Science and Metallurgy” of the Moscow State Institute of Steel and Alloys, for conducting studies of the catalysts using XPS.

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OP-III-02

Palladium-Catalyzed Allylation of Substituted Norbornenes and Norbornadienes with Hydrogen Transfer: Key Intermediates and Mechanism

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The transition metal-catalyzed allylic substitution with unactivated allylic substrates (allylic alcohols, allylic ethers and allylic amines) is an important area of research. There are several advantages to use these substrates in allylic substitution reactions due to minimization of waste by-products and amount of reaction steps, stability of these substrates and their presence in numerous biologically active compounds [1]. In addition, this reaction can be used as a protocol for enantioselective syntheses. In this aspect, enantioselective Pd-catalyzed allylic substitution is unique because not only enantioselectivity can be induced in several ways, but also many types of bonds, such as C–C, C–N, and C–O bonds, can be formed with the same catalyst with future transformation of resulting products by taking advantage of the alkene functionality [2].

Among numerous Pd-catalyzed allylic substitution reactions, the allylation of norbornene (NBN) and norbornadiene (NBD) derivatives is not similar to the well-known processes (Fig.1). The feature of this reaction is the controlled variation in the way of the addition of an allyl fragment to the NBD and NBN, which can undergo significant changes during the hydrogen transfer process, up to the breaking of the C–C bond. This reaction opens up exceptional opportunities for single-stage synthesis of a wide range of strained polycyclic hydrocarbons containing not only allyl, but methylene, vinyl, and methylenecyclobutane fragments in relatively “soft” conditions [3].

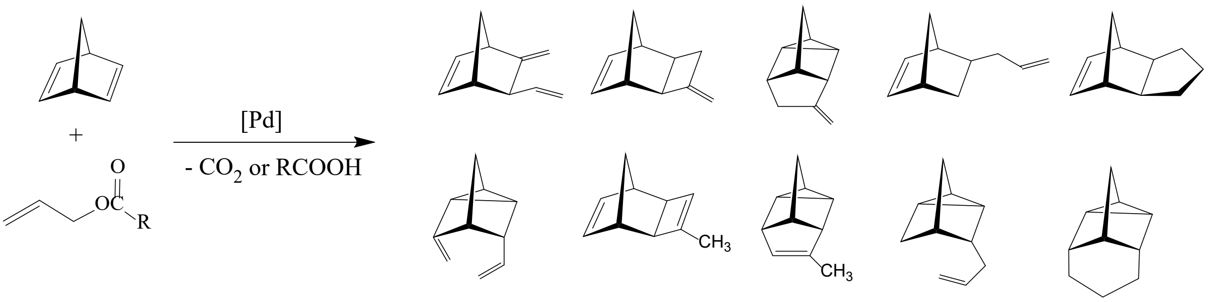

Fig. 1. Pd-catalyzed norbornadiene allylation as an example of process

Based on a combination of physicochemical, kinetic, and isotopic techniques, significant additions and clarifications have been made to the understanding of the mechanisms involved in the allylation of NBD in the presence of palladium complexes. Through experimental investigation, the directions and variability of the β-hydride transfer stages in the interaction of NBN and NBD derivatives with allylic ethers have been determined. Isotopic and kinetic methods have confirmed the pivotal role of these stages in the catalytic cycle, and strategies for controlling their directions have been proposed. It has been demonstrated that the directional preference for hydride transfer during the formation of all products is generally dependent on the C-H bond adjacent to the metal atom, specifically in the β-position. At this stage, an allylic, norbornenyl, formyl, or other active hydrogen atom may be involved.

The possibility of regulating the directions of hydrogen transfer in Pd-catalyzed allylation reaction for a wide range of NBN and NBD derivatives has been shown. The degree of influence of various factors on the direction of the process and the structure of the resulting products has been established. The opportunity of carrying out enantioselective allylation of NBN and NBD derivatives has been considered. Using quantum chemistry methods, the optimal conditions have been established and first experiments of enantioselective addition of the allyl fragment to NBD have been also conducted.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-73-00123.

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OP-III-03

Cationic Polymerization of Butadiene with Isomerization of the Initiator Structure

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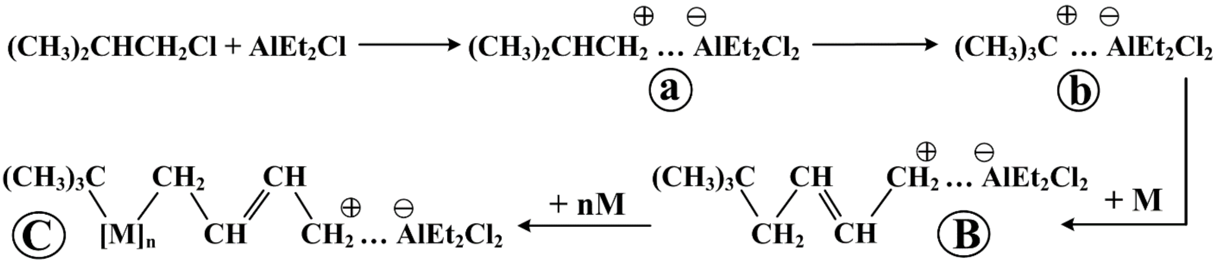
The processes of cationic polymerization of conjugated dienes (1,3-dienes) are used in industry to obtain aliphatic hydrocarbon resins (AHR) with various physicochemical characteristics. AHRs are manufactured using cationic initiating systems consisting of a Lewis acid (LA) in combination with polymerization initiators such as water, hydrogen chloride, organic acids, alcohols, and alkyl halides.

Cationic polymerizations of 1,3-dienes in the presence of initiating systems consisting of tertiary aliphatic alkyl halides (AH) in combination with $TiCl_4$, $VOCl_3$, $ZnCl_2$, $AlCl_3$, $AlEt_3$ and $AlEt_2Cl$ are described in detail in the literature [1]. It was shown for the first time in our recent studies that secondary aliphatic AHs in combination with $AlEt_2Cl$ or $AlEtCl_2$ also efficiently initiate the cationic polymerization of 1,3-dienes at a process temperature of 20 °C and higher [2]. As regards initiating systems consisting of primary aliphatic AHs in combination with LAs, such systems, as a rule, do not initiate cationic polymerization of 1,3-dienes. For example, the cationic polymerization of butadiene under the action of "pure" $TiCl_4$ or $AlEt_2Cl$ in methylene chloride, which is the primary AH, proceeds at an extremely low rate [1, 2].

The aim of this work is to study the process and mechanism of the cationic polymerization of butadiene in the presence of initiating systems consisting of diethylaluminum chloride ($AlEt_2Cl$) in combination with primary aliphatic alkyl halides, such as *n*-butyl chloride and isobutyl chloride.

It has been found that the polymerization of butadiene is initiated only by the $AlEt_2Cl$—isobutyl chloride system [3]. The butadiene polymerization process is characterized by an induction period (10—15 min) and a pronounced non-steady-state character. It was shown using the methods of one-dimensional and two-dimensional NMR spectroscopy that the head units of polybutadiene macromolecules are *tert*-butyl groups connected with the 1,4-*trans*-unit of polybutadiene. *Tert*-butyl head units are formed as a result of isomerization of the isobutyl cation into *tert*-butyl cation, which is the true initiator of the butadiene polymerization process (M-butadiene):



The absence of carbon atom signals from the head isobutyl units in the NMR spectra of polybutadiene indicates the inability of the primary isobutyl cation to initiate the cationic polymerization of butadiene. The presence in the NMR spectra of polybutadiene of the carbon atom signals of the head *tert*-butyl units indicates the isomerization of ion pair **a** into ion pair **b** containing a more stable *tert*-butyl cation. Probably, the isomerization of the primary isobutyl cation to the tertiary cation is the limiting stage of the studied process of cationic polymerization of butadiene. This is confirmed by the observed induction periods in butadiene polymerization processes. After completion of the formation of the ion pair **b**, the first butadiene molecule (**M**) is introduced to form an active polymerization center **B**. The polymer chain grows as a result of the sequential addition of monomer molecules to the active polymerization center **B**, which leads to the formation of a growing polymer chain of polybutadiene **C.**

A significant increase in the values of the average molecular weights of the polymer with a simultaneous decrease in its unsaturation was found during the process of butadiene polymerization. This indicates the transfer reaction of the growing chain to the double bond of polybutadiene with the formation of branched and partially crosslinked macromolecules. The synthesized polybutadienes are completely soluble thermoplastic polymers with reduced unsaturation (43—52 mol.%), high glass transition temperatures (64—65 °C) and softening points (162—170 °C). The resulting polymers can be used as components of adhesive and sealing compositions [3].

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OP-III-04

Activation Methods of Pd/NHC and Ni/NHC Complexes for Catalysing Carbon-Heteroatom Bond Formation Reactions

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Late-stage functionalization of heterocycles through catalytic processes, including metal complex catalysis, is currently the most promising approach for obtaining valuable heterocycles. However, the efficiency of metal complex catalysis is significantly reduced by the ability of heterocyclic compounds to form strong coordination complexes with transition metals and act as catalytic poisons. Therefore, it is important to identify the reasons for the decrease in catalytic efficiency and develop methods to activate catalytic systems. This can be achieved through the introduction of various additives or modification of the structure of NHC-ligands. This is a crucial task for the development of efficient metal complex catalysts.

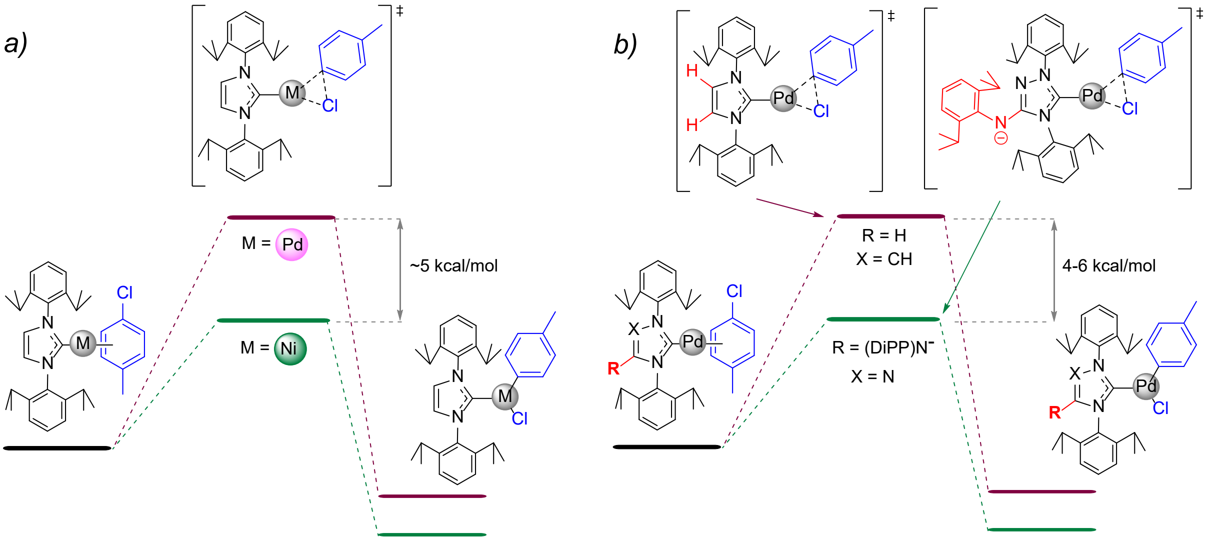

Fig. 1 Effect of the nature of the metal (a) and the NHC ligand (b) on the oxidative addition step of 4-toluyl chloride in M/NHC complexes.

This presentation compares the mechanisms of action of nickel and palladium complexes in the oxidative addition and reductive elimination stages of cross-coupling reactions for forming a carbon-heteroatom bond. The influence of the ligand's nature, metal, and various additives on the activity of Pd/NHC and Ni/NHC complexes in the functionalisation reactions of nitrogen-containing compounds will be discussed.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 24-23-00607, https://rscf.ru/project/24-23-00607.

OP-III-05

Comprehensive Study of Oxygen Exchange between MIEC Oxide and Oxygen from the Gas Phase

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Solid oxide fuel cells (SOFCs), capable of converting the chemical energy of fossil fuels directly into electricity with high efficiency, are especially relevant for Russia, since two-thirds of Russian territories (the Far East, Siberia and the Arctic) are of little use for centralized energy. Energy efficiency, as well as energy saving of distributed energy, associated with the use of fuel by the consumer in accordance with its own consumption schedule, has led in the last decade to significant progress in the development of stationary SOFC plants with a capacity of 1.5–5 kW. The main requirements for such installations are high efficiency, durability and low cost, which are implemented, as a rule, on planar SOFCs. Nevertheless, the analysis shows that there is a huge demand in the market for SOFCs with power from 1W to 1kW for mobile and portable devices (military devices, electric vehicles, gadgets, etc.). Additional requirements for such power generators are high specific power, durability and the ability to quickly start, which can be implemented on microtubular SOFCs (MT SOFCs). It was shown that MT SOFCs have a number of significant advantages compared to traditional planar and tubular SOFCs: higher values of specific power per unit volume and weight; resistance to thermal shocks, which ensures a short start-up time (~5 sec) and performance at large temperature gradients; sufficiently high mechanical strength; the ability to work in the mode of combined external and internal reforming, which can significantly improve fuel efficiency. To date, advanced scientific groups are actively searching for new, more advanced cathode materials for MT SOFC, capable of operating efficiently in the medium temperature range (500–600°C). The fact is that in order to reduce the size of mobile and portable MT SOFCs, it is desirable to have a lower temperature, and, therefore, a transition from high-temperature electrolytes based on zirconium oxide to medium-temperature electrolytes, for example, based on cerium oxide, is necessary. A decrease in the operating temperature, as is known, leads to the fact that the efficiency of the MT SOFC is limited by the cathode material consisting of an oxide with mixed ion-electron conductivity (MIEC oxide), on which the polarization resistance increases (due to a drop in the oxygen exchange rate between the MIEC oxide gas phase). To control the functional characteristics of the cathode composition, detailed information on the mechanism of oxygen exchange in these compounds is required.

Despite the large amount of experimental and theoretical information accumulated over the past decades, the detailed mechanism of the exchange is still in question. The fundamental problem of the ambiguity of solving the inverse problem of determining the transformation mechanism from its kinetics is complicated by a number of features characteristic of reactions of a solid with a gas phase: the macrokinetic nature of the process and the morphology of solid particles. The nonstoichiometry of oxides is also important - a wide range of oxygen stoichiometry leads to a large spread of kinetic parameters from 3-δ. It is known that the rate constant of the surface exchange reaction and the volumetric diffusion coefficient often follow a power law depending on the equilibrium partial pressure of oxygen ~pO_2^n. The exponent n has a characteristic value in the range of 0–1, which, however, is not explicitly taken into account when analyzing the relaxation kinetics, although pO_2 changes by a factor of two, which leads to a significant change in the kinetic parameters during relaxation.

The authors have developed a new methodology and models for studying the kinetics of oxygen exchange by two independent methods that complement each other: the study of stationary kinetics by measuring the oxygen permeability on membranes and the study of the kinetics of exchange in mixed mode by the original method of oxygen partial pressure relaxation (OPPR) [1]. At the time of application, the development was tested on 2 different compounds: ferrite $SrFe_{0.98}Mo_{0.02}O_{3-\delta}$ and cobaltite $Ba_{0.5}Sr_{0.5}Co_{0.75}Fe_{0.2}Mo_{0.05}O_{3-\delta}$ [2-4].

The work describes further development of the methodology both in terms of studying new compounds (including traditional LSCF and LSM) and technical modification (increasing the operating range, full automation, etc.). Also, comparative data to study the mechanism of oxygen exchange on the SOFC cathode materials is provided.

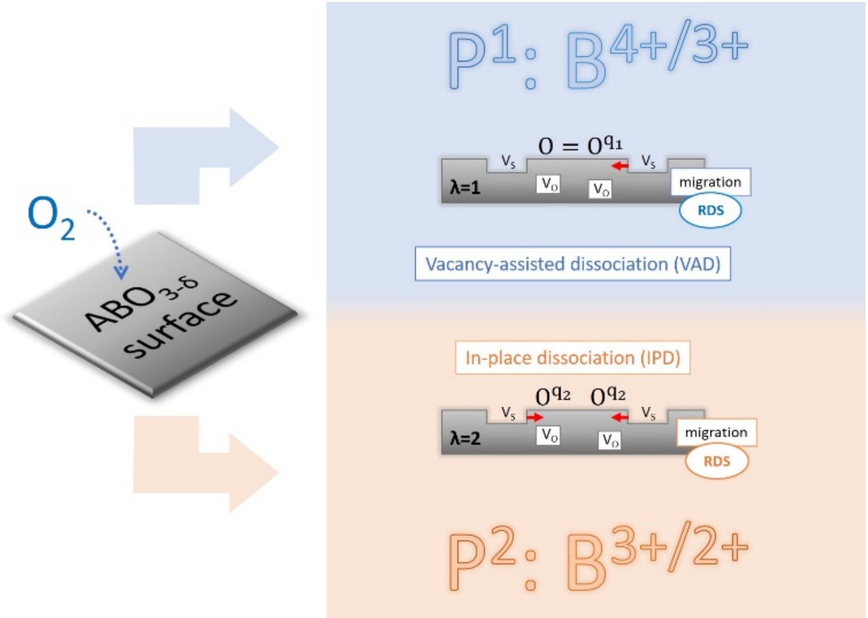

Fig. 1. Proposed RDS mechanism in BSCFM5 MIEC oxide.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 22-73-10200.

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OP-IV-01

Catalytic Properties of Protected Copper Sulfide Cluster in CO Oxidation: Active Site and Spin Effect

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The application of metal nanoclusters protected with organic ligands (PNCs) is a modern trend in heterogeneous catalysis [1]. These PNCs can solve one of the major problems of heterogeneous catalysis dealing with a wide particle size distribution on surface. But the extent of ligands shell removing and catalytic reaction mechanisms involving PNCs are open questions.

The catalytic activity of gold nanoclusters protected by thiolate and phosphine ligands in CO oxidation is well known [2]. However, high gold price leads to the search cheaper systems, i.e. based on copper. Cu nanoclusters protected by phosphine and thiolate ligands (i.e., $Cu_{12}S_6(PR_3)_8$) have been recently obtained [3]. But information on the catalytic properties of Cu PNCs is limited.

We present the simulation of catalytic activity of copper sulfide clusters in CO oxidation studied by PBE density functional theory. Pathways of sequential oxidation of two CO molecules by O_2:

$$CO^* + O_2^* \rightarrow CO_2 + O^*$$

$$O^* + CO^* \rightarrow CO_2$$

on protected $Cu_{12}S_6(PR_3)_8$ (R = -H, $-C_2H_5$) clusters corresponding to Langmuir–Hinshelwood mechanism were simulated in triplet and singlet electronic states.

First CO molecule oxidized on the cluster via spin-crossing mechanism from triplet electronic state and triplet transition states to singlet $OOCOCu_{12}S_6(PH_3)_8$ intermediate. After that, the reaction proceeded along the singlet energy pathway until CO_2 desorbed. It was shown that PH_3 ligands have positive effects on copper sulfide nanoclusters catalytic properties in CO oxidation.

Calculated regularities will be beneficial to design new efficient catalytic systems based on metal clusters and to determine appropriate conditions of catalyst synthesis.

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OP-IV-02

Kinetic Mechanism of Non-Oxidative Conversion of CH_4 over Fe/SiO_2

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Now non-oxidative conversion of methane to produce valuable hydrocarbons and hydrogen is the subject of intensive research. Previously, a superactive oxidative spin-polarized center in the four-membered ring of ZSM-5 zeolite near the intersection of the main and sinusoidal channels was studied. DFT calculations predicted a record low barrier (1.7 kcal/mol) for the abstraction of hydrogen from methane.

We examined the mechanism of methane dimerization, when the interaction of two methyl radicals, as well as the dehydrogenation of methane, occurs on the surface of the catalyst. The remaining reactions occur in the gas phase.

The simulated reaction supercell had the composition $H_{22}O_{116}Si_{53}Fe$. The formation of an Fe center from a single Fe atom surrounded by three hydroxyl groups, which arise during the sequential dehydrogenation of three methane molecules, has been calculated. The individual stages of methane activation at the Fe center were clarified by quantum chemical calculations using the VASP software package using DFT methods. Calculations of the energy barriers to the detachment of a hydrogen atom from a methane molecule at an Fe center have been carried out. The resulting activation energy was less than 150 kJ/mol.

Based on quantum chemical calculations, the stages of methane activation on Fe/SiO2 catalyst particles with the formation of ethane were determined.

Based on a compact scheme for the pyrolysis of methane-ethane mixtures and the results of quantum chemical calculations of methane activation on the active center of the Fe/SiO2 catalyst, a kinetic scheme for methane conversion with heterogeneous-homogeneous reactions was proposed and studied. The proposed reaction mechanism takes into account 20 reversible steps. In this compact scheme, the gas-phase radical reaction constants belong to the NIST database. Parametric analysis of the kinetic scheme for different activation energies of methane showed the promise of methane conversion if the activation energy of methane on nanoparticles is less than 170 kJ/mol. Preliminary experimental data for Fe/Al2O3 nanoparticles estimate this energy in the range of 140-170 kJ/mol. A parametric analysis of the kinetic scheme for different activation energies of methane was performed by changing the temperature of the gas and the surface of nanoparticles with changes in their diameter and the concentration of particles in the medium. As a result, a compact kinetic scheme for methane conversion with gas-phase radical reactions and heterogeneous catalytic reactions on the surface of Fe/SiO2 nanoparticles in a wide temperature range was developed and studied. It is suitable for gas-dynamic calculations of reactors for non-oxidative conversion of methane into two-phase flows of nanoparticles and multicomponent gas.

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov institute of Catalysis, projects FWUR-2024-0032 and FWUR-2024-0033.

OP-IV-03

Modeling the Enzymatic Reaction in N-Acetylglutamate Synthase: Role of GNAT-Conserved Structural Elements in Catalysis and Protein Stabilization

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N-Acetylglutamate synthase (NAGS, EC 2.3.1.1) is an enzyme from the large family of Gcn5-related N-acetyltransferases that catalyzes the transfer of an acetyl group from acetyl-CoA to glutamate to form N-acetylglutamate (NAG). The enzyme is found in all eukaryotes and some prokaryotes and belongs to the arginine biosynthesis pathway. As live evolved, NAG drastically changed its role from a simple intermediate in a linear pathway for arginine synthesis to an obligatory activator of carbamoyl phosphate synthase I, which catalyzes the rate-limiting step of the urea cycle. This change was also reflected in the quaternary structure of the corresponding NAGS. Meanwhile the catalytic mechanism of NAGS still needs to be refined. Therefore, both the refinement of the mechanism and the establishment of its role in the evolution of NAGS are of interest.

In this work the understanding of acetyl-CoA binding sites in NAGS of *Neisseria gonorrhoeae* (PDB ID: 3B8G) was further improved. The acetyl-CoA recognition motif (Gln364-Glu365-Gly366-Gly367-Tyr368-Gly369), which is conserved in GNAT-superfamily, was revealed to be insufficient to retain the substrate. Hydrogen bonds between acetyl-CoA and basic amino acids (Arg134, Arg151 и Lys152) from amino acid kinase domain of adjacent monomer turn out to be stronger, thus building another essential acetyl-CoA binding site.

We question the role of Glu353 as general base for glutamate amino group deprotonation, which was widely attributed to this GNAT-conserved residue in literature. Glu353 forms a salt bridge with Arg416, thus becoming ineffective proton acceptor. Similar salt bridges are found in all bacteria-like NAGS with determined crystal structure. We argue, that Glu353, establishing the salt bridge, acts as the stabilizer of the tertiary structure of the protein and, moreover, as the stabilizer of oxyanion hole conformation. The decrease in enzymatic activity of E353D and E353A mutants of NAGS is explained within the framework of the suggested model.

We determined free binding energies of glutamate with protonated and non-protonated amino group to NAGS and showed, that the protein has greater binding-affinity for the non-protonated form. Together with the absence of the suitable proton acceptor in the active site this implies, that the deprotonation of glutamate amino group happens before the substrate reaches the catalytic site. A surface binding site of glutamate was found at the edge of the tunnel, leading inside the protein to its active site. It consists of Ser326, Glu327 и Thr345, and we assume, that the deprotonation could be carried out there.

We suggest, that the enzymatic reaction proceeds trough three steps. Throughout the first step enzyme-substrate complex is formed: substrates approach each other along the

C(acetyl-CoA) –N(glutamate) line. The second step progresses through proton transfer from the amino group of glutamate to its α-carboxyl group, which is associated with the cleavage of C-S bond. This proton is then transferred to acetyl-CoA anion along the H-bond network The negatively charged intermediates of the reaction are stabilized in the oxyanion hole, formed by Cys356 and Leu357.

We discovered, that in the course of NAGS evolution the chemical nature of its active site changes radically. However, the geometry of the oxyanion hole remains the same. This suggests, that the active site of the protein has evolved in such a way as to preserve its geometry rather than amino acid composition and it is possible to attribute the mechanism, established for NAGS from Neisseria gonorrhoeae, to NAGS from more highly organized organisms.

The acetyl-CoA binding sites of NAGS and the mutant proteins were studied via molecular dynamic simulation with the applied CHARMM36 force field. The molecular mechanism of the reaction was revealed using the QM/MM approach.

Acknowledgement: This work was supported by the Russian Science Foundation (project #23-13-00011). We acknowledge the use of supercomputer resources of the Joint Supercomputer Center of the Russian Academy of Sciences and the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University.

OP-IV-04

DFT Study of the Structure and Properties of Nanosized (Bi)metallic Catalysts

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Modern quantum chemical methods make possible accurate calculations of realistic models of nano-sized catalytic systems [1-4]. Calculations of model nanoparticles contribute to the interpretation of experimental data, including those obtained by spectral methods [2], and make it possible to predict the influence of various structural factors on the catalytic properties, including the ratio of components in bimetallic nanosystems [2,3], as well as to identify size effects [1, 4].

In this work, based on calculations of model nanoparticles, a comparative analysis of bimetallic nano-sized systems PdAg and PdAu at different component ratios was carried out. General structural principles have been established and features of the PdAu system have been identified with respect to the possibility of stabilizing Pd monomers on the surface even in the absence of an adsorbate at certain Pd:Au ratios. Various structural motifs for the internal ordering of PdAg and PdAu particles and their relation to surface activity are discussed.

In agreement with experimental data, our calculations show stabilization of the palladium component on the surface of PdAg and PdAu particles upon interaction with various adsorbates. Based on calculations, it is proposed to attribute the experimentally observed frequency of 1980-1990 cm^{-1} not to single CO molecules adsorbed on surface Pd2 dimers, as previously assumed in the literature, but to vibrations of an ensemble of CO molecules co-adsorbed in bridging positions on the chains of Pd atoms, formed on the edges of PdAg or PdAu nanoparticles during the process of surface enrichment with palladium due to interaction with CO.

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OPs-01

Thermally and Adsorption-Induced Surface Structure and Morphology Evolution in Bimetallic HOPG-Supported Nanoparticles as Probed Using XPS and STM

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Most heterogeneous catalytic processes occur at the gas-surface and liquid-surface interfaces, so of high interest for research is the intentional tailoring of surface structure in catalytically active materials. The use of bimetallic nanoparticles allows to construct the active sites with a specific geometry on the catalyst surface, providing an extra degree of freedom for catalyst design. Owing to the modification of the electronic properties of active component (ligand effect) and the geometry of active sites (ensemble effect), bimetallic catalysts often demonstrate improved catalytic properties compared to their monometallic counterparts [1]. The mutual configuration of two metal species on the surface of bimetallic catalysts have a decisive effect on the occurrence of adsorption and catalytic processes, so a particular attention is to be paid to the methods of controlled tuning of the surface structure. However, a detailed surface structure investigation is rather limited for real catalytic systems due to their complex morphology and the low content of active component. In order to facilitate the investigation of atomic distribution in the near-surface regions, real catalysts can be mimicked by corresponding model systems with nanoparticles deposited onto planar conductive supports, such as a highly oriented pyrolytic graphite (HOPG). The response of the structure of such model supported systems to different external factors (temperature, gaseous medium) can be examined using the combination of spectroscopic and microscopic techniques.

The aim of this work was to investigate a series of model bimetallic HOPG-supported catalysts and the evolution of their surface structure during different temperature and gas treatments using scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). The bimetallic samples were prepared by consecutive thermal vacuum deposition of metals on the surface of a HOPG specimen preliminarily bombarded with low-energy Ar^+ ions in order to generate the defects serving as anchors for nanoparticles. All the studies were carried out *ex situ*, *i.e.*, after each temperature/gas treatment the samples were first brought back to ultrahigh vacuum (UHV) conditions and room temperature, what was followed by the photoelectron spectra recording and STM measurements.

The effect of CO treatment was demonstrated to noticeably differ for two bimetallic HOPG-supported Pd-based systems of a different type [2]. For a substitutional solid solution of Pd and Au, the exposure to a CO atmosphere induced a significant redistribution of metals with Pd segregating towards the surface of nanoparticles, disturbing the initial alloy structure. The process of Pd segregation was interpreted to be driven by the formation of stable Pd_x–CO moieties as a result of CO adsorption. According to the variations in Pd/Au atomic ratios derived from XPS, the segregation enhanced with temperature of CO treatment, achieving the largest Pd/Au atomic ratio in the performed experimental cycle after treatment at 150 °C. Nevertheless, the observed changes were reversible: annealing of the Pd-Au/HOPG sample in UHV at 450 °C was shown to restore the initial surface structure of the catalyst. In contrast, the stoichiometric intermetallic compound of Pd and In practically did not change the surface structure when exposed to CO atmosphere independently of the treatment temperature. Thus, tuning of the surface structure under CO treatment is possible for the Pd-Au nanosized substitutional solid solution and does not take place for the Pd-In intermetallic compound nanoparticles.

The other part of the study was devoted to the investigation of the alloying proneness of bulk-immiscible elements under different temperature conditions. The miscibility gap observed for the bulk Pt-Ag and Pt-Au systems was shown to be overcome for the corresponding HOPG-supported bimetallic nanoparticles already at the stage of their preparation. For the Ag-Pt/HOPG nanoparticles, a stepwise heating up to 300–400 °C caused a thermodynamically favored segregation of silver towards the surface, yielding the Pt-rich core/Ag-rich alloy shell arrangement [3]. The increase in temperature or duration of treatment did not succeed in the enhancement of the extent of Pt-Ag alloying: annealing of the sample at 450–500 °C led to Ag sublimation, whereas increasing the annealing time resulted in the partial separation of monometallic species from bimetallic nanoparticles. In contrast, thermal annealing of the Pt-Au/HOPG nanoparticles up to 350–500 °C enhanced the alloying degree of the metals, but further increase of the treatment temperature gave rise to the sintering of nanoparticles [4]. The experimental X-ray photoelectron spectra measurements were accompanied by the theoretical simulation of XPS signal intensities to enable a more meticulous analysis of compositional distribution in bimetallic nanoparticles, representing an approach which can be helpful for other researchers from a methodological perspective as well.

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for SRF SKIF Boreskov Institute of Catalysis (FWUR-2024-0042).

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OPs-02

Alkoxyamines as a Convenient Probe for Unveiling the Role of Chemical Structure in Plasmon Catalysis

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Plasmon active metals (Au, Ag, and Cu) have been attracting great attention as efficient catalysts, particularly for catalytic reactions involving organic molecules. The plasmon active substrates capture the light and transfer that energy to form that can initiate reaction. The usage of plasmon energy as a new stimulus has already shown promising results in terms of improving selectivity, enhancing reaction rates, and providing milder conditions [1-3]. However, the exact mechanism of interaction between the plasmon substrate and organic molecules is still a topic of debate. Currently, three main hypotheses have been proposed: (1) acceleration of reactions by plasmonic heating, (2) transfer of "hot" electrons to the molecule leading to the formation of highly reactive species, and (3) intramolecular excitation [4]. None of these mechanisms thoroughly considers the influence of the chemical structure of organic molecules on plasmon-assisted transformations. Alkoxyamines have been proven to be excellent probes for investigation of the plasmon catalysis mechanism due to their first-order reaction kinetics and single-component composition [5]. This uniqueness of the system has allowed us to investigate the impact of the chemical structure of the molecules on the kinetics of the plasmon-assisted reaction.

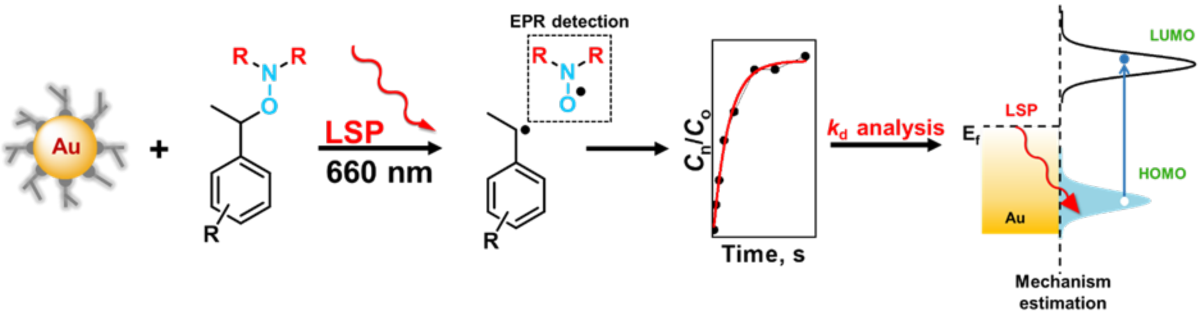

Fig. 1. The general concept of the mechanism revealing plasmon-driven homolysis.

In this work, we investigated the plasmon-driven C-ON bond homolysis of alkoxyamines in the presence of spherical gold nanoparticles (Figure 1). The concentration of released nitroxide was easily and precisely monitored by electron paramagnetic resonance spectroscopy. Further analysis of rate constants k_d obtained from kinetic curves enabled us to establish the importance of the electronic features of organic molecules in plasmon-assisted transformations.

Thus, having plasmon-assisted homolysis rate constants in our hands, we began seeking the correlation between rates and parameters responsible for a specific mechanism. First, we excluded the plasmonic heating mechanism because of the lack of relationship between k_d of plasmon-induced homolysis and activation energy of thermal homolysis. Furthermore, the calculation of local heating claimed that the increase in temperature was $\Delta T \approx 0.038$ °C that was not enough to carry out the reaction with so high k_d. Second, there was no correlation between the rate constants and the energy of the low unoccupied molecular orbitals that participate in the realization of the “hot” electron transfer mechanism. Additionally, we did not observe the formation of products that corresponded to the anion-radical pathway. Finally, the linear dependence between rate constants of plasmon-driven homolysis and the energy of highly occupied molecular orbital demonstrated a direct intramolecular excitation mechanism. In addition, we have shown that hybridization between molecular orbitals of organic compounds and metal surfaces occurs that decreases the energy gap and favors the homolysis. Additional DFT calculations of local densities of states of conjugates metal-molecule demonstrated that HOMO of an organic molecule hybridized with the Fermi level of the metal more active than LUMO. This argument proved the importance of HOMO in plasmon-induced reactions [6].

Therefore, the experimental and theoretical studies allowed us to suggest a possible mechanism that explained the role of the HOMO in the plasmon-driven homolysis of alkoxyamines. The obtained results open the prospects for fine-tuning plasmon-assisted reactions that allow chemical engineering and medical science to be more efficient, cheaper, and safer.

Acknowledgement: This work was supported by the Russian Science Foundation, grant no. 23-73-00117.

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OPs-03

Bronsted Acidic Catalysts Based on the Porous Aromatic Framework for Effective Oxidative Denitrogenation

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To date, all types of motor fuels are subject to fairly strict requirements for the content of total sulfur due to the negative impact of sulfur-containing compounds and their combustion products on the environment, human health, and process equipment. Although there are no requirements for the nitrogen content in motor fuels and petroleum products, their presence is indirectly regulated through fuel characteristics such as gum content, thermal stability, and storage stability. Today, nitrogen-containing compounds are removed from petroleum products in a hydrotreatment process designed primarily to reduce the sulfur content. It should be noted that nitrogen-containing compounds compete with organosulfur substrates for the active sites of hydrotreatment catalysts. A decrease in the efficiency of the desulfurization process leads to the necessary tightening of process conditions in order to obtain products that meet modern environmental standards for residual sulfur content.

At the moment, the development of heterogeneous catalysts based on porous aromatic frameworks is relevant and it is a relatively new area of research. Their hydrophobic properties allow the transport of organic substrates into the pores to be simple, and their ordered structure can influence the selectivity of the process. In recent studies, catalysts containing immobilized Bronsted acids in the form of sulfo-groups [1] allow the oxidation of sulfur-containing substrates with hydrogen peroxide with high efficiency. Considering that nitrogen-containing compounds are also typical Lewis bases, catalysts with an acid component will allow the oxidation process to be carried out with high efficiency.

In this work, a catalyst with sulfo-groups was used for the first time in the oxidation reactions of various nitrogen-containing substrates. Sulfonic groups immobilized on support, which are Brønsted acid sites, can form active peracid in presence of hydrogen peroxide and on the other hand can efficiently coordinate both nitrogen- and sulfur containing compounds, which are Lewis bases (fig.1).

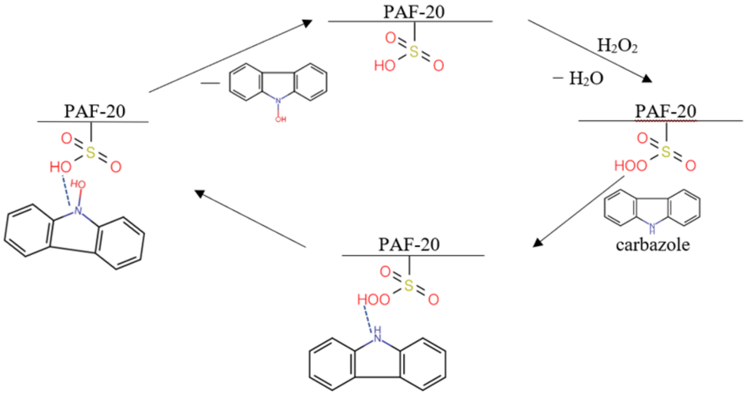

Fig. 1. Possible reaction scheme.

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The main factors affecting the process consisting of sulfonic groups content, catalyst dosage, temperature, hydrogen peroxide amount as well as concentration were investigated in detail. In presence of the most active catalyst PAF-SO3H 500 (fig.2A) under optimal reaction conditions relatively inert carbazole was removed by 95% in just 10 min. In this work, a catalyst with sulfo-groups was used for the first time in the oxidation reactions of of mixtures with sulfur-containing compounds (fig.2B). Sulfonic groups are strong bonded to support which allows to prevent their leaching and retain catalyst activity up to 5 cycles of oxidation-regeneration.

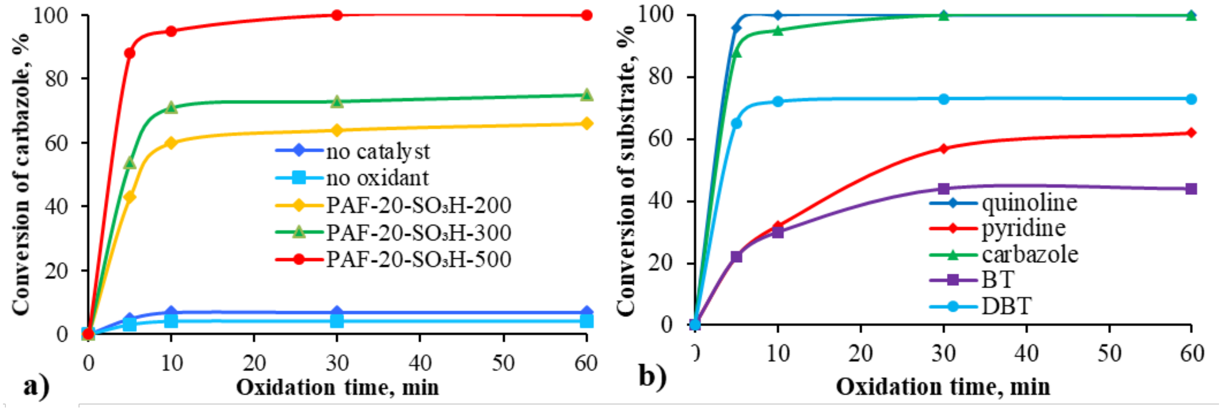

Fig. 2. A. Catalysts activity test cycles (oxidation conditions: 2,0 wt% of catalyst, H_2O_2:N molar ratio of 4:1, T 80°C). B. Oxidation of various substrates (oxidation conditions: 2,0 wt% of catalyst PAF-20-SO_3H-500, H_2O_2:N molar ratio of 4:1, T 80°C).

The use of catalysts containing acidic catalytically active centers immobilized on a support opens up wide opportunities for the development of the oxidation process of nitrogen-containing compounds, including in combination with desulfurization.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 22-79-10044.

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OPs-04

Diverting Mn Catalyzed Epoxidations towards *syn*-1,2-Acyloxylations

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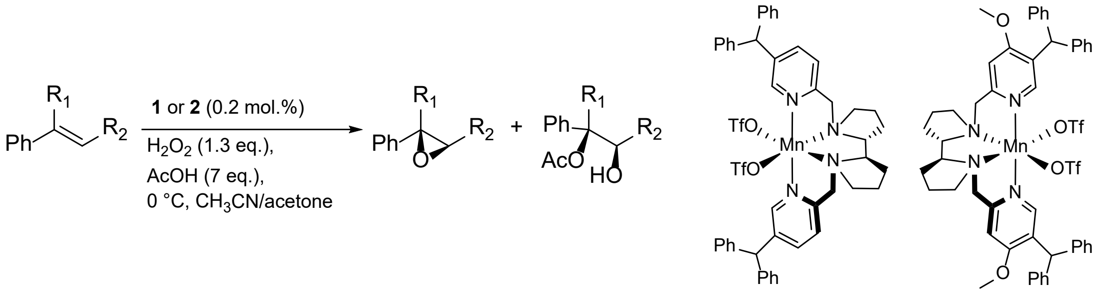
Asymmetric epoxidation of olefins is a challenging transformation, leading to chiral epoxides, widely used as building blocks. In recent years, bioinspired manganese(II) complexes with chiral N_4 *bis*-amino-*bis*-pyridylmethyl ligand have been considered as arguably the most promising transition metal catalysts for asymmetric epoxidations with "green" oxidant H_2O_2. Here we report the novel catalytic reactivity of two manganese complexes (**1** and **2,** *Fig. 1*), bearing bulky benzhydryl substituents at the pyridine moieties, in asymmetric epoxidation reactions. Complexes **1** and, particularly, **2**, have been found to convert olefinic substrates into the products of *syn*-addition to the C=C bond, hydroxy-carboxylates, that can prevail under certain conditions.



1 **2**

Fig. 1. Asymmetric epoxidation/syn-dihydroxylation reaction. OTf^- = $CF_3SO_3^-$.

The reaction is rate-limited by electron transfer to the Mn^VO intermediate to form a short-lived acyclic (presumably carbocationic) intermediate [1]. Based on the oxidation of various substrates and the linear free-energy relationships, we conclude that the presence of bulky benzhydryl substituents in combination with the strongly electron-donating substituents in the catalyst structure switches the reaction towards radical mechanism, thus stabilizing the acyclic intermediate. This creates prerequisites for alternative pathways, such as rotation around the C_α–C_β bond and *syn*-1,2-hydroxyacyloxylation. The novel catalytic reactivity of nonheme Mn complexes, reminiscent of natural metalloenzymes, contributes to establishing the mechanism of biosynthetic 1,2-dixydroxylations by Rieske dioxygenases.

Acknowledgment: The authors thank the Ministry of Science and Higher Education of the Russian Federation for financial support.

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OPs-05

Organocatalysts in the Electrochemical Oxidation of H_2S and RSH

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The development of new catalytic methods to convert H_2S into hydrogen and sulfur is a promising area in the oil and gas industry and ecology. The involvement of low-molecular thiols in the synthesis of organosulfur compounds is relevant from the point of view of recycling waste from oil and gas desulfurization into products with high added value. The decomposition of H_2S and the oxidation of thiols to disulfides can be carried out under electrochemical conditions, both under direct electrolysis or using redox-mediator (electrocatalytic) systems [1,2].

At the first time, natural organic compounds such as gallic acid (**1**), L-ascorbic acid (**2**) and their esters (methyl gallate (**3**), octyl gallate (**4**), L-ascorbyl palmitate (**5**)) have been considered as electrocatalysts (Med_{red}) in the process of indirect oxidation of hydrogen sulfide, aliphatic (aromatic) thiols in the compared with early studied substituted *o*-aminophenols (**6-8**) [1] (Fig. 1).

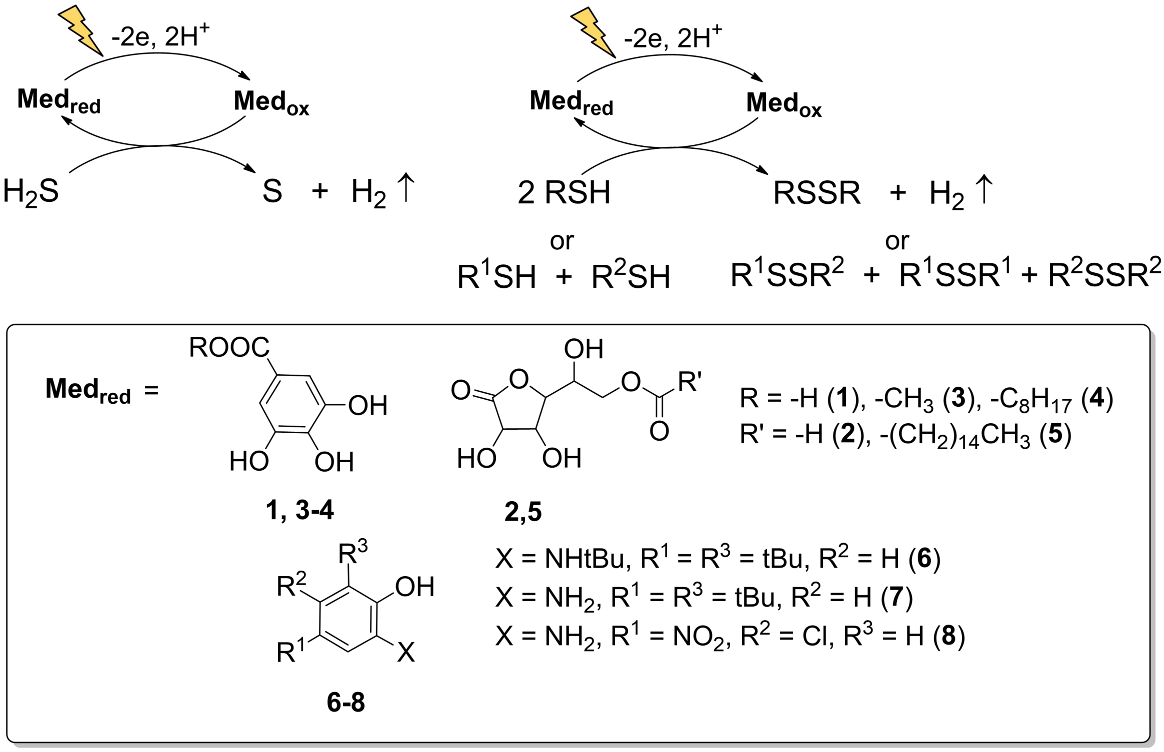

Fig. 1. Redox-cycle of studied compounds.

The main advantage of using the studied compounds is the transfer of the one-electron stage of H_2S or RSH oxidation from the electrode to the solution. This leads to a decrease in adsorption processes on the electrode. In other words, if direct electroactivation of H_2S (RSH) is a heterogeneous process at the electrode, then in the presence of compounds **1-8**, sulfur reagents react with the electrogenerated form of the mediator (Med_{ox}) in a solution.

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Electroactivation of **1-8** leads to the corresponding *o*-(imino)benzoquinones (Med_{ox}). These compounds act as dehydrogenating agents with respect to H_2S and RSH and can promote their transformations.

Electrolysis of H_2S in the presence of compounds **1-5** at the anodic potential of the electrocatalyst in a mixture of N-methylpyrrolidone–acetonitrile leads to the formation of sulfur (14-30%) and hydrogen (1.3-2.6 cm^3). The highest yield of target products was obtained using gallic acid (**1**) as an electrocatalyst. Electrolysis of n-C_3H_7SH in the presence of **1-5** leads to corresponding disulfide (n-$C_3H_7S)_2$ (27-56%). During electrolysis with substituted *o*-aminophenols **6-8**, effective formation of (n-$C_3H_7S)_2$ (62-72%) occurs at lower values of the anodic potential (0.7-1.2 V). To carry out indirect electrolysis in the presence of **1-9** makes it possible to transform thiols into disulfides while reducing the anodic overvoltage of the RSH oxidation reaction by 0.5-1.2 V. In addition, the oxidation of a mixture of disulfides of different structures in the presence of a redox mediator leads to the formation of unsymmetrical disulfides (R^1SSR^2) with potential bioactivity.

Thus, the electrochemical transformations of H_2S and RSH in the presence of organocatalysts **1-9** were studied. For the first time, the possibility of using of natural compounds (gallic acid, L-ascorbic acid) and their esters as electrocatalysts for the decomposition of hydrogen sulfide to sulfur and hydrogen, the oxidation of thiols to disulfides has been discovered.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-13-00201.

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OPs-06

C-H Bond Breaking in Methane on Protected and Unprotected Ni-Cu-S and Ni-Cu-O Nanoclusters: Doping and Ligand Effects

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A current trend in chemical industry is an effective conversion of natural gas into valuable chemical raw materials. To achieve this task, in particular, steam reforming of methane (SRM)

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

and dry reforming of methane (DRM)

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$$

are used, which makes it possible to obtain synthesis gas (a mixture of CO and H_2), which is an important raw material for the synthesis of methanol [1] and the Fischer-Tropsch process [2]. In addition, DRM is also important from an environmental point of view, since it allows efficient utilization of the greenhouse CO_2, helping to reduce its emissions into the atmosphere. Development of catalytic systems with high efficiency, stability and reasonable cost is an important task. One of the key steps in SRM and DRM is methane activation by C-H bond breaking on the catalyst surface. Ni–Cu bimetallic systems have high perspectives due to low activation energy of C-H breaking and high stability [3].

Simulation of catalytic properties of new type of catalysts based on protected Ni–Cu nanoclusters is of high interest. Systematic studies of CH_4 activation on protected Ni-Cu-X-PR_3 and unprotected Ni-Cu-X clusters have not been conducted. Here we present the results of simulation of C-H bond breaking on $NiCu_{11}X_6(PH_3)_8$ and $NiCu_{11}X_6$ (X = S, O) clusters obtained by density functional theory (PBE level). These models are based on copper sulfide clusters $Cu_{12}S_6(PR_2R')_8$ (R = Et, Ph; R' = Et, “Pr, Ph) obtained experimentally and characterized by X-ray diffraction analysis (Fig. 1) [4]. Firstly, the structures of the $Cu_{12}S_6(PH_3)_8$, $Cu_{12}S_6$, $Cu_{12}O_6(PH_3)_8$, $Cu_{12}O_6$ clusters were optimized. Then the structures of all possible isomers of bimetallic clusters including $NiCu_{11}S_6(PH_3)_8$, $NiCu_{11}S_6$, $NiCu_{11}O_6(PH_3)_8$, and $NiCu_{11}O_6$ were simulated and optimized. Activation energies and energy changes of C-H bond breaking of CH_4 on the model catalysts were calculated to study doping (S or O) and PH_3 ligand effects. The lowest activation energy was observed for the $NiCu_{11}O_6$ cluster (99 kJ/mol), which gives grounds to consider this system as a promising one for methane activation.

OPs-06

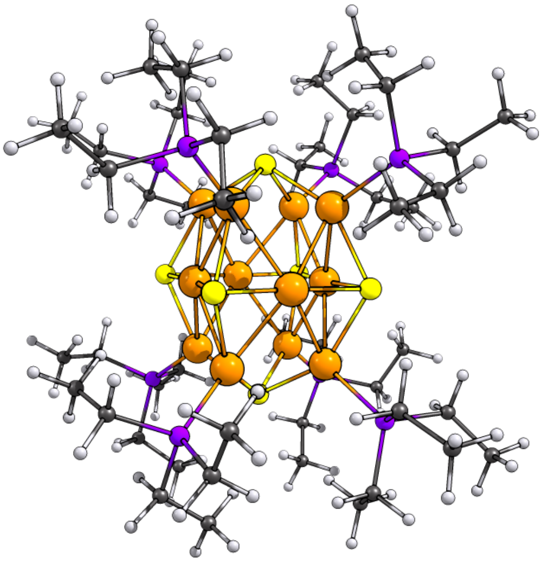

Fig. 1. Calculated structure of the $Cu_{12}S_6(PEt_3)_8$ cluster.

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OPs-07

Selective C(sp^3)–H Hydroxylation/Alkoxylation in the Presence of Palladium Aminopyridine Complexes

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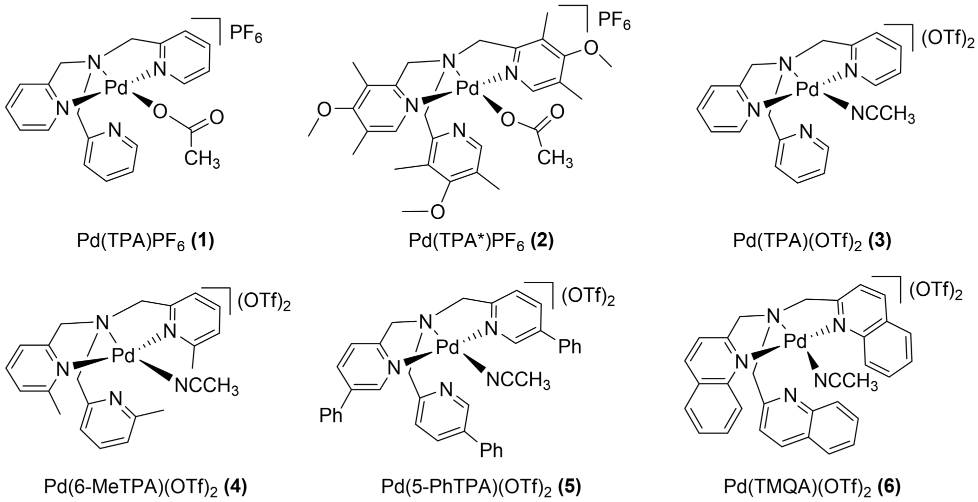
Direct transition metal-catalyzed oxidation of C–H groups remains one of the main trends in the late-stage functionalization (LSF). Site-selective and deliberate C–H functionalization has been envisioned as a promising tool for the alteration of key chemical and pharmacological properties of natural products, as well as for the synthesis of complex molecules in general [1]. In recent years, catalyst systems based on non-heme iron and manganese complexes have dominated the area of regio- and stereoselective C(sp^3)–O bond formation [2]. However, in some cases catalysts based on complexes of late transition metals such as nickel and palladium have demonstrated competitive or even superior results in terms of turnover numbers (TONs) and regioselectivity.

Previously, we demonstrated that palladium complexes with tris(pyridylmethyl)amino ligands (Figure 1) mediated benzylic C–H oxidation with peroxycarboxylic acids (AcOOH, *m*CPBA) in acetonitrile, providing the corresponding alcohols or ketones in up to 100% selectivity and yield [3].



Pd(TPA)PF$_6$ **(1)**   Pd(TPA*)PF$_6$ **(2)**   Pd(TPA)(OTf)$_2$ **(3)**

Pd(6-MeTPA)(OTf)$_2$ **(4)**   Pd(5-PhTPA)(OTf)$_2$ **(5)**   Pd(TMQA)(OTf)$_2$ **(6)**

Fig. 1. Structure of synthesized palladium complexes ***1-6***

In this work, the reactivity of palladium catalysts in the media of polyfluorinated alcohols toward direct oxidation of C(sp^3)–H sites has been examined. It has been found that replacing CH_3CN with TFE dramatically enhanced the substrate conversions and improved the selectivity. In addition, it allows expanding the substrate scope at the expense of compounds with non-activated aliphatic C–H groups. Pd(TPA)-mediated direct selective C–H hydroxylation of organic molecules proceeds smoothly under mild conditions (0…+10°C), demonstrating unprecedentedly high regiopreference for the most electron-rich tertiary $(3^\circ : 2^\circ > 300)$ sites in the molecule.

Depending on the reaction conditions, either alcohols or ethers can be selectively obtained by oxidation of 2° or 3° benzylic C–H groups. The use of TFE or HFIP:primary alcohol mixtures as solvents provides access to a variety of alkoxy derivatives on demand, while in poly-β-fluorinated alcohol:H_2O mixtures the C–H hydroxylations occurs with improved selectivity and efficiency compared to the reaction in acetonitrile.

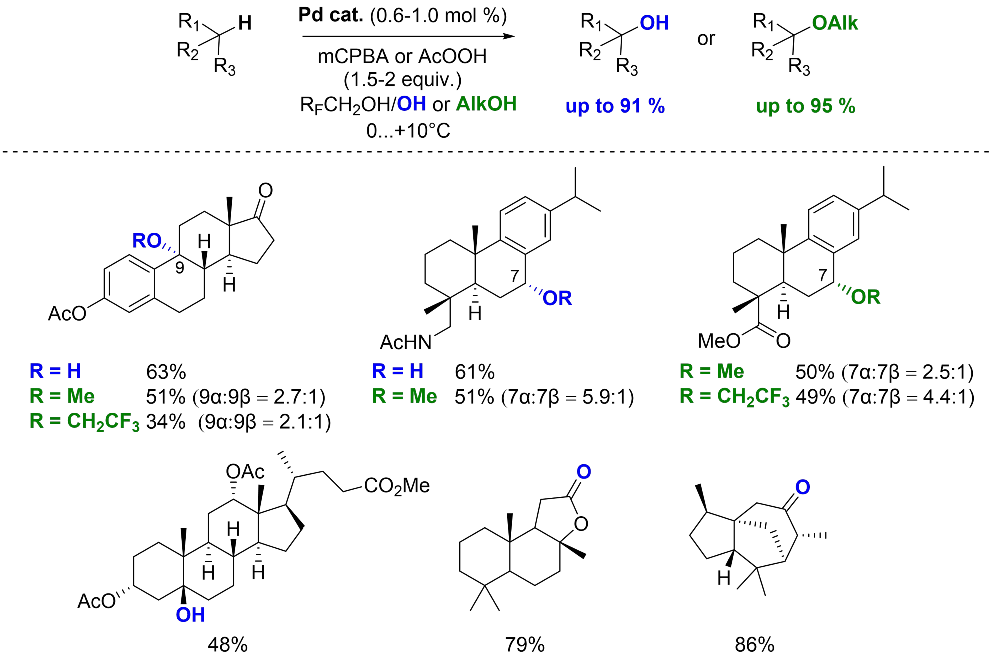


Fig. 2. Oxidative functionalization of complex substrates of natural origin.

The developed catalytic approaches demonstrate high stereospecificity and regioselectivity, enabling applications in the selective oxidative C–H functionalizations of complex substrates of natural origin. Thus, a variety of oxidations of complex substrates (steroids and terpenoids) has been achieved in synthetically useful yields (Figure 2). Mechanistic studies provide evidence in favor of transition metal mediated H–C bond breaking, followed by competitive OH/OAlk transfer to the intermediate C-centered radical.

Acknowledgement: The authors thank the Ministry of Science and Higher Education of the Russian Federation for financial support.

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OPs-08

Extractor Mode on Membrane Catalysts

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The extractor mode of membrane reactor has attracted the most attention of researchers in the all history of membrane catalysis. For a long time, the reactor (extractor) with a stationary or fluidized catalyst bed and a selective membrane was considered as the most promising. Traditionally [1], a change in the ratio of retentate and permeate flows is considered as a way of influencing the equilibrium state of a reversible reaction. It is assumed that the removal of one of the reaction products through the gas-selective membrane should compensate for the decrease in reaction temperature by a change in equilibrium in the reversible reaction. The main mechanism for achieving selectivity of gas separation membranes is to reduce the pore size. However, it was not possible to achieve a significant change in equilibrium in a reactor with a porous gas-selective membrane. The expected effect was observed reactant mixture using at extremely low flow that have no practical significance.

In [2], the change of equilibrium in a reactor with a membrane catalyst was explained by different states of the reaction mixture in porous channels. Gas flows have been found to arise and coexist in states of continuity and rarefaction in the pore channels of a membrane catalyst under conditions of non-isothermal Knudsen diffusion.

The aim of this work was to establish the possibility of influencing on equilibrium in the process of carbon dioxide conversion of methane on a porous membrane catalyst.

In this study, in a reactor with a membrane catalyst, the equilibrium of the DRM reaction was also altered by way of the same permeate-to-retentate ratio (P/R). All other parameters were remained unchanged (T – 850 °C, reagent flow rate 320 nscm^3/min, [CH_4]:[CO_2]=1:1). The changes in concentrations with contact time that were established by changing R:P from 0 to 1 in the reaction volumes for P and R, respectively, were considered as two kinetic dependencies. At the same time, it was assumed that the DRM reaction in both reactor volumes takes place on the same catalyst, but in different adjacent volumes of the reaction space. The rate constants of direct and reverse reactions (columns No. 3 and No. 4) in both volumes of the reactor in the extractor mode were represented as the transition states between the two limiting modes of the contactor – the modes of "diffusional" and "forced" transport of reactants to the catalyst surface (columns No. 2 and No. 5 at the Table).

In the considered modes of the reactor with a membrane catalyst, heterogeneous reactions at all stages of the DRM occur irreversibly, except for the methane cracking reaction in the extractor mode. The reaction was reversible in both adjacent reactor volumes and took place near equilibrium. It should also be noted that in extractor mode, heterogeneous reactions proceed with greater intensity. The rate constants of methane cracking in extractor mode are higher than that in contactor mode.

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Table 1. Specific rate constants of the intermediate stages of the DRM

Reaction	Rate constant, $\frac{sm^3}{g \cdot s}$	Contactor, (diffusion transport)	Extractor-Retentate	Extractor-Permeate	Contactor (forced transport)
Column No.	1	2	3	4	5
$CH_4 = C + 2H_2$	$k_1 \rightarrow$	29	87	70	40
	$k_2 \leftarrow$	0	67	60	0
$C + CO_2 = 2CO$	$k_3 \rightarrow$	20	30	30	15
	$k_4 \leftarrow$	0	1	2	0
$CO_2 + H_2 = CO + H_2O$	$k_5 \rightarrow$	2	2	20	2
	$k_6 \leftarrow$	2	10	40	2
$C + H_2O = CO + H_2$	$k_7 \rightarrow$	15	80	120	15
	$k_8 \leftarrow$	0	7	1	0

The irreversibility and intensification of the heterogeneous intermediate stages of the DRM in the publication [2] are explained by the peculiarity of mass transfer called thermal slip. All heterogeneous stages of DRM on a membrane catalyst take place in a thermal slip stream in which the gases are in a rarefied state. If we consider that these reactions proceed with an increase in the volume of the reaction mixture, it becomes clear that the equilibrium in them is shifted towards the formation of products. In theory of Thermal slip rarefaction (δ) depends on the characteristics of the pore channels, the properties of the gases, and the thermodynamic parameters according to the equation [3]:

$$\delta = \frac{\sqrt{\pi}}{2} \cdot \frac{1}{Kn} = \frac{a \cdot P}{\mu} \left(\frac{m}{2k_B T} \right)^{0,5}$$

where: a – characteristic size of the gas flow; T – temperature; P – average pressure; μ – viscosity of the gas; m – mass of the gas molecule; k_B – Boltzmann constant.

Dividing of the reaction mixture into R and P streams in extractor mode changes the rarefaction state in the thermal slip stream, increasing the average pressure in the pore channels of the membrane catalyst.

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation, grant FSSM-2023-0004.

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OPs-09

Kinetics and Mechanism of the Liquid Phase Hydrogenation of Norbornene Family Compounds

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Chemistry of the norbornene family compounds attracts unflagging interest of researchers. These compounds are commercially available substrates obtained from by-products of petroleum refining mainly using [4+2]-cycloaddition reaction. Their unique strained norbornane structure opens wide possibilities for qualified utilization, in particular, for production of synthetic caoutchouc SKEPT, epoxide resins, components of alternative energy sources, pharmaceutics, aromatizers, as well as new composite materials [1, 2].

Hydrogenation products of substances from norbornene family represent polycyclic structures containing strained norbornane fragments. They have high density and specific combustion heat allowing use them as motor fuel components [1, 2]. The selective synthesis of saturated carbocyclic structures retaining strained carbonic skeleton and unsaturated functional groups represents most important fundamental and applied task. To solve it one needs developing of selective catalysts and finding of mild conditions for liquid phase hydrogenation of norbornene family substances based on detailed kinetic studies.

To achieve the formulated target the mesoporous core-shell catalyst ПК-25 with low active component content (0.25% Pd/γ-Al_2O_3) utilized which usually used for selective heterogeneous hydrogenation acetylenes and dienes.

The main proceeding routes of liquid phase hydrogenation of norbornadiene (ND), (*endo/exo*)-5-vinyl-2-norbornens (VNE) and *endo*-dicyclopentadiene (DCPD) in n-heptane or n-decane medium at 25 – 80 °C temperature interval and different hydrogen partial pressure [3-6].

In all cases, the selective conversion of different norbornenes into norbornanes proceeds with retaining of carbocyclic skeleton. The saturation by hydrogen of ND and VNE shown to be a complex consecutive-parallel process proceeding through formation of different compounds, mainly alkenes. In case of ND the reaction mechanism complicates by formation of minor product - nortricyclane, and for VNE – by double bond migration with participation of vinyl group. For DCPD one may observe its consecutive transformation into cycloalkane without formation of side-products. Based on the structure of the products formed one can come to conclusions about variability of coordination (adsorption) ways of carbocyclic substrates on the catalyst active centers. Variance of ND adsorption leads to formation of different products – norbornene and nortricyclane. Here 2,3-coordination of ND prevails. Chelate nature of ND 2,6-coordination confirms by formation of insignificant nortricyclane quantities.

OPs-09

Monodentate coordination of VNE and DCPD results in formation of spatial olefin isomers retaining the substrate structure. Their coordination on the catalyst active center goes exclusively by more strained double bond of norbornene fragment, but not with participation of other nature double bonds.

The steps of all processes under study neatly separated in time. In the presence of carbocyclic dienes of norbornene family inhibition takes plate of the alkene hydrogenation step. Until diene is present in the system, alkene hydrogenation completely suppressed. It relates with preferred diene adsorption on active palladium center compared to the rest system components.

In the course of kinetic studies, it became clear the practically same consumption rate of dienes and their zero kinetic order in wide interval of initial concentration. By partial pressure variation, the first kinetic order upon hydrogen established. The practically quantitative hydrogenation of norbornene bond does not affect other double bonds – cyclopentene, vinyl, and ethylidene. Shown is that *exo*- and *endo*-isomers of VNE are equally active in hydrogenation reaction of norbornene double bond [6]. Found is that for all studied dienes their hydrogenation rate weakly depends on temperature.

Based on total experimental and theoretical data using Langmuir-Hinshelwood approach the detailed kinetic model developed for every compound. Adequacy of data description by these models accessed only on assumption of multiple substrate adsorption on the same active center of heterogeneous catalyst. Supposition made that hydrogen activation nature affects the reaction kinetics in substantial degree.

Acknowledgement: The work is carried out by financial support of RSF in the framework of scientific project №23-73-00123

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OPs-10

DFT-Quality Monte-Carlo Simulations of Distribution of Hydrocarbon Pool Species in MFI Frameworks Enabled by Machine Learning Potentials

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Zeolite catalysts have been widely used in transformation of biobased substrates into essential products for the modern chemical industry [1]. For example, light olefins and aromatic hydrocarbons can be produced from methanol and ethanol in the methanol-to-olefins (MTO) and ethanol-to-hydrocarbons (ETH) processes. They are very complex and an HCP (hydrocarbon pool) mechanism has been proposed for these processes [2].

In this mechanism, carbocation spices based on alkenes, cyclopentadienes and aromatic hydrocarbons are the active catalytic site. They are included in corresponding catalytic cycles to form another alkenes, cyclopentadienes and aromatic hydrocarbons. These particles are split off, regenerating the active site and closing the catalytic cycle. The mechanism can explain the deactivation of zeolite catalysts and the distribution of resulting products during the conversion of methanol or ethanol [3].

The stability of carbocation species in the zeolite framework is possible because the framework is able to hold them through host-guest interactions [4]. However, zeolite frameworks have different channel and pore system. For example, zeolite ZSM-5 has a system of intersecting straight and sinusoidal channels, therefore these channels are not equivalent and will be differently involved in host-guest interactions. Thus, it is still an open question what species are contained in different shape of pores of zeolite, its distribution and most possible compounds.

This problem is being solved experimentally and computationally, for example, periodic calculation, Raman spectroscopy, UV-visible spectroscopy or extraction from zeolite samples dissolved in acid are used. Each approach has its own advantages and disadvantages. The most important difference between computational and experimental approach is that the extraction and spectroscopic methods are insensitive and cannot separate similar isomers of the hydrocarbon. The computational approach allows us to model the host-guest interactions of each hydrocarbon in the pore space of the zeolite framework [5].

We investigate the distribution of hydrocarbons in zeolite ZSM-5. To investigate the potential energy surface (PES), we use native Monte Carlo simulations for a wide set of hydrocarbons. However, DFT calculation host-guest interaction for all hydrocarbons in the space of pores and different regions is computationally expensive, because about 10000 single point calculation are required for each hydrocarbon. Therefore, in this work, we utilize recent developments of highly accurate and data-efficient equivariant machine learning potentials (MLPs) to describe the host-guest interaction of hydrocarbons in zeolite framework. For instance, this approach is used in the work on the study of carbon dioxide adsorption on ZIF-8 using the machine learning potential [6].

For sampling, we used a heuristic approach where different hydrocarbons and their conformers are distributed in different locations of the zeolite pores. Some of these samples are selected for the training set to obtain the DFT-level energy, and then we obtain the exact energy after training a graph neural network for the whole set.

This approach reduces computational time with slight loss of accuracy to investigate the hydrocarbon distribution in the pore space of ZSM-5 zeolite. In addition, this approach does not require calculation of forces in DFT-study.

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (project FWUR-2024-0039).

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OPs-11

The Effect of Cerium Content and Method of CeO_2 Addition on the Catalytic Properties of Cr_2O_3-ZrO_2-SiO_2 Systems in Non-Oxidative Propane Dehydrogenation

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Propylene is one of the most important products in the chemical industry, and its demand has been constantly growing over the past decades. One of the most promising methods to produce propylene is the catalytic dehydrogenation of propane. The industrial dehydrogenation catalysts usually contain Pt or CrO_x particles supported on Al_2O_3. Platinum-based catalysts are expensive and easily deactivated while high chromium content can pose a threat to human health due to the possible presence of toxic Cr^{+6} compounds [1]. ZrO_2-based systems modified with silica and small amount of CrO_x as an active component are promising catalysts for non-oxidative propane dehydrogenation (PDH). Due to the unique redox properties of ceria and the high lability of lattice oxygen in CeO_2 structure, its introduction into PDH catalysts can promote soot oxidation and improve stability under reaction conditions [2].

CrO_x-SiO_2, CrO_x-ZrO_2-SiO_2, CrO_x-CeO_2-SiO_2 and CrO_x-CeO_2-ZrO_2-SiO_2 catalysts were prepared using cetyltrimethylammonium bromide (CTAB) and TEOS as templates. After evaporation the precursors were heated up to 600°C (2°C/min) and calcined at this temperature initially in air for 4 h. The samples were denoted as CrSi, CrZrSi, CrCeSi and CrCeZrSi_x (where x=1, 2 or 4 is the (Zr+Ce)/Si molar ratio). The chromium loading was 6 wt%. The catalysts were tested in PDH at 500, 550, and 600°C on an ULCat-1 catalytic unit (UNISIT, Russia) equipped with a fixed-bed continuous-flow quartz reactor. 100 mg of catalyst was used in each test. Long-term stability tests and stability tests with two cycles of regeneration were carried out at 550°C with 200 mg of the catalyst. The feed flow composition was 40 vol.% C_3H_8 and 60 vol.% N_2 (total flow rate – 30 ml/min). The gas mixture was analyzed by GC Crystal-5000.2 (“Chromatec”, Russia) equipped with a Carboxen-1010 PLOT capillary column (30 m, id 0.32 mm, “Supelco”, USA) and a FID. The catalysts were characterized by H_2-TPR, PXRD, Raman spectroscopy, XPS, EPR, FTIR, SEM-EDA, N_2 physisorption and DSC-TG.

According to the PXRD data the ZrSi support presents in the samples as highly dispersed crystalline particles, while modification with CeO_2 increases the crystallinity and decreases S_{BET} values. Long-term stability tests at 550°C led to the deactivation of catalysts due to the coke formation. Raman spectra of the catalysts after 200 minutes in the reaction mixture contain lines related to carbon species, while bands in the region of 500-800 cm^{-1} associated with Cr^{3+} oxides become less intense. For the CrCeZrSi_1 and CrZrSi samples there were no lines characteristic for Cr^{6+} compounds. It is likely that in these samples occurs a more complete reduction of Cr^{6+} to the active form, as a result these systems were less deactivated. The regeneration of the samples by 30 min air treatment at 550°C partially recovered catalytic properties. A characteristic period of catalyst development is observed for CrCeZrSi_x systems: the rate of propylene formation increases at the initial stage, then begins to decrease, which is especially noticeable after regeneration (fig. 1a). The same trend can be seen in systems that do not contain zirconium, which clearly indicates the influence of cerium (fig. 1b). CeO_2 intrinsically promotes soot oxidation, which is confirmed by the TG data: the smallest mass loss in samples after catalytic tests is observed for the sample with the highest cerium content (fig. 1c).

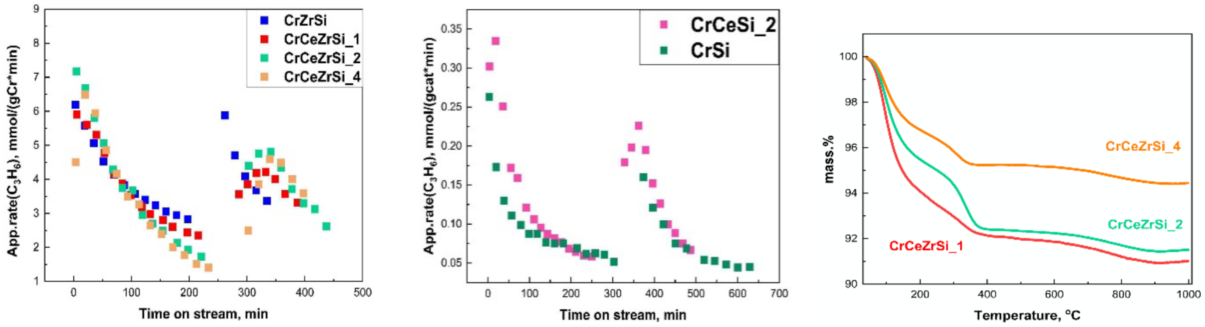

Figure 1. Apparent rate of C_3H_6 formation vs. time for a) CrCeZrSi_1, CrCeZrSi_2, CrCeZrSi_4 and b) CrSi, CrCeSi_2; c) TG-analysis results for CrCeZrSi_1, CrCeZrSi_2, CrCeZrSi_4 after long-term stability tests.

Soot oxidation is the reason for the increase of propylene formation rate at the initial period. High lability of lattice oxygen in CeO_2 structure not only promotes effective soot removal, but also affects $Cr^{3+}O_x$ species. As a result, some active Cr^{3+} sites are lost due to chromium oxidation to inactive Cr^{6+} form. This leads to a decrease in the rate of propylene formation. In the CrCeZrSi_4 sample the number of CeO_2-Cr_2O_3 contacts and, consequently, amount of Cr^{6+}, is the highest. $Cr^{3+}O_x$ species in the system with the lowest CeO_2 content were oxidised to a lesser degree, which is consistent with Raman spectroscopy data. This tendency persists after the second cycle of regeneration.

Acknowledgement: The research was supported by RSF (project No. 22-23-00445). Some scientific equipment was purchased using the Moscow State University development program.

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OPs-12

Structural Features of Supported Ru/$Ce_{1-x}Zr_xO_2$ and Mixed Ru-$Ce_{1-x}Zr_xO_2$ Catalysts for Methanation of Carbon Oxides

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Ruthenium-containing catalysts are known to exhibit a high performance in the methanation of carbon oxides (CO, CO_2). The catalytic reactions, which convert synthesis gas (CO and H_2) or exhausted CO_2 into synthetic natural gas, have attracted increasing interest.

A number of studies revealed the high activity of supported ruthenium catalysts based on cerium dioxide RuO_2/CeO_2 [1-2] or on mixed cerium-zirconium oxides Ru/$Ce_{1-x}Zr_xO_2$ [3]. This was explained by a possibility of the Ce^{4+} - Ce^{3+} transitions with the generation of oxygen-deficient centers at metal-support interface, which are considered as additional sites for activation of CO and CO_2 molecules. In addition, it was suggested that ceria – based supports are effective for formation of highly dispersed Ru species possibly due to metal-support interaction [4]. However, the question about the nature of the metal- support interaction is still open. To explore this issue, it is necessary to use methods with a high sensitivity to local structural features and the ability to detect ultrafine particles. In addition, it is useful to consider mixed catalysts with thorough component mixing.

This report presents the results of complex structural diagnostics of supported Ru/$Ce_{1-x}Zr_xO_2$ catalysts prepared by a sorption-hydrolytic deposition technique and mixed Ru-$Ce_{1-x}Zr_xO_2$ catalysts prepared by co-precipitation method. Attention is paid to the influence of the catalyst preparation techniques on the state and structure of Ru species as well as to the structural aspects of the formation of Ru species, their fixation on the $Ce_{1-x}Zr_xO_2$ surface, metal-support interaction. A wide range of methods was used, including X-ray powder diffraction, high-resolution transmission electron microscopy, X-ray photoelectron spectroscopy, CO chemisorption. The X-ray pair distribution functional (PDF) analysis was used to study the structure of highly dispersed Ru species at the atomic level of structure.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 21-73-20075.

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OPs-13

Carbon Monoxide Oxidation on the Surface of Silver- and Copper-Containing Mixed Oxides with Layered Structure

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Mixed oxides with delafossite or crednerite structure are promising materials in the field of oxidative catalysis. Layered structure of mixed oxides is often characterized by presence of stacking faults [1] and point defects [2]. Formation of defects may lead to formation of metastable active sites, which are available for adsorption of substrate and oxygen activation. The mentioned features provide a potential of mixed oxides application in the processes of catalytic oxidation. The use of transitional metals in the composition of mixed oxides ABO_2 (A = Cu, Ag, B = Fe, Co, Ni, Mn etc.) determines their economic efficiency in comparison with catalysts based on noble metals. Widely used methods of mixed oxides preparation include solid state reaction, solution combustion and co-precipitation, which may be combined with hydrothermal conditions [3]. The most suitable of them are co-precipitation and hydrothermal synthesis, since they provide relatively high surface area of final products [4] and can be easily scaled.

The aim of this work is devoted to investigation of relations between the nature of metals in composition of mixed oxides ABO_2, structural features of layered structure, chemical state of ABO_2 surface and catalytic properties in the CO oxidation reaction. In this work we prepared and investigated mixed oxides such as $AgFeO_2$, $AgMnO_2$, $CuFeO_2$, $CuMnO_2$. It was found that delafossite or crednerite structure of mixed oxides forms in a wide range of synthesis temperatures: $60°C \leq T \leq 180°C$. Using X-ray diffraction, we concluded that all of obtained samples consist of pure phases of desired mixed oxides: $AgFeO_2$, $AgMnO_2$, $CuFeO_2$, $CuMnO_2$. The preparation conditions were optimized to achieve the improved catalytic properties of these samples in the CO oxidation reaction. Structural features and phase transformations were investigated with use of *in situ* X-ray diffraction under the catalytic CO oxidation reaction conditions. It was found, that initial layered structure of mixed oxides is primarily stable up to 300°C.

To study the evolution of the surface state as a result of treatment with various reaction media (CO, O_2 and $CO+O_2$) such methods as *ex situ* XPS and TPR-CO were applied. With use of the TPR-CO study it was found, that mobility of bulk oxygen increases in the following order: $CuFeO_2 < CuMnO_2 < AgMnO_2 < AgFeO_2$. Moreover, presence of active oxygen was noted on the surface of $AgMnO_2$ and $CuMnO_2$. At the same time, in the low-temperature range (≤ 50°C) the specific catalytic activity of CO oxidation increases in the following order: $CuFeO_2 < AgFeO_2 < CuMnO_2 < AgMnO_2$. This observation illustrates the increased catalytic activity of the Mn-containing oxides over the Fe-containing ones. This data corresponds well with the presence of active oxygen on the surface of the $AgMnO_2$ and $CuMnO_2$, found with use of the TPR-CO testing.

Based on all obtained data including the results of *ex situ* XPS, we supposed about different structure of active surface of layered oxides ABO_2 (A = Ag, Cu, B = Fe, Mn) under $CO+O_2$ reaction conditions. Manganese- and iron-containing mixed oxides should be compared. It is assumed that redox lability of manganese species provides such transitions as $Mn^{2+}\leftrightarrow Mn^{3+}\leftrightarrow Mn^{4+}$ causing variety of surface adsorption sites and influencing change in state of the second cation – silver or copper. At the same time, iron electronic transitions limit the oxygen activation and decrease catalytic activity of Fe-containing oxides in comparison with Mn-containing ones. Thereafter, copper-containing layered oxides $CuFeO_2$ and $CuMnO_2$ are seriously differ in their catalytic activity. As shown in *ex situ* XPS, copper in $CuFeO_2$ is rather stable during the $CO+O_2$ treatment at different temperatures. In contrast, copper in $CuMnO_2$ is more labile and supposed to perform transition between Cu^{1+} and Cu^{2+} forms simultaneously with manganese state transitions due to the electronic exchange between Cu and Mn species. Redox lability of copper in the case of $CuMnO_2$ influences its high catalytic activity in CO oxidation. In the case of silver-containing $AgFeO_2$ and $AgMnO_2$ oxides difference in Ag state takes place. Speaking of the $AgFeO_2$, silver is mainly presented in regular form as Ag^{1+}, while more oxidized silver is observed on the $AgMnO_2$ surface as $Ag^{1+\delta}$, what could be the consequence of the electronic exchange between Ag and Mn. The presence of silver in form of $Ag^{1+\delta}$ is probably related to the stabilization of highly active oxygen forms (shown by TPR-CO), that is why $AgMnO_2$ is more active in catalytic CO oxidation than $AgFeO_2$.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-73-10127.

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OPs-14

Catalytic (de)Hydrogenation and Hydrosilylation Reactions Involving Bimetallic Complexes (^{tBu}PZCZP)Pd(μ-OC)M(CO)$_2$L

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The dehydrogenation of formic acid (HCOOH) to produce hydrogen (H_2) and carbon dioxide (CO_2) has gained substantial attention in catalysis, offering potential applications in hydrogen storage and clean energy technologies. Formic acid, a liquid at room temperature, serves as a promising source of molecular hydrogen, making it an attractive option for on-board hydrogen storage in fuel cell-powered vehicles [1]. On the other hand, CO_2 released in this and other processes requires utilization which can be achieved, e.g., by means of hydrosilylation. This reaction transforms CO_2 into valuable chemicals or fuels, such as formate ion, formaldehyde or methanol, using silanes as reducing agents [2].

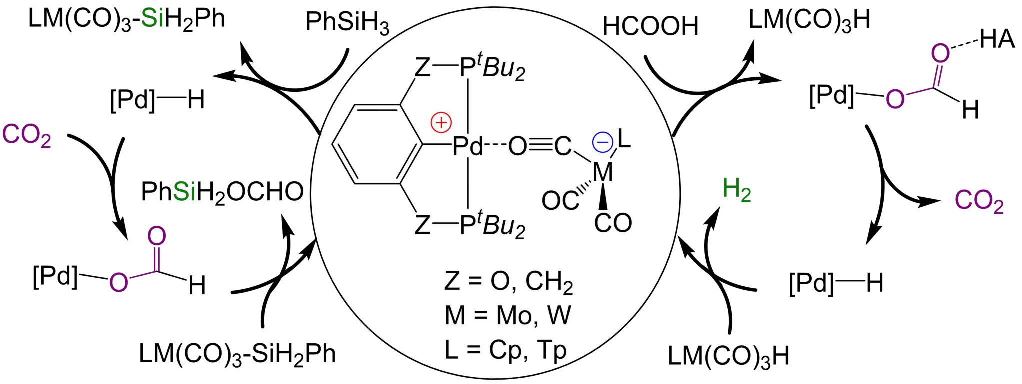
Bifunctional catalysts bearing basic and acidic sites on the same molecule demonstrate good efficiencies in a great variety of catalytic processes [3]. Hydride complexes of transition metals, depending on the polarization of the M–H bond, can display both acidic and basic properties [4]. It was recently shown that bimetallic ionic complexes (^{tBu}PCP)Pd(μ-OC)W(CO)$_2$L (L= Cp, Tp) formed by the interaction of the acidic tungsten hydride LW(CO)$_3$H and the basic palladium hydride (^{tBu}PCP)PdH could effectively dehydrogenate amine-boranes (Me_2NHBH_3, *t*BuNH$_2$BH) [5]. The presence of Lewis acidic [Pd]$^+$ and basic [W]$^-$ metal centers in these complexes triggers the cooperative BH/NH bond activation followed by the stepwise proton transfer to [W]$^-$ and hydride transfer to [Pd]$^+$ making them a transition metal analogue of frustrated Lewis pairs (FLPs).

In this work we report on the synthesis and characterization of the series of bimetallic complexes (^{tBu}PZCZP)Pd(μ-OC)M(CO)$_2$L (Z = CH$_2$, O; M = Mo, W; L = Cp, Tp (Scheme 1)) and the investigation of their catalytic activity in formic acid dehydrogenation [6] and carbon dioxide hydrosilylation [7]. The study of these processes under stoichiometric and catalytic conditions by variable temperature IR (ν_{CO}) and NMR (^{1}H, ^{31}P, ^{29}Si) spectroscopy allowed us to characterize reaction intermediates and products. The kinetic and spectroscopic data analysis enabled us to propose HCOOH dehydrogenation mechanism, where *hydride abstraction/CO$_2$ release* step is facilitated by −OCHO···H−A hydrogen bonding (HA = LM(CO)$_3$H or HCOOH). Additionally, TOF values were estimated for this catalytic reaction under constant volume conditions. The effect of ligands, metal atom and temperature on the rate of the catalytic reaction was also demonstrated.

For carbon dioxide reduction, the experimental data obtained showed that *step-wise* CO$_2$ hydrosilylation can be stopped at the formate level in presence of bimetallic complexes

(^{tBu}PCP)Pd(μ-OC)M(CO)$_2$Cp. In contrast, sole (^{tBu}PCP)PdH rapidly proceeds beyond this stage, achieving a more extensive reduction. The diffusion-controlled step involves CO_2 insertion into the Pd-H bond, making Si-H bond activation by bimetallic complex in the FLP-fashion the *rate-determining step*.

The important role of multiple non-covalent interactions at the key stages of the investigated catalytic reactions and the potential of transition metals based FLPs were demonstrated.



Scheme 1.

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation.

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OPs-15

Catalytic Systems Based on Quaternary Ammonium Compounds for Free Radical Generation

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Quaternary ammonium compounds (QAC) can be attributed to a large class of cationic biocides with a wide spectrum of antimicrobial activity [1]. Analysis of the bactericidal action of QAC combinations with various carriers presented in reviews [1, 2] showed that association of QAC fragments with polymeric materials is one of the most promising strategies to obtain antimicrobial biomaterials. Cationic surfactants (CS) which constitute an important part of QAC have been found to form mixed micelles together with amphiphilic hydroperoxides (ROOH) and catalyse decomposition of ROOH and H_2O_2 into free radicals. The study of binding CSs with ROOH by the means of NMR, DLS, tensiometry, and the measurement of the rates of radical initiation in the mixtures showed that mixed micelles {CS-ROOH} having a size of 20-500 nm were formed. Micelles can be considered as soft supramolecular nanocatalysts, generating free radicals with low activation energy (40-60 kJ/mol) suitable for initiation of radical oxidation and polymerization [3]. The kinetics of radical polymerization of styrene (St) and methyl methacrylate (MMA) initiated by mixed micelles {CS-ROOH} have been studied. Choline (Ch) and its derivatives acetylcholine (ACh) and L-carnitine (LCh) containing the tetraalkylammonium cation R_4N^+ can be attributed to endogenous QAC. Ch and ACh similar to CSs being immobilized on a solid support retain the ability to catalyse the decomposition of ROOH, producing radicals, and to initiate radical oxidation and polymerization. The effect of counterions in CSs and choline derivatives has been studied as well [3-5].

Heterogeneous catalysts obtained by chemisorption of chlorides of Ch and ACh, and bromide of cetyltrimethylammonium (CTAB) on microcrystalline cellulose were tested as catalysts for ROOH (cumene hydroperoxide) decomposition into free radicals in the model reaction of styrene polymerization and the features of kinetics of radical polymerisation in heterogeneous system have been studied. Relatively high values of the rate of radical generation upon contact of the cellulose–CTAB and cellulose–ACh, with hydroperoxides open the possibility of creating disinfectants and medical materials on a cellulose basis.

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OPs-16

Ni-Cu Bimetallic Supported Catalysts for Hydrogen-Rich Syngas Production from CO_2 Reforming with Ethanol

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In recent years, the global chemical community has been moving away from traditional chemical processes associated with large amounts of harmful waste to new, more environmentally friendly, and efficient techniques. One of these processes is ethanol dry reaction (EDR, $CO_2+C_2H_5OH=3CO+3H_2$) converts C_2H_5OH and CO_2 into syngas ($CO + H_2$), which can be used in the Fischer−Tropsch synthesis process. H_2/CO ratio is important characteristic of syngas. Alkanes, olefins, alcohols can be produced by the Fischer−Tropsch reaction on Nickel-based catalysts from hydrogen-rich syngas [1].

However, the decomposition of ethanol and disproportionate amounts of CO also promote carbon deposition [2]. Cu nanoparticles have a good ability to activate CO_2 in the CO_2 hydrogenation reaction. Consequently, Cu particles are added to Ni-based catalysts to promote dry reforming performances.

The aim of this work is to study impact of the promotion of Ni particles by copper in EDR. In this work catalysts were synthesized $1Cu\text{-}9Ni/xAl_2O_3\text{-}(100\text{-}x)[Zr_{0,88}Ce_{0,12}]O_2$ with different ratio Al/Zr in support $x(Al_2O_3)$ = 5, 50, 75 mol.% (1Cu-9Ni/5ACZ, 1Cu-9Ni/50ACZ, 1Cu-9Ni/75ACZ).

Nanoparticles of the active phase Ni^0 и Cu^0 were obtained *in situ* H_2-TPR. The stability was studied for 7 hours in EDR at a temperature 650°C with a ratio of the initial reagents $EtOH/CO_2$=1,8. Through characterizations with XRD, H_2-TPR, EPR, and Raman, the physicochemical properties and structure−performance relationship of the catalysts are investigated and discussed. It was found that unlike nickel systems, catalysts promoted by copper give a higher H_2/CO ratio, which is determined by the composition of the support (Fig.1). The highest H_2 yield (78%) observed at 1Cu-9Ni/5ACZ catalyst.

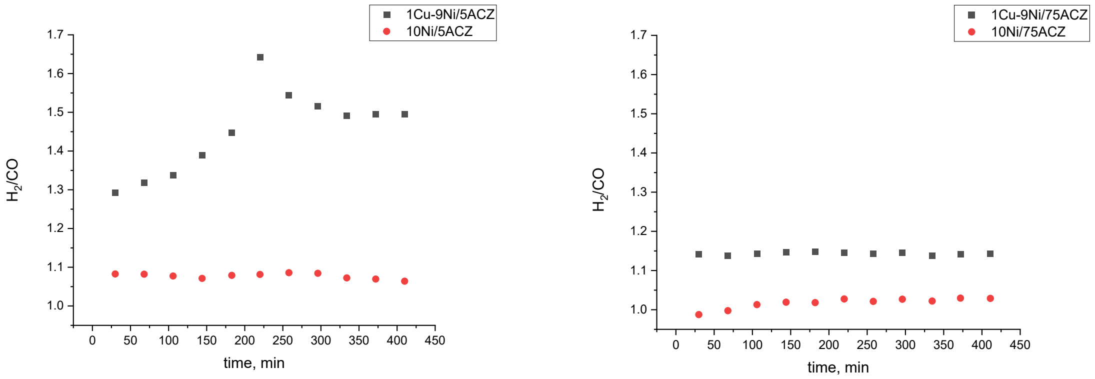

Fig.1. H2/CO molar ratio in EDR stability tests with the Ni−Cu catalysts

Acknowledgement: This work was supported by the Russian Science Foundation, project 23-29-00369.

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OPs-17

The Doping of Higher Tungsten Boride with Transition Metals for Catalytical Application

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Currently, the cost of many products is notably high due to the widespread use of catalysts made primarily of noble and rare earth metals for organic synthesis. Additionally, over 80% of the catalysts used in the domestic oil and chemical industries are imported, which can pose challenges in the current political climate.

Transition metal borides [1], [2] have been proposed as a cost-effective alternative to expensive catalysts. Tungsten borides have been investigated as potential catalysts for the hydrogen evolution reaction (HER) and the conversion of CO_2 to CH_4. They have also been suggested for use as catalysts in organic synthesis.

In our previous work, we demonstrated the effectiveness of higher tungsten boride (WB_{5-x}) in CO oxidation and photocatalytic CO_2 reduction reactions (both publications are in production). However, both reactions face energy barriers that must be overcome. One way to increase the catalyst's effectiveness is through doping with more active elements.

Due to the complicated structure of WB_{5-x}, molybdenum atoms with a radius similar to that of tungsten were proposed for doping. The material was then doped with Cr atoms, and Rh atoms were used to obtain reference data, as Rh is known for its catalytic activity.

Density functional theory (DFT) as implemented in the VASP package was used for all calculations. To avoid artificial interactions between periodic images of the slabs, a vacuum region of 25 Å perpendicular to each surface was employed. The doping atom replaced one tungsten atom from the surface layer of the (010) stable surface. At the starting point of relaxation CO, CO_2, NO, and O_2 molecules were placed 1.8 Å above the surface.

Based on the data obtained, the higher tungsten boride's ability to dissociate the O_2 molecule remains unchanged with doping, making it applicable for various oxidation reactions. Additionally, the adsorption energies of CO and NO molecules increase compared to those on pure WB_{5-x}. However, the most significant finding is that the doped samples show a reduction in the dissociation of CO_2 molecules, which was observed in pure WB_{5-x}.

Changes in electronic density and surface charges can determine the causes of unpredictable changes in adsorption energies and related energy barriers. Doped WB_{5-x} could be an alternative catalyst material for automotive motors due to its low adsorption energies of NO and CO molecules and relatively high adsorption energy of CO_2 molecule. As demonstrated in our previous study, WB_{5-x} is highly resistant to sulfur impurities in petrol, unlike traditional catalysts based on noble metals [3]. Additionally, WB_{5-x} surface facilitates the dissociation of the O_2 molecule without any energy barrier, making it a potential candidate for environmentally and industrially important reactions, such as ethylene epoxidation and hydrocarbon oxidation [4], [5].

Acknowledgement: This work was supported by the Russian Science Foundation, grant 24-23-00125.

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OPs-18

Insights into the Formation of the Flavin-N5-Oxide Reactive Species in Monooxygenase EncM from Molecular Modelling

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Flavin-dependent monooxygenase EncM catalyzes oxidation of a linear (R)-C7,O4-dihydrooctaketide in biochemical synthesis of antibiotic enterocin [1]. Employing a FAD cofactor, EncM forms a species by interacting with molecular oxygen which are capable of inserting an oxygen atom at a specific position in the poliketide substrate. The insertion launches a Favorskii-type rearrangement and subsequent cyclization reactions yielding the polycyclic structure of enterocin. It has been demonstrated experimentally that EncM reacts with dioxygen to form previously unknown oxygenating species flavin-N5-oxide [2]. The occurrence of the flavin-N5-oxide, which substantially broadens the established chemistry of the flavin cofactors, has been reported for other enzymes, e.g. sulfone monooxygenase DszA and monooxygenase RutA [3].

The molecular mechanism of the N5-oxide formation remains obscure mostly because the preceding intermediates cannot be detected in the stopped-flow experiments [4]. However, it has been suggested that the reaction is initiated by a hydrogen atom transfer from the reduced flavin to molecular oxygen leading to a biradical intermediate. The biradical recombination results in an unstable N5-OOH peroxo species that is further stabilized by elimination of a water molecule upon proton transfer from the protein. The proposed reaction steps are supported by the analysis of the O_2-containing active site structure of EncM and small-model quantum-chemistry calculations.

Here we investigated the mechanism of N5-oxide formation in EncM monooxygenase by means of molecular modelling including the classical force-field molecular dynamics, hybrid QM/MM dynamics, and quantum chemistry calculations. The formation of the oxygenating species was considered for two distinct positions of O_2 with respect to the isoalloxazine system of FAD. These two positions, as evidenced by our molecular dynamics simulations, drastically differ in the access of water molecules controlled by the protein structure and dynamics. The computed energies reveal crucial role of water molecules and protein side chains in stabilizing the biradical and peroxo intermediates. The derived reaction pathways of EncM are compared with those for RutA [5] and model system lumiflavin-O_2. The obtained results elucidate molecular mechanisms responsible for versatile oxygenation reactions catalyzed by the flavin-dependent enzymes.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 22-13-00012.

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OPs-19

Model Reactions for Plasmon Catalysis: From p-Nitrothiophenol Azocoupling to Nitroxide Homolysis

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Plasmon-active substrates are the perspective catalytic systems, that able to overcome the heterogeneous catalysis limitation, such as high temperature, pressure and complicated design of catalytic systems. However, investigation of plasmon catalysis mechanism is still challenging, one of the reasons is the absence of reliable model reactions. Model system should be simple, well-known to exclude side processes and assessment of kinetic rates of reaction will be quantitative and simple. Equally important requirement for system is multidimensional parameter space, that will allow to vary only one parameter at the time, such as excitation wavelength, power, plasmon-active substrate properties (size, shape, nature) and etc. Commonly used model reaction to study plasmon catalysis mechanism is p-nitrothiophenol (PNTP) azocoupling (Fig.1A). However, thiols chemosorbed with plasmon-active substrate surface (Au or Ag) forming Au-S bond that can destructed under aggressive conditions [1]. Thus, azocoupling of PNTP under laser excitation can provide side processes, such as desorption or replacement with other molecules, that will be affect on kinetic study of plasmon catalysis mechanism.

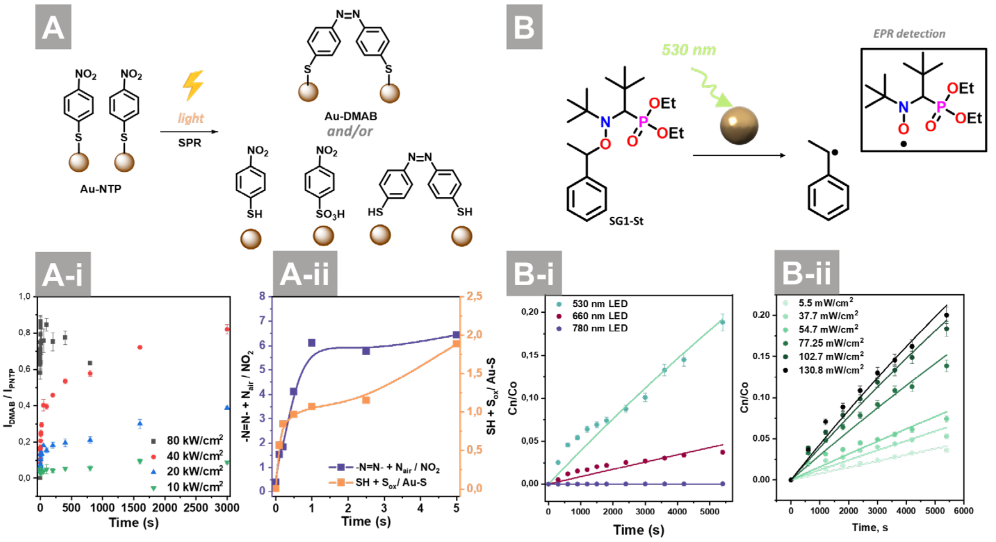

Fig. 1. Comparison of model system for plasmon catalysis mechanism study: A) Azocoupling of 4-nitrothiophenol: i - kinetic study by Raman spectroscopy at different power density, ii -kinetic study of azocoupling and side processes by XPS; B) Homolysis of alkoxyamine SG$_1$-St: I - kinetic investigation under different wavelength, ii – kinetic investigation under different power density.

However, this fact is often not considered, therefore we investigated design of appropriative model system to plasmon catalysis mechanism study through side processes detection of PNTP azocoupling by chemical state changes of surface by X-Ray photoelectron spectroscopy. Plasmon-active substrate was prepared through AuNPs modification by PNTP and its drop-casting on Si. Azocoupling was carried out under laser irradiation of Au-NTP surfaces with wavelength 633 nm. Product 4,4’-dimercaptoazobenzene (DMAB) formation after irradiation was confirmed by Raman spectroscopy (SERS) and XPS. Appearance of -N=N- signals at 1390, 1430 cm^{-1} on Raman spectra and at 399 eV on high-resolution XPS confirmed DMAB formation. Au-S bond stability after laser irradiation was controlled by chemical state of sulphur detection by high-resolution XPS in S2p region. According to obtained spectra oxidation (R-SO_4 at 169 eV) and desorption (R-SH at 164 eV) processes are observed in the same time as dimerization (Au-S at 162 eV and N=N at 400 eV). Kinetic curves obtained by SERS (Fig.1A-i) and XPS (Fig.1A-ii) revealed the complex character of reaction. First of all, the reaction has order distinguished from the first. Second, the reaction went through side processes including thiols desorption and oxidation.

In comparison with azocoupling, homolysis of alkoxyamine (Fig. 1B) is a first order and one-component reaction, that can be used for investigation plasmon-induced reaction mechanism by detecting concentration of formed nitroxide through electron paramagnetic resonance (EPR) spectroscopy [2]. Changing of nitroxide concentration over time allow to create kinetic curves and use exponential fitting of first order. In order to show potential of nitroxide homolysis as a model reaction, SG1-St homolysis driven by plasmon excitation of AuNPs was performed under different excitation wavelength (530 nm, 660 nm, 780 nm) and power density of LED with 530 nm wavelength. Due first order of reaction, kinetic curves were fitted exponentially and reaction rate was determined simple. Obtained kinetic curves of homolysis allows to evaluate influence of various parameters on plasmon-induced reaction rates due simple first-order fitting. Dependent of reaction rate from wavelength was performed, where obviously 530 nm wavelength is effective (Fig.B-i). Also power density influence on reaction rate was carried out (Fig.B-ii). This model makes it possible to simply evaluate the influence of the irradiation wavelength on the course of the plasmon-induced reaction. It should be noted that in this system one parameter can be changed, thereby the kinetic dependence of the reaction on changes in power during irradiation with a 530 nm LED was assessed.

Hereby, obtained results show that previously reported data about plasmon catalysis mechanism based on azocoupling investigation should be revised. The homolysis of alkoxyamines can become new promising model reaction to study plasmon catalysis mechanism due its well-known reactivity and simplicity of kinetic investigation

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-73-00117.

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OPs-20

Amine Catalysed Dehydrocoupling of Phenylsilanes and Alcohols in Solvent-Free Environment

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With the growing demand for diminishing the usage of fossil fuels and transition to utilizing eco-sustainable green energy the issue of chemical storage of hydrogen becomes topical. Dehydrocoupling of silanes and alcohols allows for production of not only molecular hydrogen but also alkoxysilanes, which could be used for polymer and fine organic synthesis [1-3]. Dehydrocoupling of phenylsilanes and hexafluoroisopropanol in the presence of basic catalyst (Et_3N) has been studied in low polar solvents [4-5], however such reactions in solvent-free systems are also of great interest.

In this work we present kinetic studies of the solvent-free dehydrocoupling of silanes (Ph_2SiH_2, $PhSiH_3$, $PhMeSiH_2$) and various alcohols (MeOH, CF_3CH_2OH (TFE), $(CF_3)_2CHOH$ (HFIP), etc.) in the presence of Et_3N. Based on the data obtained two different reaction mechanisms for alcohols of different acidity have been proposed (Fig. 1). More acidic alcohols can be deprotonated by Et_3N forming the real catalyst – alkoxide-anion (Fig. 1, left). However, less acidic alcohols are not able to be deprotonated by amine and form a trimolecular noncovalent complex with Et_3N and silane instead (Fig. 1, right).

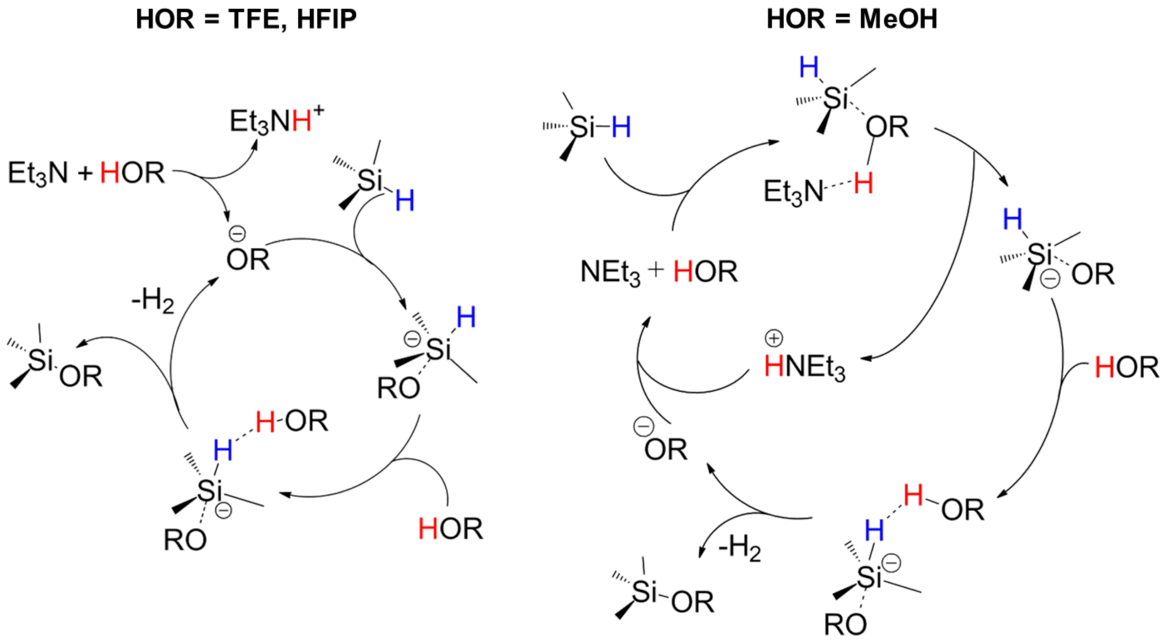

Fig. 1. Proposed mechanisms of solvent-free dehydrocoupling of silanes and more acidic (left) or less acidic (right) alcohols in the presence of Et_3N

The nitrogen atom of the PNP-pincer ligand in group 10 metal complexes (PNP)MX (PNP = bis(2-(diisopropylphosphaneyl)-4-methylphenyl)amine; M = Ni, Pd; X = Cl, H) (Fig. 2) readily accepts proton from alcohols and other Brønsted acids [6]. Thus, we tested these complexes as catalysts for dehydrocoupling of silanes and alcohols studying the reaction kinetics and mechanism. Preliminary data suggest these complexes operate rather as strong nitrogen bases than through Si-H activation by transition metals.

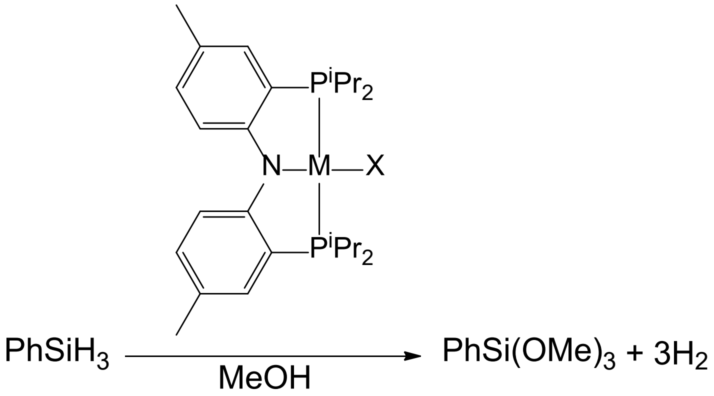

Fig. 2. Dehydrocoupling of phenylsilane and methanol catalyzed by pincer group 10 metal complexes

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation.

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POSTER PRESENTATIONS

PP-01 ÷ PP-38

PP-01

Porous Aromatic Polymers – Supports for Pd Nanoparticles: Factors Influencing Catalytic Activity and Stability in Cross-Coupling Reactions

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Last decades, the interest towards the development of porous organic polymers for immobilization of metal complexes and nanoparticles (NPs) has been continuously growing. Porous aromatic polymers (PAPs) possess high chemical and thermal stability, large specific surface area, and the ability to control the nature and concentration of functional groups [1]. Amorphous PAPs are simple in preparation, have low cost and the possibility of using readily available cheap monomers as starting materials. Tan et al. [2] developed a method for producing PAPs via the Friedel-Crafts reaction using methylal as a cross-linking agent [2]. Besides, there are methods for producing PAPs by the Scholl reaction and the solvent cross-linking [3]. It is noteworthy that naphthalene was shown to allow higher polymer yields as compared to some other monomers such as benzene, toluene, xylene [4].

In the framework of this study, a one-step synthesis of amorphous PAPs was carried out using methylal as a cross-linking agent and anhydrous $FeCl_3$ or $AlCl_3$ as polymerization catalysts. The influence of solvent nature, the type of monomers (monocyclic, polycyclic condensed, monomers containing heteroatoms) and their ratios, the nature and concentration of the catalyst and the concentration of the cross-linking agent were studied, which allowed controlling the polymers porosity. Moreover, functional groups were introduced into the polymers by sulfonation or nitration.

Synthesized polymers were used as supports for palladium catalysts (1 wt.% of Pd) of cross-coupling reactions (Suzuki, Sonogashira and Heck). It was shown that the use of Pd-containing polymeric catalysts allows achieving the conversion of aryl halides close to 100% under mild conditions without the necessity to add co-catalysts and amines (in the case of Sonogashira cross-coupling) to the reaction mixture. Moreover, it was found that the amount of cross-linking agent, as well as the presence of functional groups in the polymer composition, can affect the mean diameter of Pd NPs formed during the preliminarily reduction or during the catalytic process. The catalyst stability was also influenced by the sizes of Pd NPs and the relative hydrophobicity of the polymers.

It should be emphasized that in the case of so-called ligand-free catalysts the cross-coupling reactions are complicated by various processes such as aggregation, dissociation, and leaching of Pd. The features of the catalytic cycle of cross-coupling reactions lead to continuous mutual conversion of various forms of palladium: Pd(II) compounds, clusters, and Pd(0) nanoparticles (NPs) [5, 6].

Recently, we have proposed that the use of the starting palladium in the form of Pd(0) or Pd(II) should not affect the reaction's kinetic laws for both catalysts, but the catalysts based on Pd(II) are extremely active in the initial period of the reaction. Then the "hot form" of the catalyst is rapidly converted into the form of Pd(0), whose activity is identical to that of the preliminarily reduced catalyst [7]. However, there are still a lot of questions regarding to the dependence of observed catalytic behavior of Pd NPs sizes.

In the presented work, we found that, in some cases, too small Pd NPs allows relatively higher stability, but the low activity in cross-coupling reactions; hence the dependence of catalytic activity of the NPs sizes goes through a maximum. Therefore, we considered a series of experiments with competitive substrates (the method developed by Schmidt et al. [8, 9]) using as-synthesized (unreduced) as well as preliminarily reduced catalysts samples possessing promising activity and selectivity in chosen reactions in order to find, if the observed dependences can be due to the input of homogeneous forms.

Thus, from the one hand, it is very important to ensure the interaction of the active phase and the support, in order to preserve the activity and selectivity of the catalyst during repeated use. From the other hand, too efficient Pd-support interaction can result in low activity, which is likely determined by homogeneous Pd species.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-29-00604.

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PP-02

Cu-Containing OMS-2-Based Catalysts for Low-Temperature CO Oxidation

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In recent years, a topical problem of pollution of the environment, in particular atmospheric air, has become a consequence of the rapid development of industry. Today, air is one of the sources of toxicants such as volatile organic compounds (VOCs), CO, NO_x, soot particles, etc. Promising catalysts low-temperature oxidation of CO are systems based on MnO_2 with the OMS-2 structure [1]. The CuO_x addition to MnO_2 with a cryptomelane structure is known to increase the catalyst activity in total oxidation of benzene, toluene, diethyl ether, etc. [2]. The OMS-2 modification with Ce atoms is considered a promising approach due to the redox shift between the Ce(III) and Ce(IV) [4]. However, the systems containing Cu^{n+}/CuO_x clusters in the structure of Ce-modified OMS-2 and/or on the surface was not studied in details. These catalysts are of interest due to their enhanced activity and stability in low-temperature CO oxidation in the presence of H_2O.

The purpose of this work is to study the influence of the preparation conditions of the supported CuO_x catalysts based on the OMS-2 with and without the introduction of a Ce modifier on their activity and stability in the low-temperature CO oxidation, including in the presence of water vapor.

The OMS-2 supports were synthesized by the hydrothermal method. A $KMnO_4$ solution was added dropwise to an acidified $Mn(NO_3)_2$ solution under vigorous stirring. Then, the resulting suspension was subjected to a hydrothermal treatment at 120 °C for 24 h. The Ce (or Fe) component was introduced directly at the stage of mixing the solutions of manganese salts by adding of cerium or iron nitrates as precursors. After the hydrothermal treatment, the sediment was washed with distilled water, dried at 120 °C, and calcined at 450 °C. The Cu-containing catalysts were prepared by wet impregnation of OMS-2 supports without and with addition of Ce or Fe (molar Mn/Me ratio was 20/1). Theoretical amount of Cu was 4 wt% for all samples prepared. After drying, samples were calcined at 300 or 450 °C.

The physical-chemical properties of the obtained catalysts were studied by XRF, XRD, Raman spectroscopy, XPS, low-temperature nitrogen adsorption/desorption, SEM and TEM HR as well as TPR-H_2 and TPR-CO.

The catalytic properties were tested in the CO oxidation reaction using the catalytic unit (Katakon LLC, Russia) with a flow U-shaped reactor. The reaction mixture was an oxygen-depleted mixture of the following composition: 1 vol.% CO, 8 vol.% O_2 in He. A model mixture simulating real exhaust conditions and containing 1 vol.% CO, 21 vol.% O_2, and 10 vol.% H_2O in He was used as the initial reaction mixture to study the stability of the resulting catalysts. GHSV was 90,000 h^{-1}.

According to the XRD results, the Ce introduction at the co-precipitation stage partially destroys the tunnel OMS-2 structure. The Ce^{n+} cations are able to integrate into the OMS-2 tunnels replacing K^+ or H_3O^+ ions in them, thereby disrupting the charge ratio and destroying the tunnel structure with the formation of the tetragonal α-MnO_2 phase contrary to the one in the tunnel.

The destruction of the tunnel structure is also confirmed using Raman spectroscopy, where the intensities of the characteristic peaks of OMS-2 are noticeably reduced. The TPR-H_2 profile changes with the appearance of a new high-temperature signal.

The Cu introduction to Ce-OMS-2 by an incipient wetness impregnation makes it possible to partially restore the cryptomelane structure due to the ability of copper cations to enter into the cryptomelane structure in positions inaccessible to the Ce^{n+} ions. This is confirmed by Raman spectroscopy, where the characteristic peak of OMS-2 at 184 cm^{-1} reappears. The high-temperature signal at TPR-H_2 disappears, and the entire TPR profile is shifted towards the low-temperature region.

The Cu/Ce-OMS-2 sample features the highest catalytic activity in comparison with the Cu/OMS-2. In this case, a sample calcined at 300 °C shows greater activity than the one calcined at 450 °C. The Cu/OMS-2 sample shows similar activity in the light-off mode; however, under the stability tests in CO oxidation in the presence of water vapor, it is less active.

High activities of Cu/OMS-2 and Cu/Ce-OMS-2 are determined by the distribution of dispersed copper on the surface of these catalysts, which is confirmed by HRTEM. Moreover, the stability of the catalysts is determined by the presence of copper hydroxo-/hydroxocarbonate compounds, such as $Cu_2(OH)_2CO_3$ and $Cu(OH)_2$, on the surface. The content of such compounds is higher in the Ce-containing catalysts due to a more developed specific surface area. Thus, not only does the OMS-2 modification with cerium before the Cu introduction allow increasing the catalytic activity of the Cu/Ce-OMS-2 in comparison with the unmodified Cu/OMS-2, but also increasing the stability of the resulting catalyst during the oxidation in the presence of water vapor. The influence of both copper content and precursor will be discussed.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 19-73-30026.

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PP-03

Microfluidic Synthesis of Vinyl Iodide

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In catalysis, scientists aim to improve the performance of catalysts and increase the yield of desired products. Traditionally, they have focused on modifying the catalysts themselves. However, optimizing the reaction conditions can have an equally significant impact. Finding the optimal reaction conditions to maximize product yield is a complex task due to the multitude of factors that influence the process. This work presents a universal method to determine the conditions at which the yield of a given catalyst–product pair is maximal. In past recent years, microfluidic synthesis based on manipulates a small amount of fluids using small channels with sizes ten to hundreds micrometres have attracted a lot of attention and even largely formed new approaches to chemical engineering.[1] Microfluidic synthesis, which involves manipulating small volumes of fluids in microchannels, offers several advantages, including the ability to dynamically change reaction conditions.

In this work, we performed optimization for synthesis of vinyl iodide taking place on the surface of commercial Pt nanocatalysts (K_2PtCl_6, Sigma Aldrich) in presence of NaJ and the addition of acetylene using the microfluidic system. First, we carried out several classic experiments in a flask (80 °C) analyzing reaction products by mass-spectroscopy. Then, we have moved on to microfluidic synthesis to compare the effectiveness of this approach with the classical method. Finally, we optimized gas and liquid flows for more effective processes of catalytic reaction. Because of the unique chemical and physical features that occur in micron-sized fluids, this allows several advantages over traditional "macro" technologies. In addition, microfluidics devices are generally easy to use and produce, as well as cost-effective.

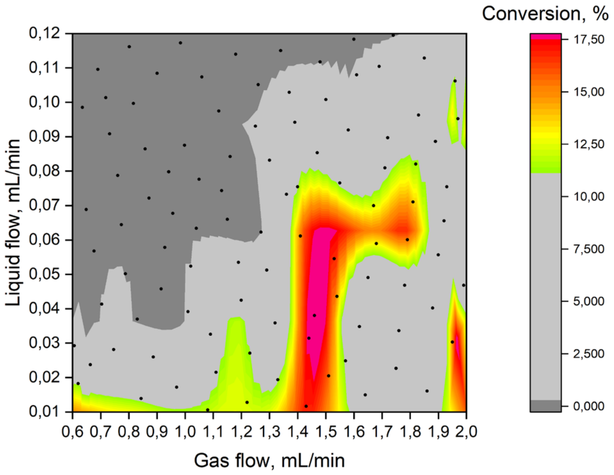

Fig. 1. Map of reaction conversion distribution. The ratios shown in gray are worse than the classical method

As a result, we obtained improved solution for more effective way to synthesize vinyl iodide. Application of microfluidics approach demonstrated their supremacy over the classic synthesis.

This methodology opens a perspective for the optimization of relevant catalytic reactions using microfluidics by rational use of reactants and varying conditions. The demonstrated approach can be expanded for optimization of many other industrially relevant reactions and catalytic systems.

Acknowledgement: The research was supported by the Strategic Academic Leadership Program of the Southern Federal University ("Priority 2030").

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PP-04

Kinetic Coupling of Stationary Methane Dry Reforming and Self-Oscillatory Methane Oxidation over Ni

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The reaction of methane dry reforming (MDR) is considered promising from the point of view of producing hydrogen and synthesis gas, as well as CO_2 utilization. It is known that metallic nickel is a good catalyst for this reaction, however, its catalytic activity in MDR is inhibited due to carbon deposition and blocking of the active surface. It was found that the combined carrying out of a stationary MDR reaction and a self-oscillatory methane oxidation reaction leads to the kinetic coupling of these processes. As a result of this coupling, the MDR reaction also begins to proceed in a self-oscillatory mode and in two different phases of oscillations, reducing and oxidizing conditions periodically exist. As a result, in the oscillation phase with reducing conditions, nickel is in an active metallic state and intensively catalyzes the MDR reaction, but gradually loses activity due to carbon deposition. In the subsequent phase of oscillation with oxidizing conditions, the nickel surface is oxidized and loses its catalytic activity, but at the same time the accumulated carbon is oxidized and the catalyst is regenerated. Under certain conditions, the average catalytic activity of nickel during the oscillation period may significantly exceed the activity of the same nickel sample in the absence of coupling with a self-oscillatory reaction (Fig.1) [1].

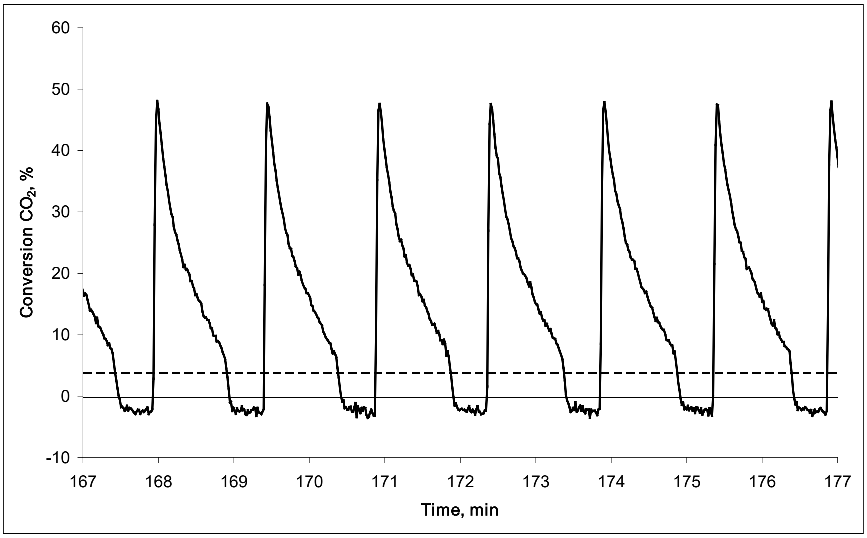

Fig. 1. Conversion of CO2 over time during the interaction of a mixture of CH4-CO2-3.5%O2 with Ni foil at 650 °C, as well as the value of CO2 conversion for a stationary reaction of MDR (dotted line)

Acknowledgement: This work was supported by the Russian Science Foundation, grant 24-23-00030.

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PP-05

Catalytic Systems Based on Metallocenes and Isobutylaluminum Aryloxides for Synthesis of Ethylene-Propylene Copolymers with Different Composition and Properties

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Ethylene-propylene copolymers are widely used in various industries such as automotive, rubber, cable, construction materials, and impact-resistant plastics. The synthesis of these copolymers is facilitated by modern and efficient catalysts such as metallocene and post-metallocene complexes [1]. To activate organometallic catalysts in polymerization processes, methylalumoxane (MAO) is commonly used as an activator. However, MAO is expensive, unstable during long-term storage, and used in large molar excess with respect to the organometallic complex ($Al/M=10^3$-10^4). Therefore, the development of new efficient activators capable of replacing MAO and catalytic systems based on them is an important task.

New effective activators of metallocene catalysts, isobutylaluminum aryloxides, have been developed [2,3]. The studies investigated catalytic behavior of metallocene systems with new activators in ethylene and propylene polymerization. The systems offer high activity in polymerization processes, comparable to MAO-activated catalysts. Isobutylaluminum aryloxide activators, which are easily synthesized, inexpensive, stable in storage, and can be applied at low molar excesses to metallocene ($Al/M \sim 10^2$). The task was to investigate catalytic systems with aryloxy isobutylaluminum activators in the synthesis of ethylene-propylene copolymers and to determine the relationship between the composition and structure of the system components, characteristics, and properties of the polymer products.

The copolymerization activity of a number of metallocene/(2,6-^{t}Bu$_2$PhO-)Al^{i}Bu$_2$ catalytic systems was evaluated. The structures of the metallocenes and activator are presented in the Figure. The zirconocene systems exhibited the highest activity in copolymerization [4]. The resulting E/P copolymers were semi-crystalline, with crystallinity no more than 39%. Copolymers with improved co-monomer incorporation, high molecular weight (Mw = 500,000), low degree of crystallinity ($\chi < 12\%$), and low melting points were synthesized using the rac-EtInd$_2$HfMe$_2$ catalyst. Mechanical tests of the polymer samples revealed that the E/P copolymer obtained on *rac*-Me$_2$Si(2-Me-Ind)$_2$ZrMe$_2$ exhibited the highest tensile strength and the values of elongation at break. The samples obtained on *rac*-EtInd$_2$HfMe$_2$ showed the best relaxation properties.

The correlation between the structure of the activator, the activity of the catalytic system in copolymerization processes, the composition, the molecular weight, the thermophysical and mechanical properties of the copolymers has been demonstrated for a number of catalytic systems *rac*-EtInd$_2$ZrMe$_2$/isobutylaluminum aryloxide (structures of aryloxydisobutylaluminum activators and zirconocenes are shown in the figure) [5]. Increasing the size of the substituent in the para-position of the aryloxy group and the number of aryloxy groups in isobutylaluminum aryloxides results in a decrease in the activity of catalytic systems, a decrease in the content of propylene units, and an increase in molecular weight of copolymers. It leads to an increase in tensile strength, tensile strain, and relative residual strain (EL) of the copolymer. It was revealed that the E/P copolymers synthesized contain phenolic residues of isobutylaluminum aryloxides as a residue of hydrolysed activators during reaction quenching. Phenolic residues determines increased thermo-oxidative stability of the copolymers.

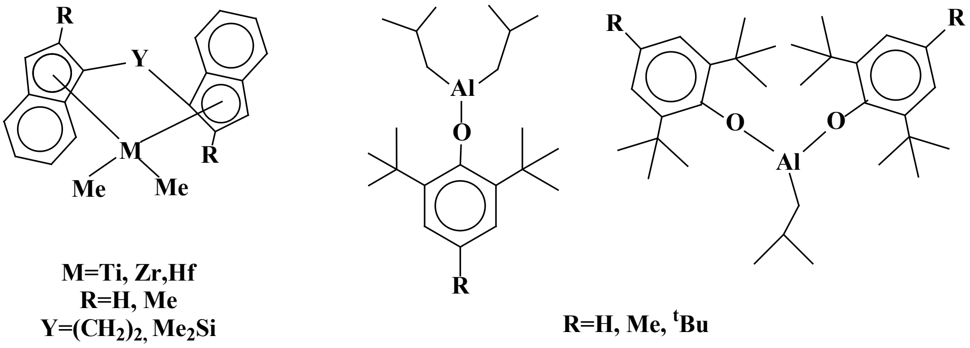

Figure - Structures of metallocenes (left) and aryloxyde-isobutylaluminum activators (right)

Thus, the structure of metallocenes and isobutylaluminum aryloxides is shown to have an important influence on the properties of the formed catalysts, the composition, structure and molecular weight of the polymer, and thus on the physical and mechanical properties of the polymer samples.

The results suggest that the new catalytic systems are efficient in synthesizing ethylene-propylene copolymers with a wide range of properties.

Acknowledgement: This work was supported by Ministry of Science and Higher Education of the Russian Federation, State task, No. registration № FFSG-2024-0007.

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PP-06

Quantum Chemistry Kinetic Analysis for Cracking Reactions of Normal and Iso Hexane Based on Transition State Energetic Evaluation for Production of n-C_4 and i-C_4 in FCC Process

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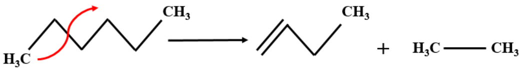
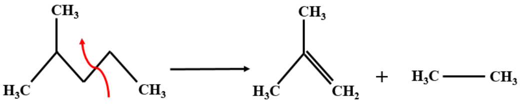
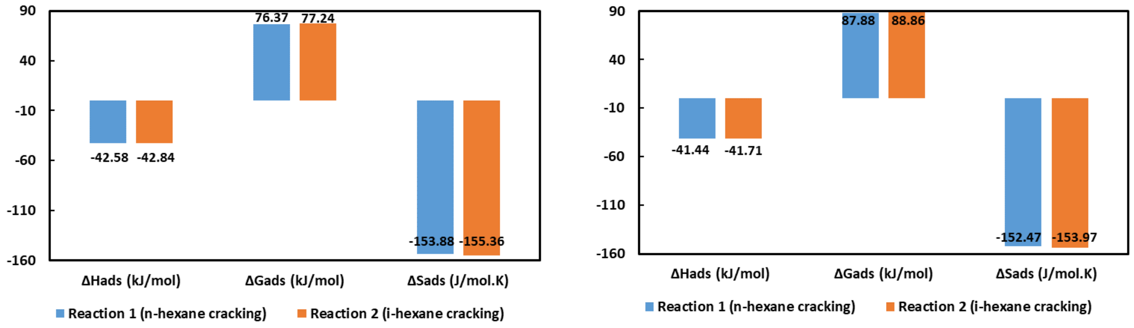
Light olefins including ethylene, propylene and butylene are key raw components in chemical and petrochemical industries. Among those, butylene has a wide spectrum of industrial applications. It functions as valuable fuel additive for enhancing gasoline octane number with improving combustion properties while reducing engine knocking. This automotive utilization attracts 44% of butylene end-use applications in 2022. Global economic market for production of butylene is projected to grow from 490 thousand tones in 2022 with growth rate of 3.12% CAGR to the horizon of 2035 [1]. In Russian Federation, 69% of oil and gas industry processing was dedicated to deep processing technologies and 12% to oil residues processing in 2022. Over 69% of butylene production is based on fluid/deep catalytic cracking process [2]. Therefore, it is our indispensable actual task to switch the mode of FCC process for production of butylene through operation optimization and configuration reconstruction.

The first step of our project was dedicated to thermodynamic study of catalytic cracking process with the aim of light olefins productions and results were presented in previous publications [3-4]. At this stage, we are about to work on kinetic pathway patterns of protolytic cracking reactions on Brønsted active site of zeolite-type catalyst based on quantum chemical modeling. In this work, two catalytic cracking reactions of normal hexane and iso-hexane (2-methyl pentane) were studied. Table 1 shows the target reactions. Normal butylene and iso-butylene (methyl propene) are produced via reaction 1 and 2, respectively.

Table 1. List of reactions

Reaction 1		n-C_6H_{14} → C_4H_8 + C_2H_6
Reaction 2		i-C_6H_{14} → i-C_4H_8 + C_2H_6

The steps of this work are: 1) calculation of adsorption parameters such as enthalpy, entropy and Gibbs energy; 2) calculation of transition state parameters, such as enthalpy, entropy and Gibbs energy; 3) calculation of activation energy reaction rate constants. For quantum mathematical calculations, method DFT combined with ωB97XD basis and 3.21G basis were applied. Figure 1 shows the result of adsorption thermochemical parameters such as enthalpy, Gibbs energy and entropy at 773 and 848 K. Results are quite precise with literature date. Thermochemical parameters for adsorption and transition state were done based on equations: $\Delta X_{ads.} = X_{complex} - (X_{cat.} + X_{reactant})$ and $\Delta X_{meas} = X_{transition\ state} - (X_{cat.} + X_{reactant})$ where *X* refers to enthalpy, entropy and Gibbs energy.



a) b)

Figure 1. Calculated thermochemical parameters of adsorption of normal and iso hexane on active site of zeolite catalyst, a) 773 K, b) 848 K

Table two shows the significant results of activation energy and reaction rate constants at 773 and 848 K according to equations $E_a = \Delta H_{int} + RT$, $K(T) = \frac{K_B T}{h}$ where K_B is Boltzmann's constant, h is Planck's constant.

Table 2. Quantum mathematical calculated activation energy and reaction rate constants

Temperature, K	Reactions	Activation Energy, Ea, kJ/mol	Constant of reaction rate, k, 1/s
773	1	199.61	1.81707E-07
	2	239.68	8.22945E-09
848	1	202.26	9.24118E-06
	2	242.36	7.32826E-07

It was obtained that activation energy for iso-butylene production is 40 kJ/mol more than n-butylene production at all studied temperatures of this work. Reaction rate constant for n-butylene production is 22 and 12.6 times more than reaction rate constant of iso-butylene production at 773 and 848 K, respectively. As the temperature increases from 500 to 575°C, reaction rate constant of n-butylene and iso-butylene production increases by 50 and 89 times, respectively.

Acknowledgement: This work was supported by the Russian Science Foundation, grant No. 19-71-10015-P.

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PP-07

Interactions of Simple Oxides with Supercritical Isopropanol: Spectrum of Products and Kinetic Regularities

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Along with other substances in the supercritical (SC) state, isopropanol (iso-C_3H_7OH) is widely used as a medium and reagent in organic and inorganic chemistry [1]. In particular, SC isopropanol is used as a reaction medium and a reducing agent in the synthesis and modification of inorganic materials based on the transformations of simple and complex oxides and their precursors [2-4]. Much less attention is paid to the transformations of isopropanol itself during the mentioned processes, although this may result in the formation of products that affect the rate of formation of target inorganic materials, as well as their composition and properties.

In this work, the composition and kinetic features of the formation of solid, liquid and gaseous products of the interaction of several simple oxides (Al_2O_3, SiO_2, La_2O_3, CeO_2, PrO_2) with isopropanol are studied and an attempt is made to analyze the mechanism of the ongoing transformations.

The experiments were carried out in static mode at temperatures above the critical point of isopropanol (235.5°C) in a stainless steel autoclave under pressure of an inert gas (nitrogen). The composition of the liquid and gas phases after the experiment was determined by gas chromatography (GC) methods, including combined GC – mass-spectrometry. The phase composition of solid oxides before and after treatment in isopropanol was determined by X-ray powder diffraction.

It has been shown that in the presence of all the studied oxides, various processes of SC isopropanol conversion occur. The only products of its transformation found in the presence of all the studied oxides in different amounts are water and acetone. The amount and composition of other products in the presence of different oxides varies substantially. Thus, in the presence of aluminum oxide, a significant amount of diisopropyl ether is formed (its yield is about 5%), which is not observed even in trace amounts in the presence of other oxides. This may be due to the relatively high acidity of alumina, which promotes dehydration towards the formation of an ether or the addition of propylene (primary dehydration product) to the isopropanol O-H bond.

In addition, cyclobutane is found in liquid samples (also only on Al_2O_3, the yield is about tenths of a percent) and, in much smaller amount, polyunsaturated hydrocarbons and cyclic compounds (2,5-dimethyl-2,5-dihydrofuran – on La_2O_3, 3,3,5-trimethylcyclohexene – on Al_2O_3). The largest amount of such condensation and isomerization products is formed in the presence of Al_2O_3 and La_2O_3, which have pronounced acidic and basic properties, respectively.

The largest amount of gaseous products is observed in the presence of Al_2O_3 and La_2O_3. In the first case, a high concentration of propylene – over 10 vol. % – and hydrogen are observed. In the case of La_2O_3, large amounts of hydrogen are found in the absence of propylene. The data obtained indicate the high activity of La_2O_3 in the dehydrogenation of isopropanol and the bifunctional nature of the catalytic properties of alumina. The smallest amount of isopropanol conversion products is formed in the presence of SiO_2, apparently due to the lack of acid-base properties.

With the exception of SiO_2 and CeO_2, all the studied oxides hydrate to form hydroxides. In the case of praseodymium, PrO_2 is reduced to form $Pr(OH)_3$. It is interesting to note that the same product is formed when PrO_2 is treated even in water vapor at the same temperature [5]. In the case of SiO_2, in SC isopropanol a significant decrease in the specific surface area occurs. And CeO_2 does not undergo any changes (neither chemical/phase composition, nor specific surface area). The differences in the behavior of CeO_2 and PrO_2 are due to differences in the value of the 4th ionization potential (36.7 and 39.0 eV for Ce and Pr atoms, respectively).

It was concluded that hydration and structural changes in oxides occur under the influence of water, which in turn is a product of the isopropanol conversion.

The kinetic features of the formation of isopropanol transformation products were studied by varying the amounts of reactants loaded into the autoclave. These features and differences in the qualitative composition of organic products clearly indicate the catalytic nature of their formation.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-13-00360.

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PP-08

Application of Vermiculite-Based Catalysts for Solving Environmental Problems

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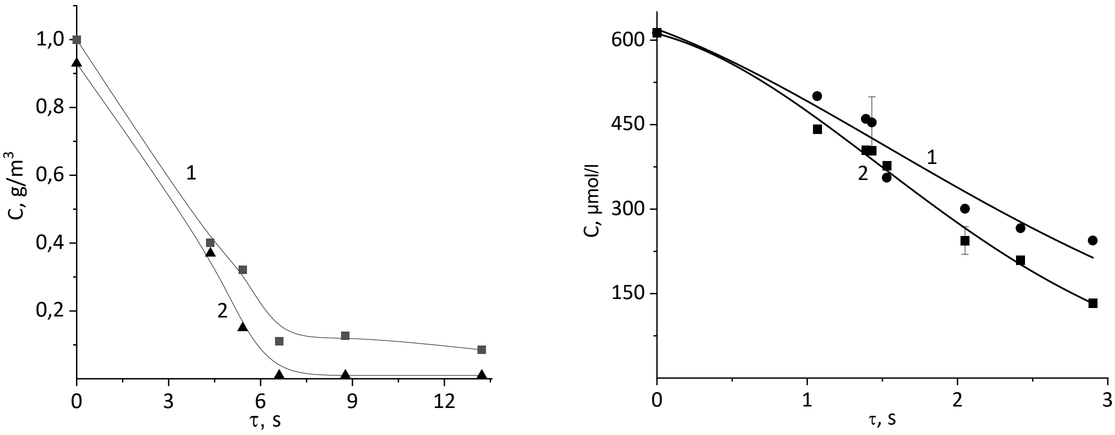
Environmental pollution with highly toxic compounds has become global and is damaging both natural ecosystems and public health. Traditional purification systems cannot cope with the requirements placed on them in terms of both environmental and economic parameters. Therefore, the development of improvement of existing and development of new approaches implemented in environmental protection systems is an urgent task.

One of the promising areas in water and air purification technologies is plasma-chemical methods, which are characterized by high cleaning efficiency and low relative energy costs, but have one significant drawback - low productivity [1, 2]. This problem can be solved by using plasma catalyst systems [3, 4].

The purpose of the work: to study the processes of destruction of organic compounds present in gas and aqueous media in plasma-chemical reactors that implement a dielectric barrier discharge with catalysts located inside.

A detailed description of the experimental laboratory setups was given in [3, 4]. Vermiculite impregnated with zirconium oxide was used as a catalyst. Vermiculite as a material for applying a catalyst is a very promising material due to its low cost (natural vermiculite is a fairly common and promising material), has a relatively high sorption capacity, developed surface properties and structural features in comparison with related materials of this group of hydrosilicates. Modification of vermiculite with zirconium dioxide (ZrO2) was carried out by the method of mechanochemical activation [5]. ZrO_2 is one of the promising photocatalysts due to its redox potential and higher chemical stability than traditional catalysts, for example, containing Mn, Zn, Ti. The object of the study was gas mixtures and aqueous solutions containing 2,4-dichlorophenol, which are highly toxic volatile organic compounds.

Experiments have shown (Fig. 1) that a dielectric barrier discharge makes it possible to effectively remove 2,4-DCP from vapor-gas mixtures and aqueous solutions.



a) *б)*

Fig. 1. Changes in the content of 2,4-DCP in vapor-gas mixtures (a) and aqueous solutions (b) in plasma (1) and plasma-catalytic (2) processes.

The results obtained (Fig. 1) made it possible to estimate the effective constants, rates and energy consumption for the decomposition of 2,4-DCP in DBD and the combined plasma-catalytic process (CPCP), which are presented in Table. 1.

Table 1

Rates, effective rate constants and energy efficiency of 2,4-DCP decomposition

2,4-DCP destruction process	Initial concentration, µmol/l	Effective rate constants, s^{-1}	Decomposition rate, molecules/(cm^3·s)	Energy efficiency, molecules/100 eV
Vapor-gas mixtures				
DBD	6,1	0,234	$4{,}4 \cdot 10^{14}$	0,03
CPCP	5,7	0,313	$5{,}5 \cdot 10^{14}$	0,04
Aqueous solutions				
DBD	62	0,22	$8{,}2 \cdot 10^{15}$	0,04
CPCP		0,51	$1{,}9 \cdot 10^{16}$	0,05

Thus, from the results presented in Table. 1 it follows that the rate of decomposition of 2,4-DCP in CPCP is less than 1.25 times higher than when processing model objects in DBD, and energy consumption is 20% lower.

Acknowledgement: This work was supported by the was carried out within the state assignment for the implementation of research work (Theme No. FZZW-2024-0004).

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PP-09

Adsorption and Catalytic Properties of Nanoparticles Fe_3O_4-Ag in Relation to Various Types of Organic Dyes

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The adsorption of organic dye molecules on the surface of various adsorbents and the dye degradation in the presence of catalysts are effective methods of water purification. The idea of using nanoscale materials for these purposes is justified by the colossal increase of the nanoparticles (NPs) surface area and, consequently, the number of centers of interaction with pollutants. The use of magnetic NPs enables their easy extraction from the environment using a magnetic field and allows for multiple reuses. Thus, a trend has emerged in a field of research into new methods of water purification using magnetic NPs. Excellent adsorption and catalytic properties of magnetite-silver NPs have already been pointed in several studies, such as, [1]. This is particularly important considering that the fact that the properties and performance characteristics of NPs are greatly dependent on synthesis conditions and the search for optimal synthesis conditions for specific applications is an urgent task.

In this study, comparative research of the adsorption and catalytic properties of Fe_3O_4-Ag NPs obtained by the solvothermal method in various modes (maintained in an autoclave at 200°C for 6 hours, sample 1, and 8 hours, sample 2) were carried out in relation to organic dyes: cationic Methylene blue (MB) and Rhodomin C (RhC) and anionic Congo red (CR) and Methyl orange (MO) .

The obtained values of the sorption capacity of the investigated NPs in an aqueous solution of dyes differ both between samples 1 and 2, and for dyes of different types. In figure 1(a) the adsorption isotherms of MB dye are shown. The higher adsorption capacity for sample 1 indicates a great number of adsorption sites for positive cations that formed on the surface of this sample during the synthesis. For sample 2, rapid initial growth leads to reaching the equilibrium adsorption value at the low amount of adsorbed dye, not dependent on the concentration of the dye in the solution. In both cases, the data are best described by the Langmuir adsorption equation [2], confirming the formation of a monomolecular layer of dye molecules on the surface of the NPs. It is evident that these NPs are most effectively used at low concentrations of pollutants. The adsorption capacity for anionic dyes is several times lower, with a saturation value of 2-4 mg/g, suggesting the predominance of electrostatic interactions of organic dyes with the surface of the investigated NPs. In such a case, it can also be assumed that the total surface area in sample 1 is significantly larger than in sample 2.

PP-09

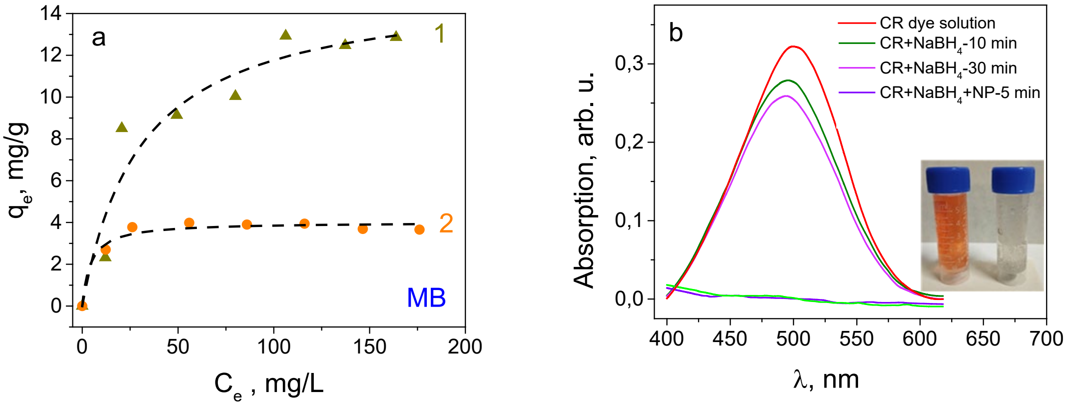

Fig. 1. a – adsorption isotherm for MB dye, dashed lines are the result of fitting the Langmuir equation, (curve numbers correspond to sample numbers). b - Optical absorption spectra of CR solution depending of mixture composition and interaction time for sample. Insert: solution of the initial dye solution and after the catalytic reaction

The catalytic activity of NP samples in the process of degradation of organic dyes was investigated in the presence of sodium borohydride $NaBH_4$. To determine the change in the reaction rate of degradation, the experiment was conducted both in the presence of NPs in solution and without NPs. Complete decolorization of the solutions of all used dyes in the simultaneous presence of NPs and $NaBH_4$ occurred in less than 5 min, while in the absence of NPs a noticeable color change in the solution occurs only in the case of Rh, but with significantly slower rate. The change in intensity of the characteristic absorption peak of the CR dye is shown in Fig. 1(b). In the case of CR and MO dyes, during the procedure, irreversible degradation of the dyes occurred; the dye molecules were destroyed along the N=N bond, on individual aromatic amines, as evidenced by the disappearance of the absorption band at 505 nm and the appearance of a weak band in the UV region, characteristic of aromatic amines. For MB and Rh, a different picture is observed. Under the influence of NPs and $NaBH_4$, the solutions also rapidly decolorize, but gradually, over approximately 30 min, the color is restored. This behavior can be associated with the transition of MB and Rh molecules into leuco forms (colorless and less toxic). Thus, the leuco form of the MB dye has a characteristic absorption band at a wavelength of 257 nm, and such a band appears during decolorization. Therefore, additional measures are necessary for the stable decolorization of MB and Rh solutions. No noticeable differences in catalytic properties were detected between the two samples.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-22-10025, https://rscf.ru/project/23-22-10025/ and by the Krasnoyarsk Regional Science Foundation.

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PP-10

New Approaches to the Synthesis of Complex Oxide Catalysts MO_2-SiO_2 Modified with Copper or Manganese for the Preferential Oxidation of Carbon Monoxide in Excess Hydrogen

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Ceria-based materials has attracted much interest as an alternative oxidation catalysts owing to in oxidation processes due to its unique redox properties, relatively high thermal stability and low cost. Recent researches are focused on the development of ceria-based systems for preferential CO oxidation (PROX-CO) required for effective CO removal from H_2-rich streams below the 10−100 ppm of CO-tolerance level accepted for proton exchange membrane fuel cells [1]. The catalytic performance of such oxide systems can be tuned using additives improving textural and structural properties of such materials [2 – 4], and by addition of a second active component. In our work we used silica as a texture stabilizer and CuO_x or MnO_x as a second active component to investigate the effect of the addition and the nature of the modifiers on the catalytic efficiency in PROX-CO.

CeO_2-SiO_2 oxide (Ce:Si = 4:1) was prepared by template method using cetriltrimethylammonium bromide (CTAB) and tetraethoxysilane (TEOS) and calcined at 500°C for 4 h. Cu or Mn (nominal metal loading was 5 wt.%) were supported by impregnation method using metal nitrates as precursors. The prepared systems were designated further as Cu/CeSi and Mn/CeSi. Catalytic tests in PROX-CO were performed on ULCat-1 catalytic unit (“UNISIT”, Russia) equipped with fixed-bed continuous-flow stainless steel reactor in the temperature range from 50 to 450°C using 150 mg of catalyst and the reaction mixture comprising 4 vol.% CO, 3 vol.% O_2, 13 vol.% N_2 and 80 vol.% H_2, at 95 ml/min. The reaction products and unconverted reagents were analyzed by GC Chromatec-Crystal 5000.2.

The catalytic results are presented in fig.1 (a and b). It is seen that both Cu/CeSi and Mn/CeSi systems are active in CO oxidation in the presence of hydrogen. However, in spite of the same metal content, CO and O_2 conversion, as well as CO_2 selectivity over Cu/CeSi were significantly higher than for Mn/CeSi in whole studied temperature range. The highest CO conversion value (77%) at sufficiently high selectivity of CO_2 (60%) was achieved on Cu/CeSi at as low temperature as 200°C. Several reasons of such behavior can be explained by using TPR-H_2 data, as shown in fig.1 (c).

PP-10

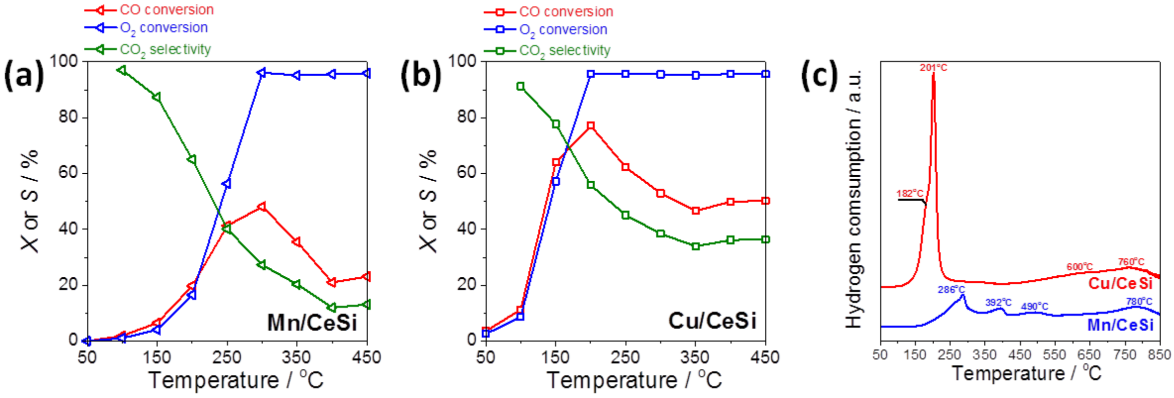

Figure 1. CO conversion (%), O_2 conversion (%), CO_2 selectivity (%) vs reaction temperature for Mn/CeSi – (a) and Cu/CeSi – (b); TPR-H_2 results (c).

The positions of high-temperature reduction peak (~ 760–780°C) associated with the reduction of subsurface and bulk Ce^{4+} are almost the same in the H_2-TPR profiles of both catalysts, but the position of low-temperature peaks of Cu or Mn reduction is different. The TPR-H_2 profile for Cu/CeSi has one low-temperature peak centred at 201°C and small shoulder at 182°C, indicating the presence of highly dispersed copper oxide species contacted with silica surface and ceria particles, respectively. According to TEM and XPS results this sample have unique structure, comprising fine CeO2 particles with a narrow size distribution of 2–3 nm well dispersed on a large surface area and high concentration of the most active in CO oxidation Cu+ sites, formed on CuOx-CeO2 interfaces. The TPR profile of Mn/CeSi contains several less intense low-temperature reduction signals, which can be associated both with the stepwise reduction of manganese in different oxidation states and with the reduction of surface and subsurface layers of MnO_x of various sizes.

Thus, modification of ceria-silica composite systems with copper led to formation of easy reducible highly dispersed copper oxide species on the surface, which can possess the superior catalytic properties. A detailed analysis of catalysts by XPS, Raman spectroscopy, EPR, FTIR of adsorbed CO, TEM, and the other methods confirmed the conclusions made on the basis of TPR-H_2 data. Long-term catalytic tests with H_2O and CO_2-containing feed mixtures proved high stability of the prepared samples.

Acknowledgement: The work was carried out using scientific equipment purchased under Lomonosov Moscow State University development programme.

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PP-11

Applicability of Fridman-Macheret α-Model to Heterogeneous Processes in the Case of Dissociative Adsorption of N_2 on Ru Surface

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The efficacy of vibrational excitation for reaction promotion can be well-described by Fridman-Macheret (F-M) α-model [1], which was initially developed for processes ingas phase. However, it is widely used for analysis of efficacy of vibrational excitation of heterogeneous processes, such as NH_3 synthesis, reduction of CO_2 and activation of CH_4. For plasma-assisted heterogeneous processes, the contribution of species with high vibrational excitation into reaction is emphasized. The aim of this paper is to check the applicability of F-M model for the case of activation of N_2 molecule on the Ru(113) and Ru(0001) surfaces using molecular dynamics with machine learning potential (MLP).The results show that F-M model appears to be a reasonable approximation for estimate of vibrational efficacy of highly excited states ($v \geq 7$) which are important under nonequilibrium plasma conditions. Applicability of Fridman-Macheret α-model to heterogeneous processes in the case of dissociative adsorption of N_2 on Ru surface.

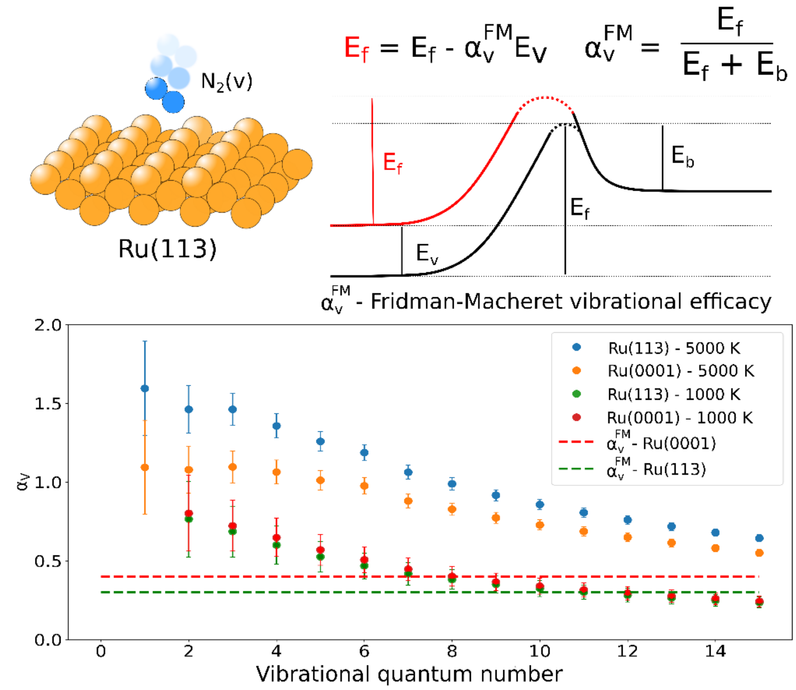

Fig. 1: The dependence of alpha-v on vibrational quantum number for T = 1000, 5000 K for Ru(0001) and Ru(113)

Acknowledgement: This work has been carried out using resources of the federal collective usage center Com-plex for Simulation and Data Processing for Mega-science Facilities at the NRC "Kurchatov Institute".

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PP-12

Formation of Ni(0)/NHC Active Species from Ni(II) Precatalysts in Alkene Hydroheteroarylation and Cross-Coupling Reactions

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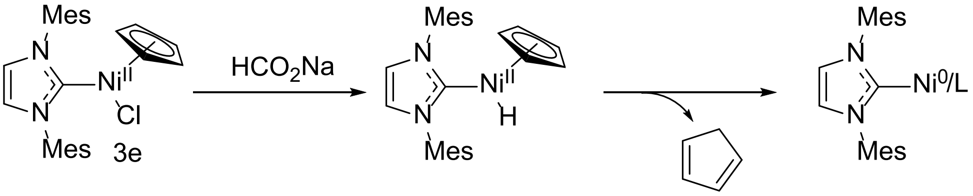
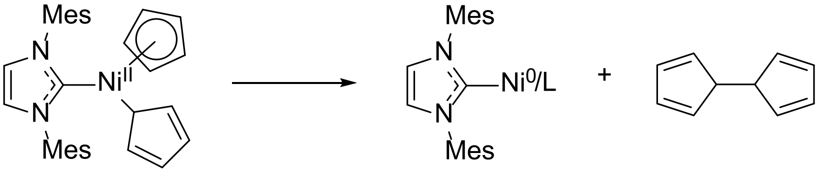
Catalytic systems based on Ni complexes with NHC ligands (Ni/NHC) have received much attention in the catalysis of olefines hydroheteroarylation, C-C and C-heteroatom cross-coupling reactions. The reaction mechanisms often involve the participation of Ni^0/NHC active species. However, most of well-defined Ni^0/NHC complexes, as well as free NHCs and $Ni(COD)_2$, are expensive and extremely air-sensitive compounds which requiring the use of a glovebox.

In this report discusses recently developed approaches to the generation of active Ni^0/NHC catalytic species from cheap and air-tolerant Ni^{II} precatalysts in the Ni/NHC catalysis of alkene hydroheteroarylation. These approaches include:

formation of active Ni^0/NHC complexes using sodium formate as *in situ* reductant;

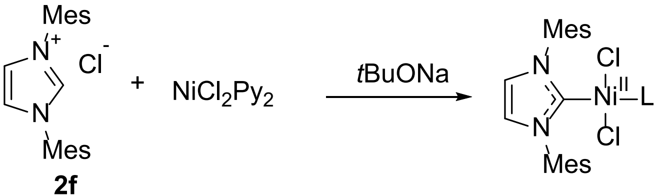


using Ni^{II}/NHC precatalysts with cyclopentadienyl-anion co-ligands serving as internal Ni(II) to Ni(0) reductants;



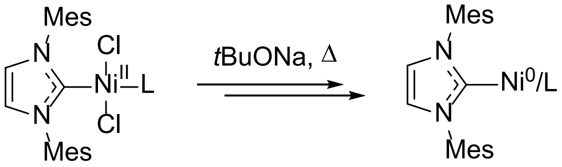
using sodium *tert*-butoxide both as base and Ni(II) to Ni(0) reductant

Formation of Ni(II)/NHC complexes



L = IMes, Py, solvent, etc.

Ni(II)/NHC to Ni(0)/NHC reduction



The developed approaches provide high efficiency of Ni/NHC systems generated form cheap and bench-stable precatalysts in alkene hydroheteroarylation, azole C-H arylation with aryl chlorides, C-N cross-coupling and etc.

Acknowledgement: This work was supported by the the Ministry of Science and Higher Education of the Russian Federation, project FENN-2024-0002.

PP-13

Application of Prussian Blue Nanocatalysts as Labels in Immunoassays

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The nanozymes are nanomaterials that exhibit catalytic activity similar to that of enzymes. Nanozymes are catalysts based on artificial nanomaterials capable of mimicking the functions of enzymes. Their physical and chemical stability, low cost, and adjustable properties make them a promising alternative to horseradish peroxidase (HRP), alkaline phosphatase, and β-galactosidase, which are used as labels in colorimetric immunoassays. Colorimetric immunoassays include enzyme-linked immunosorbent assay (ELISA), immunochromatography (ICA), immunofiltration, dot immunoassay, and other less common modifications. In these analyses, the role of enzymes and their artificial analogs is to convert a colorless substrate into a colored product. Currently, colorimetric immunoassays are one of the key analytical tools in medicine, food quality control, and biotechnology. Despite the insufficient technological maturity of nanozymes, they are a promising alternative to enzymes in the field of biosensing [1].

We synthesized albumin nanoparticles loaded with varying amounts of Prussian blue nanozymes. The nanoparticles were functionalized with monoclonal antibodies against the prostate-specific antigen (PSA) tumor marker. The properties of the obtained diagnostics were characterized, and they were subsequently used as labels in an ELISA-like colorimetric quantitative sandwich immunoassay for PSA.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-75-01093.

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PP-14

Unravelling the Mechanism of Dihydroxyacetone Isomerization into Lactic Acid over Ti^{4+}/Sn^{4+}-Substituted UiO-66

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The isomerization of dihydroxyacetone (DHA) into lactic acid (LA) is known to occur over the Lewis acid sites [1,2]. The metal-organic framework (MOF) UiO-66 feature the presence of such acid sites, namely, uncompensated Zr^{4+} cations, that appear due to the formation of a missing linker defect. Besides, of interest are the secondary building units (SBU) doped with other cations that exhibit the properties of Lewis acids, e.g., Sn^{4+} and Ti^{4+}.

The geometries of reagents, intermediates, and SBU of M_2-$Zr_4O_4(OH)_4$, where M = Zr, Sn or Ti, with a single missing linker defect were proposed and optimized. The binding energy of intermediate compounds in the dihydroxyacetone isomerization into lactic acid on Zr^{4+}, Sn^{4+} and Ti^{4+} active sites was estimated. The calculations were carried out using the Orca 5.0.3 software package at the B3LYP-D3/def2-tzvp level of theory for O, C, H, Ti atoms and B3LYP-D3/SARC-ZORA-def2-tzvp level of theory for Zr and Sn atoms to account for the relativistic interactions in transition metals.

It has been shown that the energy of binding of carbonyl intermediates on Sn^{4+}- and Ti^{4+}-containing active Lewis acid sites is by 3-10 kcal mol^{-1} lower than on those containing Zr^{4+}. Moreover, the energy of binding of carbonyl compounds depends on the geometry of active site of SBU in the substituted UiO-66. This report will discuss the effect of Sn^{4+} or Ti^{4+} ions and also the influence of geometry of active sites in M_2-$Zr_4O_4(OH)_4$ (M = Zr, Sn or Ti) on the binding energy of intermediates. The mechanism of DHA isomerization into LA on heterogeneous catalytic systems comprising UiO-66, Sn-UiO-66 and Ti-UiO-66 will be discussed. A combined theoretical and experimental catalytic studies will allow us to determine the most effective catalyst for the described reaction and reveal the catalytic roles of Sn^{4+} and Ti^{4+} substitution on the mechanism of the DHA isomerization into LA.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 19-73-30026, https://rscf.ru/en/project/19-73-30026/.

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PP-15

Aspects of the Mechanism for Single-Walled Carbon Nanotube Growth via Aerosol CVD Method

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Due to the unique set of structural, mechanical, electronic and optical properties, carbon nanotubes are a promising component for devices of science and technology: aerospace and medicine, functional materials and communication. Carbon nanotubes are actively employed to create structural and composite materials, antistatic agents and battery components, but their use in the fields of optoelectronics, photovoltaics and medicine requires an increased level of control. One of the key features of nanotubes is the impossibility of their non-destructive separation after agglomeration. Indeed, the energy of the lateral interaction of two nanotubes can reach 1000 eV/μm.

Aerosol chemical vapor deposition (CVD) method – is one of the promising approaches to overcome this limitation as it refers to a case of floating bed with an extreme dilution of the catalyst. Nevertheless, one of the key barriers to scaling and optimizing this process is the inability to "fix" a nanodisperse aerosol particle for a detailed study of the mechanism. Here we discuss, our recent studies towards analyzing the kinetic patterns in aerosol CVD [1,2] as well as mechanism aspects for single-walled carbon nanotube growth [3-5], namely phase composition, rate-limiting steps, activation and deactivation patterns.

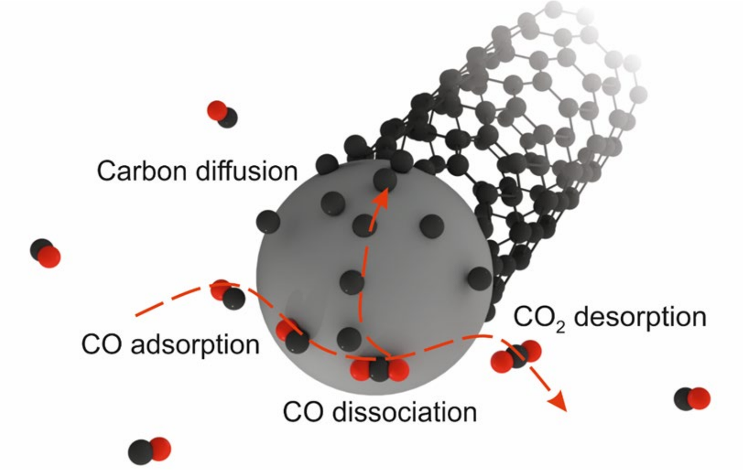

Fig. 1. Scheme for the carbon nanotube growth

Acknowledgement: The authors acknowledge Russian Science Foundation grant No. 20-73-10256.

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PP-16

Influence of Reaction Conditions on Catalytic Properties of *rac*-Et(2-MeInd)$_2$ZrMe$_2$/(2,6-^{t}Bu$_2$PhO-)Al^{i}Bu$_2$ in Ethylene-Propylene Copolymerization

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Metallocene and postmetallocene catalysts are used for copolymerization of ethylene with propylene with specified characteristics. Thermal and physicalmechanical properties of copolymers, determined by their microstructure, molecular-mass characteristics, etc., depend on the type of catalyst, methods of its activation and synthesis conditions. Earlier in our works it was shown that bisindenyl complexes of metallocenes activated by isobutylaluminum aryloxides are effective catalysts for copolymerization [1,2].

This study investigates the influence of copolymerisation conditions on the activity and properties of the resulting copolymers, using the highly active catalytic system *rac*-Et(2-MeInd)$_2$ZrMe$_2$/(2,6-^{t}Bu$_2$PhO-)Al^{i}Bu$_2$ as an example.

The study demonstrates that the following factors are crucial: the composition of comonomers feed, the value of Al/Zr molar ratio, and solvent used as reaction medium (toluene or heptane). Reducing the reaction pressure from 11 to 3 atm results in a 1.6-fold increase in specific activity (from 3030 to 4840 kg copolymer/(mol Zr*h*atm)), an increase in the value Mn of from 38 to 89 kg/mol, and an increase in the ethylene content in the copolymer from 87 to 92 mol%. Increasing the molar ratio of ethylene/propylene from 0.7 to 2 does not significantly affect the activity. However, it does lead to an increase in the ethylene content of the copolymer from 92 to 97 mol%, resulting in an increase in the copolymer's crystallinity from 43 to 48%. The catalytic activity of the systems is greatly influenced by the change in the molar ratio of Al/Zr. In the series Al/Zr = 100, 150, 200, 300 mol/mol, the lowest activity of 80 and the highest of 8550 kg copolymer/(mol Zr*h*atm)) are observed at molar ratios of 100 and 150, respectively. Additionally, we have demonstrated that catalytic systems with isobutylaluminium aryloxide activators are effective in copolymerization in an aliphatic solvent (heptane).

Acknowledgement: This work was supported by Ministry of Science and Higher Education of the Russian Federation, State task, No. registration № FFSG-2024-0007.

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PP-17

Study of the Mechanism of Methyl Ethyl Ketone Coupled Condensation-Hydrogenation in the Presence of a Pd/C Catalyst

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The processes involving the formation of new carbon-carbon bonds are of considerable interest for fine and basic organic synthesis. Among the numerous methods, the reactions of aldol and croton condensation of aldehydes and ketones occupy an important place. Lower aldehydes and ketones are very available as reagents, they can be obtained from various raw materials, including renewable ones.

One of the most promising base compounds for these purposes is methyl ethyl ketone (MEC). It has a high potential for the development of catalytic methods for the production of synthons for medicines and general-purpose products, as well as effective additives to motor fuels [1]. As a rule, homogeneous catalysts are used in condensation processes, for example, acids [2-4], including amino acids [5], as well as other classes of chemical compounds.

Recently, two independent groups have found a way to increase selectivity by coupling MEC condensation with the hydrogenation process [6].

The idea of our group was to organize a new coupling node and transform the primary unsaturated condensation products into the same saturated carbonyl dimer with a reduced ability to further transformations.

Thus, it was supposed to suppress the sequential reactions of the transformation of unsaturated dimeric ketones, the primary products of aldol-croton condensation. The idea was implemented in the “one pot reaction” variant, where MEK condensation takes place in a hydrogen atmosphere with the participation of a multifunctional condensation/hydrogenation catalyst [7].

The purpose of this work was to develop a bifunctional catalyst capable of selectively conducting the process of condensation of MEC followed by hydrogenation of its products.

The experiments were carried out in flowing metal and quartz reactors (the volume of the reaction zone is 12 ml.) with a stationary catalyst layer (the volume of the layer is 8 ml) in the temperature range of 250-350 °C at atmospheric pressure of hydrogen. The molar ratio of MEC to hydrogen is 1:1. The duration of the experiment is 40-60 minutes. The volume of the catalyst and the feed rate of the reagents were selected based on the condition of the same contact time of the reagents with the catalyst (~ 7 seconds).

The condensation and hydrogenation catalyst (palladium on activated carbon) was prepared by impregnation. The required amount of palladium acetate was dissolved in acetone at room temperature in a glass with constant stirring for 5-10 minutes. The solution was poured into a porcelain cup with a carrier attachment and the solvent was slowly evaporated with stirring. Palladium acetate deposited on activated carbon was reduced in a flow reactor in a hydrogen current.

PP-17

Aldol-croton condensation, coupled with hydrogenation, proceeds sequentially. At the first stage, an aldol is formed, which undergoes dehydration to form at least two isomeric ketones. Their hydrogenation leads to the formation of a single 5-methyl-3-heptanone. For 3-methylheptan, the conversion scheme is similar, but the hydrogenation proceeds more deeply with the formation of an alkane.

This scheme, presented in Fig. 1, allows us to explain the suppression of successive transformation reactions of unsaturated dimeric ketones formed during MEK condensation, but does not clarify the mechanism of the almost complete disappearance of competing dimers, as well as the absence of their hydrogenation products. Perhaps palladium in the presence of hydrogen stimulates the formation of aldol from MEC.

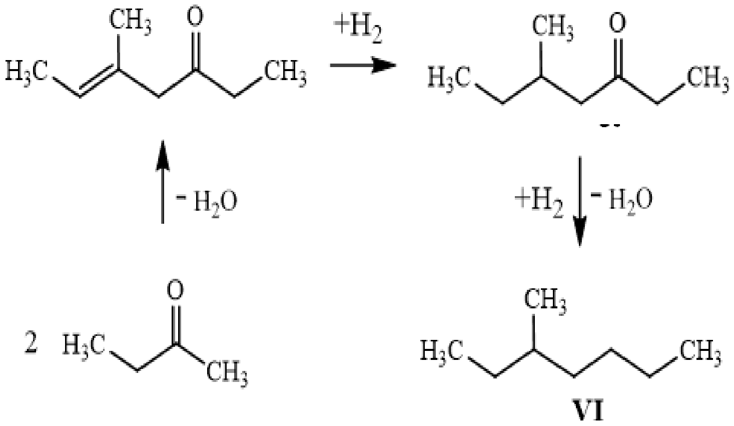

Fig. 1. The scheme of the main products formation

Thus, the coupling of the processes of MEC condensation and hydrogenation of intermediately formed products on the Pd catalyst/C allows a targeted effect on the process, increasing the selectivity for 5-methyl-3-heptanone.

The technique we used - the coupling of various processes on a multifunctional catalyst in one reactor - seems to be of a general nature and can be used to improve the technological performance of similar processes.

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PP-18

The In Situ Formation and Characterization of 2D Carbon Layer Armored La_2O_3 Catalyst for Oxidative Coupling of Methane

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Oxidative coupling of methane (OCM) is one step process converting methane into ethylene and ethane. La_2O_3 is an OCM catalyst with good potential in application. In our previous research, the change of selectivity from CO_x (CO and CO_2) to C_2 products depending on temperature has been found [1]. To increase C_2 selectivity the O_2/CH_4 reactants ratio need to be decreased, but at less oxidizing conditions the catalyst surface was found to be coked which led to deactivation. In this work, formation and chemical stability of the coking layer on La_2O_3 surface are thoroughly studied and mapped. The results demonstrate an ultrathin, sub-nanometer-thick 2D carbon layer is formed on the catalyst surface at high temperatures. This layer provides a highly compact protection to the La_2O_3 surface, preventing it from carbonation and hydroxylation at low temperatures. It is also found that the armored surface can be easily reactivated under the OCM reaction conditions, exhibiting an activation behavior similar to the pristine surface. It provides a simple method maintaining high reactivity of spent La_2O_3 catalysts in OCM reaction. In addition, analysis of the catalyst surface after repeating in situ methane treatments reveal a “memory effect”, which suggests the seed-growing mechanism of 2D carbon layer formation. This growth model is further supported by the lattice match between La_2O_3(001) surface and graphene after a structure comparison, which resembles the epitaxy process.

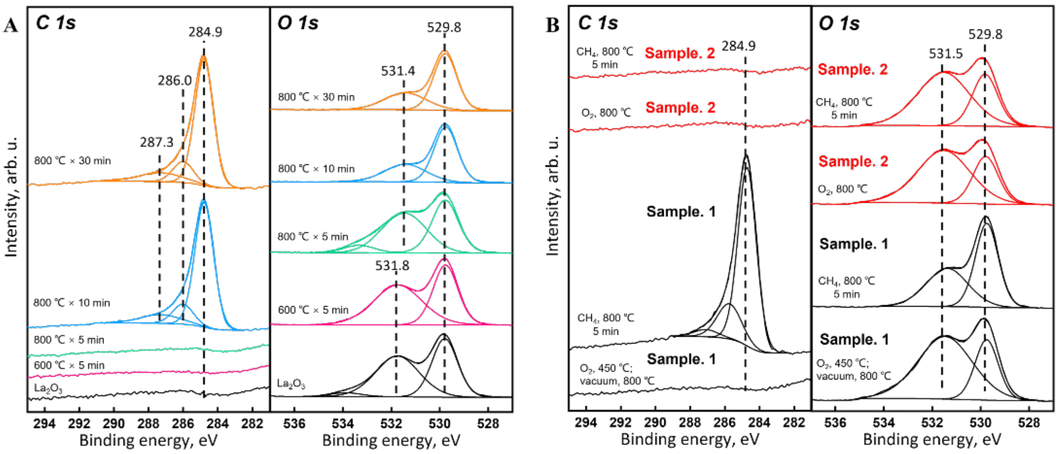

Fig. 1. (A) Coking formation over La_2O_3 by heating in CH_4 and cooling in vacuum. (B) Coking formation over La_2O_3 with different pretreatment in oxygen (O_2 : Ar = 1:4).

Acknowledgement: This work was supported by the National Natural Science Foundation of China, grants No. 22272107, No. 22072092, No. 92045301.

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PP-19

Dynamic Scheme of Iomerization-Disproportionation Conversion of a Mixture of Gaseous C_{4-} and Liquid n-C_{6+} Alkanes

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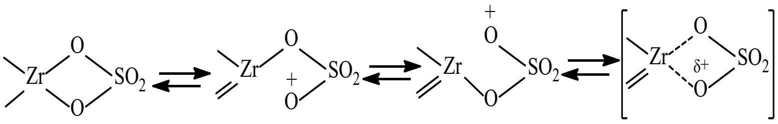
In this work, the hydroisomerization of gseous C_{4-} and liquid n-C_{6+} alkanes and their mixtures on a composite catalyst consisting of cobalt-modified zeolite and sulfated zirconium dioxide was studied. The process was carried out in a flow-through laboratory installation at atmospheric pressure and a temperature of 140-220°C in the presence of hydrogen. The results show that the main product of the process is i-C_5-C_6 alkanes. Sometimes C_1-C_5 and C_{7+} alkanes are also formed at this time. These data indicate the formation of monomolecular and bimolecular intermediates and their subsequent isomerization or hydrocraking to the corresponding products. As the temperature rises, the yield of isomeric products decreases. The decrease in the yield of isomeric products and the increase in the selectivity for C_1 - C_5 hydrocarbons indicate that the hydrocracking activity of the catalyst increases with the increase in temperature.

Theconversion of alkanes over CC can be described by a multi-step scheme. The activation of alkane is related to its interaction with the active centers of CC. Such centers in CC can be Lewis acid centers consisting of electrophilic oxygen atoms, which can be formed as a result of dynamic equilibrium in the SO_4^{2-} - ZrO_2 system:

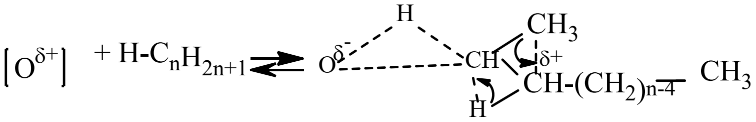


(1)

or

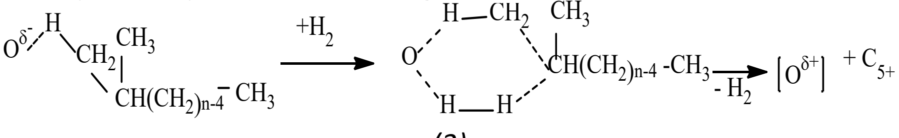
$$[O] \rightleftarrows [O^{\delta+}]$$

The interaction of n-alkane with such centers leads to the formation of alkoxy groups that have a positive charge and their subsequent stabilization by the migration of the methyl group and the transfer of hydride ions, characteristic of their skeletal isomerization:



(2)

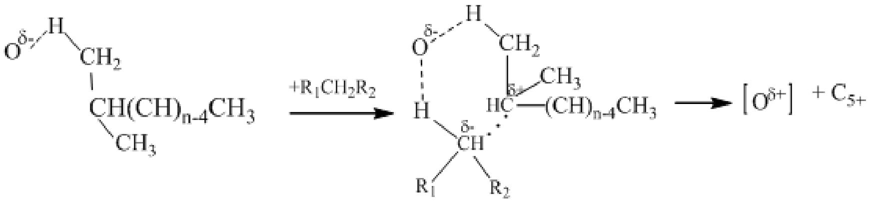
The interaction of the obtained monomolecular intermediates with hydrogen molecules enables the desorption of products according to scheme (3):



(3)

Hydrogen hydrogenates the C-C bond with the formation of low molecular mass products (β-splitting), and the share of this reaction increases with increasing temperature.

The conversion of a mixture of alkanes on CC follows a mechanism similar to the conversion mechanism of individual alkanes, in which H_2 is replaced by other lower molecular weight alkanes. The main products of the conversion of mixtures are C_5-C_6 alkanes (mainly isoalkanes), and by-products are C_1-C_3 hydrocar-bons. In this case, high molecular weight C_{7+} hydrocarbons with isostructure are also formed. The presence of C_{7+} hydrocarbons and isomeric alkanes can be explained by the initial formation of bimolecular intermediates, their isomerization, and subsequent decomposition-disproportionation into low and high molecular hydrocarbons:



(4)

Scheme (4) with an intermediate cyclic state explains the co-conversion of n-alkanes. In this case, the interaction of hydrogen molecules with SZ according to scheme (3) is replaced by the second – low molecular n-alkane molecules: low-molecular n-alkane molecules are already strongly polarized as a result of the shift of the positively charged hydrogen atom towards $O^{\delta-}$, the alkyl group with excess negative charge is attracted by the positively charged carbon atom of the intermediate formed by the primary alkane. The second low molecular weight alkane can compete with the high molecular weight primary alkane for interaction with SZ according to scheme (2) due to the bifunctional nature of the transformation. For example, as in the conversion of a mixture of n-butane and n-hexane. In this case, the presence of C_5 and propane in the conversion products of n-butane, and the decrease in the conversion of n-C_6H_{14} over CC confirm this possibility. However, highly reactive n-C_6H_{14} may show higher activity at this stage of the reaction. Blocking the interaction of hydrogen with SZ by n-butane leads to a change in the composition of the formed isomeric hexanes. The conversion products of n-hexane in the presence of n-C_4H_{10} are enriched with polyisomers, which easily undergo hydrocracking compared to normal and monoalkyl-substituted alkanes, formed in the absence of n-C_4H_{10}.

PP-20

Alkylation of Triazolic Heterocyclic Aldehydes

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Development of new approaches to functionalized of heterocyclic compounds is an important task due to their widespread distribution in nature and biological activity.

We studied the interaction of some aldehydes based on 1,2,3-triazole with diisopropyl zinc and found that in some cases spontaneous generation of chirality is possible for these reactions [1].

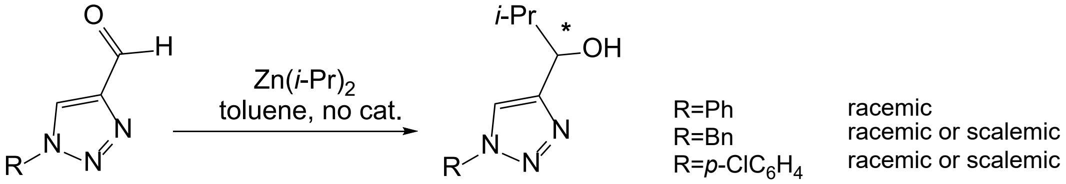

Fig. 1. Reaction of 1,2,3-triazoles with diisopropyl zinc

Furthermore, allylboration of triazoles with triallylborane or dipropylpentadienylborane afforded corresponding homoallylic alcohols with good to excellent yields.

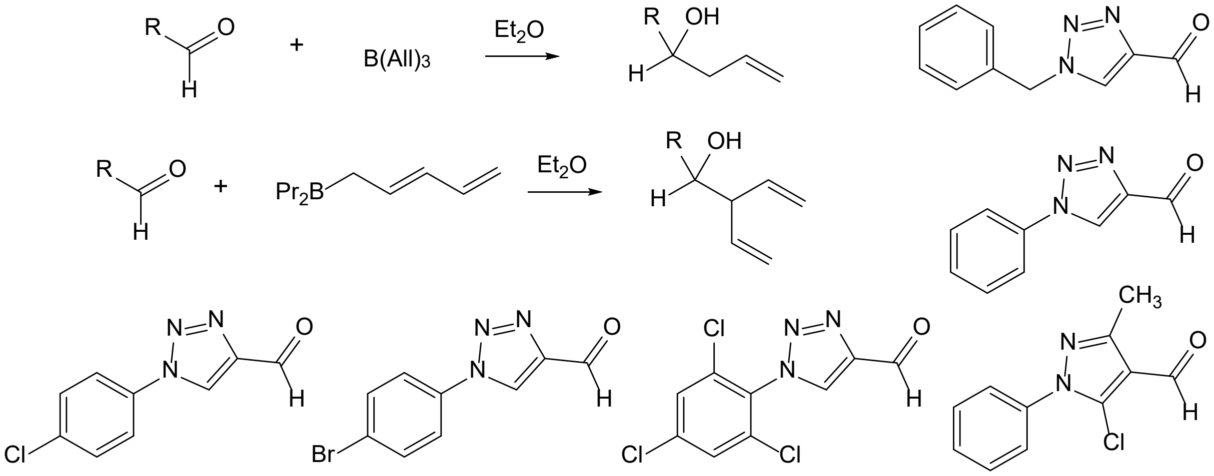

Fig. 1. Reaction of 1,2,3-triazoles with allylboranes

Acknowledgement: This work was supported by the Russian Science Foundation, grant 22-13-00275.

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PP-21

Short Spacer Bis-Imidazolium Salts for Micellar Catalysis

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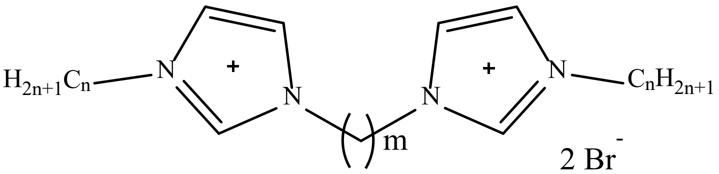
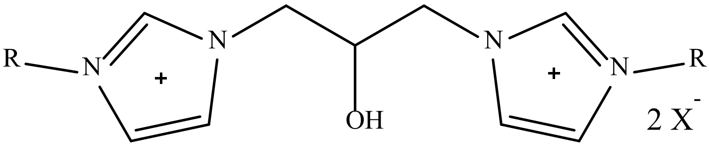
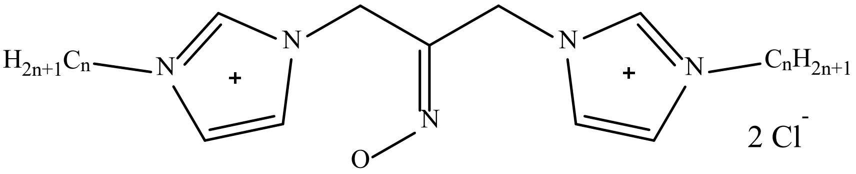
An acceleration of nucleophilic reactions in the presence of bis-imidazolium salts (BIS) micelles is known for years, but mainly for long-spacer-short-tails salts easily attainable from commercially available precursors. BIS with short spacers and long tails (SSLT) are much less studied. By the development of effective synthetic protocols [1], broad set of SSLTs was prepared in order to evaluate their aptness to construct micellar systems with catalytic activity in the eradication of stable esters-ecotoxicants.



I: n = 8,9,10,12,14,16;



II: R = H, C_nH_{2n+1}, n = 8,9,10,12,14,16; X = Cl, Br



III: n = 1,12,14,16

There is a number of properties that are shared for all compounds, and a number of features special for individual groups. At room temperature, salts of type III look as amorphous solid; salts of type I and II behave predominantly as ionic liquids or ionic plastic crystals [1]. Light weight members of all families dissolve easily in water. Solubility in water decreases catastrophically with elongation of tail.

Salts of type I and II effectively solubilize nonpolar organics, and bind to lipid membranes disrupting them and provoking cell lysis. Low toxic to warm-blooded, these compounds are active against Gram-positive and Gram-negative bacteria, and some fungal pathogens [2].

All compounds are strong electrolytes in diluted water solutions. Concentration dependences of molar conductivity under critical aggregation concentration (***cac***) are typical for strong electrolytes, with high limiting values indicating full dissociation of 2-1 electrolytes into dication and two monoanions. Kinks on a Kohlrausch curves usually lay very close to ***cac*** found by other methods [3].

PP-21

All compounds with tails long enough tend to reduce surface tension of water solutions. Measured by different methods based on different physical principles (drop shape analysis, force measurement), surface tension vs concentration demonstrates usual quasi-sigmoidal curve with saturation after ***cac*** (sufficiently lower compared with monocationics) arrived. Typically, surface pressure at flat region of saturation exceeds usual values for a monocationic congeners of the same tail lengths; Langmuir limiting surface concentration is very high, too; large modulus of elasticity of these densely populated surface layers [4] resemble the ones of biopolymers, not low molecular weight compounds.

Rotation around ordinary C-C bonds in aliphatic tails looks unrestricted for all compounds I-III in NMR time scale. Expectedly for unsymmetrical central fragment of salts III with hydroximino group, sp^2-carbon planarity leads to visible difference in geometry and magnetic properties of syn- and anti- oriented imidazolium cycles. Unexpectedly, symmetrical spacer of salts II bears non-equivalent methylene hydrogens. Sufficient barriers preclude free rotation of imidazolium fragments in salt II and III. Not so strained, type I salts polymethylene spacers do prefer fully stretched (*all trans*) conformations [5].

These observations provide a good basis for a search and creation of organized micellar-like systems for a catalytic destruction of hydrolyzable pollutants. Hydrolytic reactions of highly stable esters of phosphorous, phosphonic, and sulfonic acids were studied [6]. Pseudophase approximation reliably describes kinetics observed, with kinetically evaluated ***cac***s in reasonable accordance with conductometric and surface tension measurements. It was found that hydrolysis of armine, paraoxone, 4-nitrophenyl 4-toluenesulphonate may be enhanced by 1÷3 orders of magnitude due to pronounced concentration of hydrophobic esters in micellar pseudophase (mainly for salts of type I and II) and, additionally, functionalization of surfactant molecule (salts of type III) with powerful nucleophilic group.

Acknowledgement: This work was supported partially by the Ministry of Science and Higher Education of the Russian Federation, grant FRES-2023-0001.

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PP-22

Cu-and Fe-Containing Catalysts for CH_4 Purification from C_2H_6

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The natural gas mainly consisting of CH_4 always contains from 1.8 to 5 mol% of ethane (C_2H_6). The oxidative dehydrogenation of C_2H_6 or its transformation in C_2H_4 through steam cracking is economically profitable if ethane fraction is large enough. Otherwise, CH_4 purification from C_2H_6 is realized through catalytic combustion providing heat to refinery processes [1]. Cu or CuO doped CeO_2 catalysts are among the best for alkane combustion, contrary to previously applied Fe or Fe_2O_3 doped CeO_2 [2,3]. The new trend is an application of Cu-Fe/CeO_2 catalysts for this purpose [4]. The reason is to replace more expensive Cu with a cheaper Fe. As is assumed, solid-solution-like (Cu-O-Ce, Fe-O-Ce or Cu-O-Ce-O-Fe) two-dimensional surface structures are the real active phases suitable for the process realization.

The aim of this study is to clarify effect of iron introduction in CuO/CeO_2 and Cu/CeO_2 composites produced by mechanochemical synthesis on catalytic efficiency in C_2H_6 full degradation individually or mixed with CH_4.

The ball-milling technique was applied for preparing CuO/CeO_2 with various CuO concentration, αFe_2O_3/CeO_2, CuO-αFe_2O_3 /CeO_2, Cu/CeO_2 and Cu-Fe /CeO_2 catalysts. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (STEM) with electron diffraction and EDX were applied to study surface properties of composites. Iron state was tested by Mössbauer spectroscopy. Redox properties towards H_2 were studied by temperature programmed reduction (H_2 -TPR). Catalytic activity was measured in a flow quartz-tube reactor. The following reaction mixtures were used: (1) 0.5 vol.% C_2H_6 + 5 vol.% O_2 and 94.5 vol.% N_2 for balance or (2) 0,66 vol% C_2H_6 + 33 vol.% CH_4 + 6.36 vol.% O_2 and 59.7 vol.% N_2 for balance.

Among the oxide dopants, CuO was found to be the best for C_2H_6 total oxidation. A decrease in CuO fraction is accompanied by a gradual decrease in C_2H_6 conversion, but addition of αFe_2O_3 compensates insufficient number of Cu-containing surface active sites (Table 1). As follows from Table 1, catalytic activity in C_2H_6 oxidation was in line with a fraction of low-coordinated “surface” (O_s/O_s+O_l) oxygen and a fraction of oxygen vacancies. No change in Fe state in as-prepared αFe_2O_3-CuO/CeO_2 was detected. Also, H_2-TPD spectrum of this sample was a superposition of two individual H_2-TPD curves belonging to $\alpha Fe_2O_3/CeO_2$ and CuO/CeO_2 (not shown). Thus, contrary to [4, 5], it can be assumed that both oxides are localized separately on the CeO_2 surface, forming a mosaic structure (that was supported by STEM data), rather than forming mixed solid solutions.

Table 1. C_2H_6 conversion at 450 °C and some parameters of surface state (from XPS data).

Sample	C_2H_6 Conversion at 450°C (in 2% C_2H_6+CH_4 mixture)	O_s/O_s+O_l	Ce^{3+}/C^{4+}	Fe/Cu
10% CuO/CeO_2	92.4%	58%	0.11	
5% CuO/CeO_2	~61%			
2.5% CuO/CeO_2	~38%			
2.5% CuO-5% Fe_2O_3/CeO_2	~70% (48%)	~47%	0.08	3.7
10% Fe_2O_3/CeO_2	56%	44%	0.06	
4% Cu-7% Fe/CeO_2	~ 89% (89%)	50%	0.05	1.8
8% Cu/CeO_2	100%	~65%	0.08	

Two Fe-containing catalysts: 2.5% CuO-5% Fe_2O_3/CeO_2 and 4% Cu-7% Fe/CeO_2 were tested in preferential oxidation of C_2H_6, when 2% of C_2H_6 was admixed to CH_4. The best was found to be the second one consisting on CeO_2 modified originally by Cu and Fe metallic powders. After mechanochemical synthesis, both metals were in X-ray amorphous state being oxidized to Cu^{1+}, Cu^{2+}, Fe^{2+} and Fe^{3+}, respectively. Approximately 89% of C_2H_6 and ~ 7% of CH_4 were oxidized. Especially high selectivity in C_2H_6 oxidation could be associated with significantly higher content of Cu ions on CeO_2 surface in the case of 4% Cu-7% Fe/CeO_2 composite, as compared to 2.5% CuO-5% Fe_2O_3/CeO_2. This is evident from previous experiments: the most effective catalysts for C_2H_6 total oxidation were Cu/CuO-CeO_2 samples.

Conclusions.

Iron metal or oxide dopants can compensate a decrease in Cu-containing fraction of Cu/CuO-CeO_2 catalysts. Some experimental data point to separate arrangement of Fe- and Cu-containing phases on the surface when both oxides are added to CeO_2. CeO_2 modified by Cu and Fe metals was more effective in CH_4 purification from C_2H_6 than CeO_2 modified by CuO and Fe_2O_3 due to higher fraction of Cu ions on the surface.

Acknowledgement: This research was funded by the State Assignment of N.N. Semenov FRC for Chemical Physics RAS (topic 122040500058-1) and the State Assignment of NRC «Kurchatov Institute» in the part of TEM investigations.

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PP-23

The Structure of the Active Site and the Mechanism of Methane Oxidation in the Presence of the $Au_{25}(SR_{18})$ Cluster

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The gold clusters $Au_{25}(SR)_{18}$ catalyse the oxidation of methane by hydrogen peroxide and molecular oxygen in an aqueous medium with the formation of CH_3OH and CH_3OOH [1]. This reaction is of great interest. The structure of the active site and the mechanism of methane oxidation in this reaction have been studied in this work within the framework of the density functional theory. The geometric structures of compounds are optimized using the PBE functional using the Priroda program. The metastable form of a cluster of the composition $Au_{25}(SR)_{12}$ form interacts with the reagent. The $Au_{25}(SR)_{12}$ structure, R=CH_3 or R=G (glutathione), has been optimized. It is to consider two Au atoms linked to each other due to aurophilic interaction in one of the six CH_3S–Au–Au–SCH_3 "staples" on the surface of the $Au_{25}(SCH_3)_{12}$ cluster as an active site. A possible reaction O_2 and methane with model $Au_{25}(SCH_3)_{12}$ cluster is shown in the Figure 1.

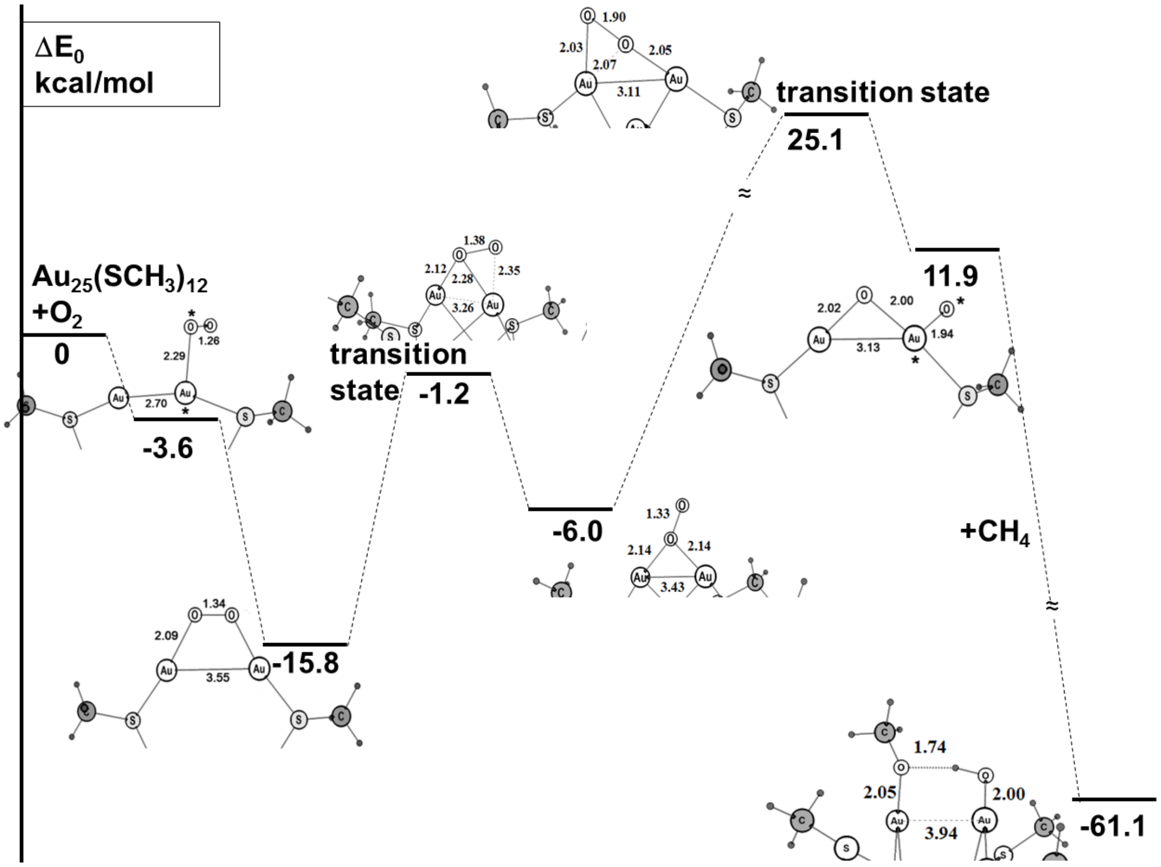

Fig. 1. The energy diagram of the reaction of a $Au_{25}(SCH_3)_{12}$ cluster with O_2 and CH_4 (the fragments of the active site)

New active site containing 4 gold atoms appear on the surface of the $Au_{25}(SG)_{12}$ cluster, where another mechanism of interaction with the reagents can be realized.

Acknowledgement: The calculations carried out using the computational capabilities of the Joint Supercomputer Center of the Russian Academy of Sciences were supported by the Ministry of Education and Science of the Russian Federation, project no. FFSG-2024-0004 (124020200104-8).

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PP-24

Use of Wool Fibers as a Biotemplate in the Hydrothermal Synthesis of Highly Efficient TiO_2 Photocatalyst: Effects of Ti^{3+} Self-Doping and Inheritance of the Secondary Structure of Keratin

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Titanium dioxide remains the focus of attention for researchers as one of the most efficient photocatalytic materials for solving a number of problems in ecology, energy, and medicine. One of the promising strategies for the synthesis of TiO_2 is based on biomimetic principles, which allow for obtaining a target material with a complex hierarchical structure using templates of biological origin. This approach was successfully used in the hydrothermal impregnation of cellulose [1] and flax [2] fibers with a solution containing titanium polyhydroxocomplexes. Developing this approach, it is of interest to move from plant fibers to fibers of animal origin, in particular wool. The properties of wool fibers are unique due to their extremely complex morphology with a hierarchical variety of nano- and microstructures formed by a multilayer cuticle and cortex, as well as the chemical composition of keratin proteins. The sulfur content in wool (up to 5%) is mainly due to the presence of cystine, which can play an important role in the crystallization of TiO_2. This amino acid usually connects two adjacent peptide chains with a covalent disulfide bond, which can be broken under hydrothermal conditions, thus forming the sites for chemisorption of TiO_2 precursor and also leading to a partial reduction of Ti^{4+} to Ti^{3+} (i.e., Ti^{3+} self-doping effect).

This work is aimed at: 1) obtaining biomorphic titanium dioxide fibers by hydrothermal saturation of sheep wool fibers with a solution containing titanium hydroxo complexes; 2) studying their phase composition, texture, morphology, and defect structure; 3) testing the photocatalytic properties of TiO_2 fibers in the decomposition of Rhodamine B dye, which a representative of the group of fluorescent dyes, under exposure to UV and visible light.

Samples of native wool, intermediate hybrid wool-TiO_2 material and final crystalline TiO_2 powders were characterized by X-ray diffraction, IR spectroscopy, thermal analysis (DSC and TG) with mass spectral analysis of gas evolution, scanning electron microscopy, nitrogen adsorption-desorption, diffuse reflectance spectroscopy in UV-visible regions, XPS, and ESR. The photocatalytic activity of the synthesized TiO_2 samples was estimated as the degradation rate of Rhodamine B (RhB) in an aqueous solution when exposed to UV and visible radiation. The highest photoactivity (Fig. 1) was demonstrated by the sample with the phase composition of anatase (60%) and rutile (40%), which was prepared via wool impregnation with TiO_2 precursor in an autoclave at 115°C for 0.5 h followed by annealing at 600°C for 1.5 h.

PP-24

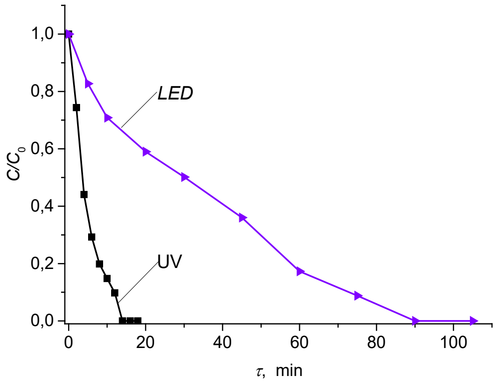
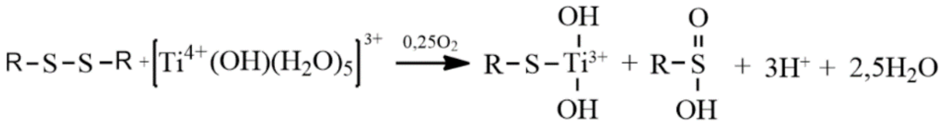


Fig. 1. *Photocatalytic degradation of Rhodamine B (20 mg/l of RhB; 0,6 g/l of TiO_2)*

It has been suggested that disproportionation of the disulfide bond is the most likely mechanism for the reduction of Ti^{4+} to Ti^{3+} when wool is impregnated with hydrolyzed forms of titanium:



$$R{-}S{-}S{-}R + \left[Ti^{4+}(OH)(H_2O)_5\right]^{3+} \xrightarrow{0,25O_2} R{-}S{-}\overset{\displaystyle OH}{\underset{\displaystyle OH}{Ti^{3+}}} + R{-}\overset{\displaystyle O}{\underset{\displaystyle OH}{S}} + 3H^+ + 2,5H_2O$$

Also, this report discusses an experimental result associated with the probable inheritance of the secondary structure of the polypeptide chain of wool keratin by titanium dioxide because of a topochemical reaction and crystal nucleation during crystallization under hydrothermal conditions. XRD analysis shows that diffuse halos at $2\theta = 8.7^{\circ}$ and 19.6°, characteristic of the secondary structure of wool containing α-spiral and β-folded keratin configurations, are preserved both for hydrothermally TiO_2-impregnated wool and the samples annealed at 600 °C and 800 °C, but a shift toward smaller angles of $2\theta = 6.3^{\circ}$ and 13.2° is observed. This indicates the stretching of keratin fibers during hydrothermal impregnation, on the one hand, and indicates that the crystallinity domains of the secondary structure of the biotemplate are preserved in the annealed samples representing a mixture of well - crystallized phases of anatase and rutile, on the other hand.

The interpretation of this effect is based on the assumption that the centers of TiO_2 crystallization are located along the turns of the α - helix or folds of the β - structure and their spatial arrangement is in a certain sense a replica of these structures, and nucleation is due to the interaction of monomeric forms of titanium hydroxocomplexes with carbonyl and carboxyl groups of the polypeptide chain with further growth of anatase and rutile crystallites by reactions of olation/oxolation under hydrothermal conditions.

Acknowledgement: this work was supported by the grant FZZW-2024-0004

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PP-25

Theoretical Study of the Mechanism of Catalytic Methane Decomposition on the Carbon Catalyst

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Hydrogen H_2 is one of the most promising energy carriers and is considered as the greenest fuel [1]. Today H_2 is generated by steam methane reforming (SMR), partial oxidation of hydrocarbons, catalytic methane decomposition (CMD), coal gasification and water electrolysis [2]. Currently, the main process of hydrogen production is steam reforming of natural gas [3]. The SMR process has several advantages, including high efficiency, low cost, and the ability to use a wide range of feedstocks. The main disadvantage of the SMR process is the production of greenhouse gases such as carbon dioxide (CO_2) and carbon monoxide (CO). Catalytic methane decomposition can be considered as an alternative chemical process for hydrogen from natural gas with zero CO/CO_2 emissions as the methane molecule CH_4 is decomposed directly into hydrogen H_2 and carbon $C_{(B)}$ homogeneously or in the presence of catalyst. In the present work we perform a systematic study of CMD on the graphene edge as a model of the carbon catalyst surface. Atomistic first-principles calculations (DFT level of theory) were performed to obtain the parameters of elementary reactions including the formation of active sites, interaction of methane molecule with these active sites and regeneration of the carbon catalyst surface. Our findings show that methane pyrolysis on the carbon catalyst is a unique heterogeneous radical chain process in which active sites are migrating over the catalyst surface via gas phase radical transport. Based on quantum-chemistry calculations, detailed kinetic mechanism of CMD on the carbon catalyst was developed and verified with respect to the latest experimental data. Calculated effective activation energies of CMD are in the range 2.1-3.2 eV, which is in reasonable agreement with experimental activation energy. Predicted methane conversion in the considered temperature range 890-990 oC is consistent with experimental values. The present investigation of the catalytic methane decomposition on carbon extends the understanding of complex catalytic processes on carbon structures and can be also applicable for the description of other processes in the carbon-based materials.

Acknowledgement: This work has been carried out using resources of the federal collective usage center Com-plex for Simulation and Data Processing for Mega-science Facilities at the NRC "Kurchatov Institute".

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PP-26

Scientific Basis for the Selection of Aluminum Oxide-Based Substrates for Nickel Catalysts with Specified Adsorption Properties

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Reactions involving hydrogen-containing gases form the basis of many large-scale chemical production, as well as the production of products and intermediates of fine organic synthesis. The reduction of a number of molecules containing various functional groups is carried out on supported and massive nickel catalysts in almost any case, aluminum oxide of various modifications is used as a substrate for the catalyst. The original aluminum oxide can be in the thermodynamically stable phase α-Al_2O_3 (corundum), as well as in a number of metastable phases (γ, θ, χ, δ-modifications and some others). When aluminum oxide can have two different structures: face-centered cubic and hexagonal close-packed. Depending on the method of obtaining a substrate based on aluminum oxide, one of its many crystalline forms is realized, differing from each other in textural properties, the number of defects and, as a consequence, the energy heterogeneity of the surface [1]. It should also be noted that the stages and conditions of most methods of applying nickel to a substrate described in the literature are quite similar; as a rule, it is the stage of preparation of the carrier that differs. Thus, it can be argued that the greatest contribution to the formation of the active surface, and as a consequence, the determination of the adsorption properties with respect to hydrogen and its acceptor, of the hydrogenation catalyst is determined by the structure of aluminum oxide and its textural properties.

The goal of this work was to search for correlations between the crystal structure and textural properties of aluminum oxide used as a support for a nickel catalyst in the liquid-phase reduction reaction of molecules of various geometries and containing one multiple carbon bond.

During the work, a whole complex of physicochemical methods of analysis was used: IR spectroscopy was performed on an Avatar 360 FT-IR ESP device in the range of 350-4000 $cm^{-1,}$ X-ray phase analysis was carried out on a Bruker D8 Advance diffractometer using CuKα radiation (λ = 0.15406 nm, voltage 40 kV, 20 mA, diffraction angles 2Θ=10º÷90º, scanning speed 4°/min, discreteness – 0.01º. To identify the X-ray phase analysis data, the MINCRYST crystallographic database was used), the method of low-temperature nitrogen adsorption. Microphotographs were taken using a VEGA 3 TESCAN scanning electron microscope. Measurement of the adsorption values of individual forms of hydrogen and their thermochemical characteristics was carried out using adsorption calorimetry, as well as a complex of simultaneous thermal analysis and mass spectrometry, which includes: a simultaneous thermal analysis device STA 449 F3 Jupiter® NETZSCH and a mass spectrometer

QMS 403 C Aëolos ®, PulseTA® reaction gas dosing systems, vacuum systems, as well as a high temperature oven and sensor for the STA 449 F3 Jupiter®.

The kinetics of the liquid-phase hydrogenation reaction was carried out using a static method in a batch reactor, which made it possible to measure the amount of hydrogen absorbed during the experiment. The dynamic operating modes of the paddle mixer ranged from 55-60 rpm, thus it was possible to remove the influence of external mass transfer on the experimental results. Water was used as a solvent. The following series of model unsaturated compounds was selected in this work: prop-2-en-1-ol, hexene, decene-1, oleic acid. The reduction kinetics of the listed compounds is well known; during hydrogenation, practically no by-products or intermediate products are formed; the selected compounds can be considered model compounds.

In a separate series of experiments, the influence of catalyst pre-reduction modes (maximum temperature, holding time, rate of temperature rise) was studied. The reduction was carried out in a separate reactor in a stream of hydrogen, after which it was transferred to a liquid-phase reactor under a layer of solvent, excluding contact with air. The catalyst activation method is described in detail in [2]. The objects of study in this work were supported nickel catalysts with a NiO concentration of 7.0±0.5 wt.%.

The work obtained a whole complex of kinetic and adsorption data that allows us to draw a number of conclusions about the influence of the textural properties of the catalyst substrate on its activity. The influence of the structure of aluminum oxide on the formation of active centers on the surface of the catalyst and, as a consequence, its adsorption properties with respect to hydrogen, has been experimentally proven. Thus, by selecting the nature of the substrate, it is possible to purposefully influence the concentration of adsorption forms of hydrogen on the surface of the catalyst.

Acknowledgement: The work was carried out within the framework of the state assignment for research work (Topic No. FZZW-2024-0004). The work plan has been agreed upon with the research work of the Scientific Council of the Russian Academy of Sciences on physical chemistry for 2024.

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PP-27

Application of Prothium Ortho-Para Conversion and Deutero-Hydrogen Exchange Reactions for Determination of the Presence of Magnetic Centres on the Surface of Metal Nanoparticles

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Reducing a macro object to the size of nanoparticles changes its properties, such as adsorptive, catalytic, optical and magnetic properties. Determining the magnetic properties of metallic nanoparticles requires unique and expensive equipment, and analysis on this equipment is not available to every laboratory. It is possible to determine the presence of magnetic properties of nanoparticles by studying the catalytic activity in prothium ortho-para conversion and deutero-hydrogen exchange reactions.

There are two spin isomers of hydrogen in nature: ortho-hydrogen and para-hydrogen. The equilibrium ratio of these modifications in a gas mixture is determined by its temperature. At temperatures above ~230 K, ortho-hydrogen with parallel spin orientation predominates with a fraction of 75%. As the temperature decreases, the equilibrium shifts towards vapour hydrogen with antiparallel spins, so that at 20 K the ortho isomer is virtually absent [1]. Without a catalyst in the gas phase, there is no change in spin [2]. On catalysts, conversion can occur by two mechanisms: magnetic and chemical. The first gives a 1-2 orders of magnitude higher rate of the process and takes place only on magnetic centres. Therefore, in order to determine the magnetic properties of the object under study, it is necessary to use a technique that allows us to distinguish between the magnetic and chemical mechanisms of the process. For this purpose, the deutero-hydrogen exchange reaction, which proceeds by a chemical mechanism, is used. The comparison of the rates of both reactions under the same conditions (taking into account the kinetic isotope effect) allows us to conclude that the reactions proceed by the same or different mechanisms. On this basis, a conclusion can be drawn about the conversion mechanism. If the conversion proceeds by a magnetic mechanism, this indicates the presence of magnetic centres in the catalyst under investigation [3-6].

As an example, the results of studies on silver nanoparticles deposited on aluminium oxide are presented. Figure 1 shows the temperature dependence of the specific catalytic activity in deutero-hydrogen exchange reactions and ortho-para conversion of protium. Isomeric conversion is indicated by white dots and hydrogen isotope exchange is indicated by black dots. The low (-196 - -163 °C), intermediate (-130 - 0 °C) and high (> 0 °C) temperature regions are highlighted in Fig. In the low temperature region, the rate of ortho-para conversion is 30-40 times higher than that of isotope exchange, so the reaction mechanisms are different. In the transition region, the catalytic activity for both reactions decreases with increasing temperature, indicating a gradual loss of magnetism by the nanoparticles for isomeric conversion and a change in the process mechanism for deutero-hydrogen exchange. At a temperature of ~0 °C, the catalytic activities in isotope exchange and para-ortho conversion are practically equal, indicating the same mechanism of the processes. The activation energy values confirm the transition from the magnetic (E = 0.2 kJ/mol) and Elley-Rideal (E = 2.5 kJ/mol) mechanisms to the high-energy Bongoffer-Farkas mechanism.

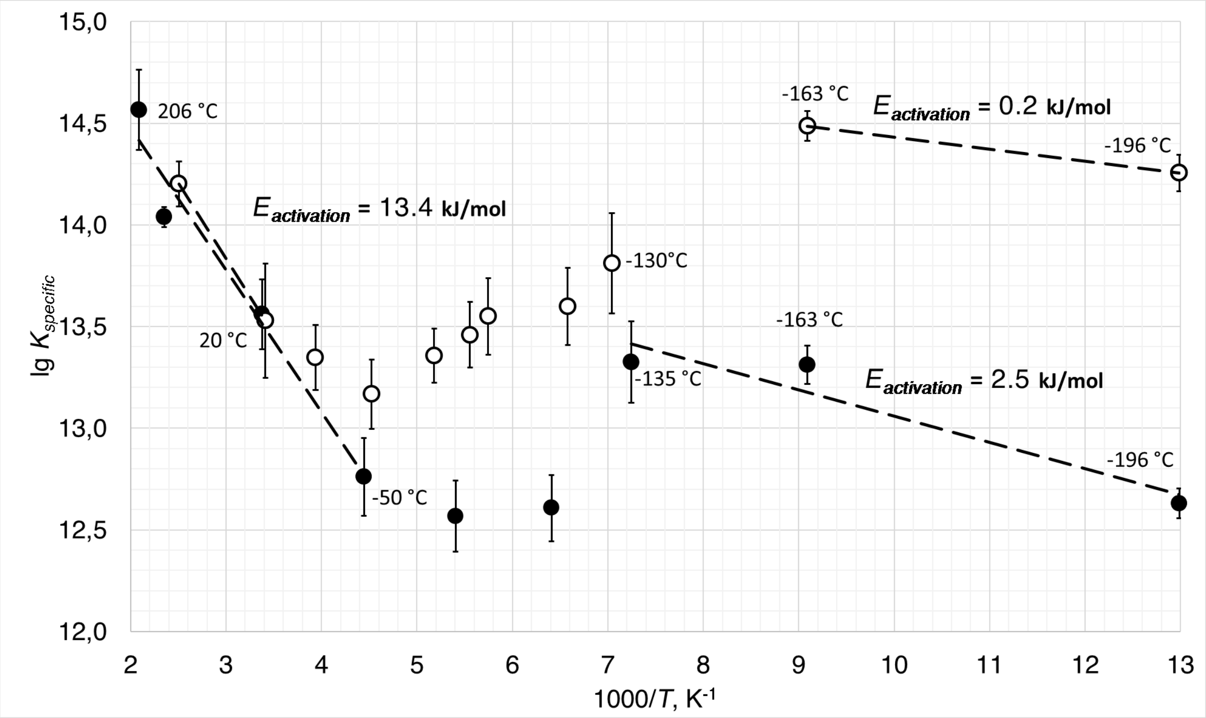

Figure 1 - Results of studies of catalytic properties of silver nanoparticles, given in Arrhenius coordinates: white dots - isomeric conversion; black - deutero-hydrogen exchange

Thus, by comparing the ratio of reaction rates in ortho-para conversion of protium and deutero-hydrogen exchange, it is possible to determine the presence of magnetic properties in the investigated catalytic systems.

Acknowledgement: The work was carried out with financial support within the framework of the development program “Priority-2030” of the Mendeleev University of Chemical Technology of Russia.

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PP-28

The Effect of the Production Method on the Physico-Chemical and Catalytic Properties of $CuO/ZnO/Al_2O_3$ Catalysts of the Large-Capacity Methanol Synthesis Process

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According to the forecast of experts who spoke at the Methanol-2018 conference, by 2027 global demand for methanol could reach 135 million tons, with annual growth of about 5.5%. Russia produces about 5% of the global volume of methanol, being among its largest exporters. Every year, the domestic market for the production of this product grows within 1.5-2%. Attention should be paid to the fact that the market for methanol synthesis catalysts is occupied by three main manufacturing companies: Haldor Topsoe (Denmark), Perstorp (Sweden), Clariant (Switzerland).

Currently, industrial methanol synthesis is carried out by processing synthesis gas obtained by catalytic reforming of natural gas. This is the most rational and cheapest way to get it. This process is implemented on copper-zinc-aluminum and copper-zinc-chromium oxide catalysts. The first studies on copper-containing catalysts for the synthesis of methanol appeared in print about a hundred years ago. Despite the fact that research on these catalysts has been going on for quite a long time, interest in them has not waned. Over the past 5 years, more than 500 scientific papers have been published in various sources on the technology and catalyst for the synthesis of methanol. This is due to the great importance of these catalysts for industry and the development of new technologies and methanol synthesis units, including large unit capacity. Quite a lot of works have been devoted to the synthesis of methanol [1-3], including those published in recent years [4-6], while, despite the various variations proposed by the authors, the compositions of catalysts are the leading compositions based on copper-zinc-aluminum and copper-zinc-chromium oxide systems with different ratios of individual components, the nature and amount of additives introduced [7]. Catalysts containing copper exhibit their maximum activity at a temperature of 220-280 ° C and a pressure of 3-5 MPa. Methanol synthesis on copper-containing catalysts can be carried out both from CO, CO in the presence of CO_2, and from CO_2. In copper oxide catalysts, copper ions, under the influence of hydrogen, are reduced to metal with the formation of protons and oxidized by the interaction of protons with hydrogenated molecules, which gives them high activity [7]. The presence of zinc and aluminum oxides in the copper-containing catalyst helps to maintain a high dispersion of copper particles and prevent their sintering during the reaction.

It is necessary to pay attention to the fact that data on the regulation of the activity and selectivity of $CuO/ZnO/Al_2O_3$ for the production of methanol are very limited. In addition, there is practically no data on non-traditional methods of their production, such as mechanochemical, sonochemical and microwave synthesis.

The report will reflect the results of work on the laws of synthesis of $CuO/ZnO/Al_2O_3$ catalysts based on the methods of mechanochemical and "soft" mechanochemical synthesis combined with microwave processing. Synthesis was performed from anhydrous oxides ($CuO/ZnO/Al_2O_3$); hydrated nitrates $Cu(NO_3)_2 \cdot 3H_2O/Zn(NO_3)_2 \cdot 6H_2O/Al(NO_3)_3 \cdot 9H_2O$; with mechanochemical interaction in $Cu(NO_3)_2 \cdot 3H_2O/Zn(NO_3)_2 \cdot 6H_2O/Al(NO_3)_3 \cdot 9H_2O$ – $H_2C_2O_4$; $Cu(NO_3)_2 \cdot 3H_2O/Zn(NO_3)_2$ 6H2O/$Al(NO_3)_3 \cdot 9H_2O$ – $(NH_4)_2CO_3$; $CuO/ZnO/Al_2O_3$ – $H_2C_2O_4$. It is shown that samples with the best characteristics are obtained by mechanochemical treatment of a mixture of $Cu(NO_3)_2 \cdot 3H_2O/Zn(NO_3)_2 \cdot 6H_2O/Al(NO_3)_3 \cdot 9H_2O\text{-}H_2C_2O_4$ and $Cu(NO_3)_2 \cdot 3H_2O/Zn(NO_3)_2 \cdot 6H_2O/Al(NO_3)_3 \cdot 9H_2O\text{-}(NH_4)_2CO_3$ taken in a stoichiometric ratio from the calculation of the formation of metal oxalates and hydroxocarbonates of copper and zinc, respectively. Processing leads to intensive interaction already in the initial period of activation time. The maximum value of the specific surface corresponds to 65.4 and 77.2 m^2/g, respectively. A comparison of the properties of the obtained catalysts with catalysts prepared by traditional methods and industrial analogues of leading manufacturers showed their similar characteristics. The report will reflect the influence of the method of preparation, the nature and intensity of processing on the physico-chemical properties of the resulting catalysts. The effect of the preparation method on the phase composition and structure, specific surface area and porous structure, formation of the active phase of the catalyst and its dispersion, acid-base properties, activity and selectivity, thermal stability, pre-operational recovery processes, etc. has been established.

Since one of the main goals of the work is the development of analog catalysts and methods for their production, special attention in the research will be paid to the interpretation of the causes of changes in activity and selectivity. In this regard, a number of characteristics have been determined using methods of thermoprogrammed reduction, thermoprogrammed oxidation, and thermoprogrammed desorption. The main surface properties and activation energy were determined using the thermoprogrammed desorption method using probe CO_2 molecules. The adsorption properties of the catalyst with respect to hydrogen have been studied using a complex of synchronous thermal analysis and mass spectrometry. The correlation of physico-chemical properties with activity and selectivity is shown.

Acknowledgement: This work was supported by the Russian Science Foundation,
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PP-29

Glycerol Valorisation into Chemicals over Zeolite Catalysts

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Biomass is a rich source of renewable carbon, which can be converted using a range of technologies into environmentally friendly fuels and chemicals. A successful example is the biodiesel industry, which has been booming since 2000. In 2019, its consumption amounted to about 40 billion tons, which led to a sharp increase in the production of crude glycerol, the main by-product (about 10 wt.%) of the biodiesel industry. Overproduction of crude glycerol reduces its economic value. In this regard, effective methods of its valorisation trough transesterification, dehydration, carboxylation and other processes are highly required. Both the effectiveness of glycerol conversion and its selectivity are determined by a catalyst. Oxides of transition metals such as Cu, Mn, Zr, Ti, Fe, etc., both simple and complex, are quite successfully used in reactions of conversion of glycerol to acetol, acrolein and other products with high added value. The choice of the support and the method of immobilization of a catalyst on it also affect the efficiency of the catalytic reaction. Zeolites can act as such a support, which in itself is a catalyst for a number of important reactions. The combination of microporosity with acidic properties makes zeolite a unique catalyst. Microporous zeolites modified with Ag, Fe and Cu are well-known catalysts for various reactions [1-3], including glycerol conversion [4]. It is known that, along with acidic properties, the presence and structure of mesopores are important for increasing the kinetics of the reaction. There are various strategies to introduce mesoporosity: (i) microporous zeolites undergo additional processing in an alkaline medium to create disordered secondary porosity; (ii) pillaring of 2D zeolites with SiO_2 [5,6] etc.

In this contribution we report the results of our study of the conversion of glycerol to chemicals through dehydration on various microporous and mesoporous zeolite catalysts modified with Ag, Fe and Cu and provide a comparative analysis with other results available in literature focusing on the role of zeolite topology and secondary porosity.

Acknowledgement: This research was funded by the Russian Federation represented by the Ministry of Science and Higher Education of Russia, Agreement No 075-15-2023-611 dated August 30, 2023.

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PP-30

Advanced PtCo Catalysts Based on Platinum Acetate Blue for the Preferential CO Oxidation in H_2-Rich Mixture

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Zeolites modified with Co and Pt cations are of particular interest as catalysts for the selective oxidation of CO as part of the production of ultrapure hydrogen [1]. The selection of promoters, support and synthesis conditions can improve the catalyst characteristics and reduce the content of noble metal in them. Platinum acetate blue (PAB) of the empirical formula $Pt(CH_3COO)_{2.5\pm0.25}$, prepared according to [2] was used as a novel precursor for the synthesis of Pt/ and PtCo/ZSM-5 catalysts for the oxidation of carbon monoxide. The impregnation of ZSM-5 (Si/Al=15, 28 and 40) with PAB and its decomposition at 200°C results in the stabilization of highly dispersed PtOx particles on the zeolite surface. The properties of Pt-modified zeolite were improved by the addition of $Co(CH_3COO)_2$ followed by calcination at 450°C. Prepared samples were tested in total (TOX) and preferential (PROX) oxidation of carbon monoxide in H_2-rich mixture. According to SEM and TEM data, Pt and Co are distributed uniformly over the catalyst surfaces. Changes in the electronic state of the metals upon application to the zeolite surface and under catalytic tests were analysed by XPS and DRIFT spectroscopy of adsorbed CO. The XPS spectra of the Pt-catalyst ($Pt4f_{7/2}$), include two components, the binding energy of one of which is close to the value of 74.3 eV ($Pt^{2+\delta}$) in the original PAB, and the other with an energy of 72.7 eV (PtO). In bimetallic systems 2.5Co/0.1Pt/ZSM-5, a reduced form of Pt^0 (E = 71.4 eV) appears, and the proportion of oxidized forms of Co^{3+} increases compared to the monometallic analogue.

The relationship between synthesis conditions, structure, and catalytic behaviour of composites is discussed. The best synergistic effect of Pt and Co was observed when they both were located together on the zeolite surface. The reason is the formation of new active sites for the CO oxidation at the Pt-Co species interface. PtCo/ZSM-5 catalysts with only 0.1-0.2 wt.% Pt and 1-2.5 wt.% Co are extremely effective for the hydrogen purification. In the H_2 excess they provide the 100% CO conversion in the wide temperature range from 50 to 130°C that corresponds to the operating mode of proton exchange membrane fuel cells.

Acknowledgement: This work was performed within the framework of the state budget agreements (AAAA-A21-121011590090-7; 122040500058-1) and MSU Development Program.

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PP-31

Mechanism of Electrocatalytic Alkanethiols Transformations into Symmetric Disulfides in Ionic Liquids

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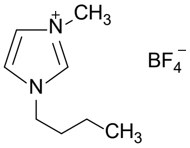
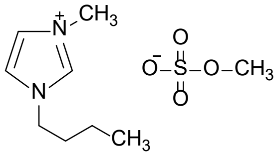
Recently, electrocatalysis has been used quite widely to stimulate organic transformations due to its high efficiency and selectivity [1]. The redox electrocatalysts make it possible to control the reactive intermediate compounds formation and reduce energy costs for chemical reactions compared to conventional organic synthesis [2].

Ionic liquids (IL) have high chemical stability and ionic conductivity, and are also characterized by wide "electrochemical windows". Due to these properties, ILs are successfully used in electrosynthesis, for example, of organic disulfides, as solvents. Additions of ILs to traditional solvents can significantly increase the efficiency of electrocatalysts (mediators) [3]. Dialkyl disulfides have antiproliferative, antiseborrheic, antieczematic and antitumor activity, anti-inflammatory, antipicornavirus effects [4]. Therefore, the development of new convenient and effective methods for the synthesis of disulfides is an urgent problem.

In this work we have proposed an electrocatalytic method for the production of isomeric dibutyl disulfides and dihexyl disulfides in a mixture of acetonitrile and **IL1** (**IL2**) at volume ratio 3:1. The ionic liquids under study contain the same cations (1-butyl-3-methylimidazolium) and different anions (tetrafluoroborate, methyl sulfate).

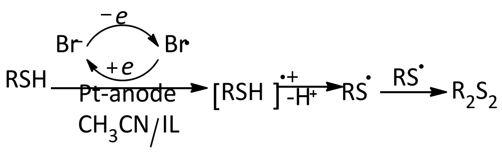


IL1



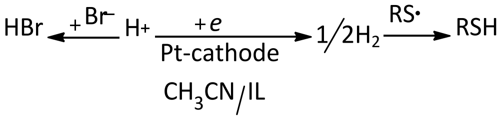
IL2

This method of dialkyl disulfides (R_2S_2) synthesis is implemented on Pt-electrodes, at room temperature, in the presence of a mediator – tetrabutylammonium bromide, that is easily regenerated during electrosynthesis. The mechanism of electrocatalytic transformations of alkanethiols (RSH), studied by the CV method, is described by the following scheme:



R = Alkyl (*n*-C_4H_9, *t*-C_4H_9, *n*-C_6H_{13})

$Br^-/Br^\bullet$ ((*n*-C_4H_9)$_4$NBr) – Mediator



The use of a mediator for the electrooxidation of RSH to R_2S_2 leads to a decrease in the anodic overvoltage of the electrode process by 0.8 V compared to the direct oxidation of alkanethiols. The results of the disulfides synthesis under electrocatalytic conditions are presented in the table.

Table - The dependence of disulfide yield, obtained by oxidation of RSH in the presence $N(n\text{-}C_4H_9)_4Br$ on various factors (CH_3CN/IL1(IL2) = 3:1, T = 298 K, τ = 90 min, E = 1,0 V).

RSH	**η (R_2S_2), %**		**φ, %**	
	IL1	**IL2**	**IL1**	**IL2**
n-C_4H_9SH	53,3	50,0	69,6	60,0
t-C_4H_9SH	46,7	33,3	84,3	66,7
n-$C_6H_{13}SH$	58,6	35,7	72,3	63,5

Note: **η** – the yield of the target reaction product (R_2S_2), **φ** – the degree of mediator's regeneration

When using **IL1** as a cosolvent, a higher yield of disulfides was observed than in medium **IL2**. This is due to the higher viscosity of **IL2** compared to **IL1** by (≈ 2 times). The efficiency of electrocatalysis is also influenced by the different electrical conductivities of ionic liquids: for an IL2 this parameter is 1,4 times lower. The structure of the alkanethiol has an ambiguous effect on the yield of disulfides and is limited by the nature of the ionic liquid.

Of the three thiols studied, the least reactive in the oxidative process was the tertiary RSH, which is explained by the branched structure of the alkyl radical. When comparing the ability of linear thiols for electrocatalytic oxidation, it was found that the yield of dibutyl disulfide is less affected by the **IL** structure and its values are comparable for **IL1**, **IL2**. In the case of using hexanethiol, the maximum yield of the reaction product is achieved in **IL1**, while in **IL2** the process of dimerization of hexylthiyl radicals is clearly hindered.

The degree of mediator regeneration in **IL1** was higher than in **IL2**. The losses of the mediator in the electrocatalytic cycle are explained by the presence of a chemical stage, as a result of which the proton generated from the alkanethiol radical cation interacts with the bromine anion. Therefore, varying the degree of mediator regeneration is consistent with changing the yield of disulfides. The consequence of the low value of this characteristic is the higher ability of the thiol to undergo electrooxidation under the conditions under consideration.

Thus, the work has developed an electrocatalytic method for the production of biologically active disulfides, characterized by environmental safety and energy saving.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-13-00201.

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PP-32

Mechanisms of Vegetable Oils Conversion in Catalytic Processing

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Significant growth and constant development of the transport system currently lead to great demand for commercial motor fuels.

An increase in the consumption of motor fuels leads to a reduction in non-renewable natural energy sources, in particular oil reserves. In addition, there is a deterioration in the quality of extracted feedstock, which entails an increase in capital and operating costs associated with its extraction and processing [1].

The actively developing direction of the "green economy" determines the prospects for the development of alternative energy, which will preserve mineral reserves and also have a positive impact on the environment [2].

In [3] it is shown that the processing of plant feedstock using a hydrotreating catalyst makes it possible to obtain hydrocarbons with properties identical to fuel hydrocarbons. However, the hydrotreating process produces long-chain hydrocarbons with unsatisfactory physicochemical and low-temperature properties. It is possible to improve the properties of products by carrying out a process based on cracking reactions. One such process is catalytic processing using zeolite catalysts [4].

This work shows the possibility of obtaining environmentally friendly components of motor fuels as a result of the catalytic processing of vegetable oils sequentially on two catalysts – on a hydrotreating catalyst, and then on a zeolite catalyst.

The following vegetable oils were selected as feedstock: rapeseed oil (RO), sunflower oil (SO) and corn oil (CO). Oil processing was carried out in a laboratory catalytic unit with the following technological parameters: temperature 375 °C, pressure 7 MPa, feedstock flow 0.08 ml/min, hydrogen flow 35 ml/min.

The possibility of obtaining motor fuel components from vegetable oils is confirmed by determining the composition of catalytic processing products using gas chromatography-mass spectrometry (table).

Table. Composition of products obtained by catalytic processing of vegetable oils

Compounds	pRO	pSO	pCO
n-alkanes	3.47	7.58	5.95
iso-alkanes	3.14	17.63	18.75
cycloalkanes	1.81	6.86	6.37
alkenes	1.99	2.23	2.31
alkynes	0.00	0.05	0.04
aromatics	68.31	48.26	48.58
oxygen-containing	1.45	2.33	2.31
unidentified	19.83	15.04	15.69

**pRO, pSO, pCO – processed products of RO, SO, CO*

The results of determining the of products obtained by catalytic processing of vegetable oils show that the composition of all products is represented to a greater extent by fuel hydrocarbons.

The mechanism of conversion of vegetable oils sequentially on a hydrotreating catalyst, and then on a zeolite catalyst, explains the results obtained when determining the group composition.

Fatty acids that make up vegetable oils are first hydrogenated during hydrotreating and then undergo thermal decomposition reactions to form predominantly monobasic fatty acids. The resulting monobasic acids, in turn, undergo decarbonization, decarboxylation and hydrodeoxygenation reactions, which result in the formation of long-chain n-alkanes [5-6].

On a zeolite catalyst, long-chain n-alkanes undergo skeletal isomerization and cracking. These reactions lead to the formation of iso-alkanes and alkenes. Alkenes, in turn, enter into diene synthesis reactions with the formation of naphthenes and in hydrogen transfer reactions with the formation of aromatic hydrocarbons and alkanes, as well as hydrogen. The occurrence of hydrogen redistribution reactions in alkenes with the formation of aromatic hydrocarbons and hydrogen, in turn, explains the high content of aromatic compounds in the composition of the resulting products [5-6].

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-23-00101.

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PP-33

XAFS Spectroscopy and DFT Modelling for Investigation of Cu-Zeolites Structure

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Zeolites are materials of the group of microcrystalline aluminosilicates. They have a framework structure consisting of aluminum and silicon atoms and may include transition metal atoms. Due to their structural features, zeolites are often used as catalysts in various industries including the processes of methane to methanol conversion [1,2].

In this work we investigated the structures of copper active centers in Cu-MOR zeolites at different stages of the catalytic cycle, which includes the oxygen activation step and interaction with methane at 200°C [3]. The copper centers in Cu-MOR were synthesized by solid-phase ion exchange using CuCl and H-MOR. X-ray absorption spectroscopy and computer modeling were used for studying of local atomic structure of active centers in Cu-MOR.

The calculation of Cu K-XANES spectra for a set of possible structural models of copper centers was performed by the finite difference method realized in the FDMNES software package [4]. Geometric optimization was performed using density functional theory (DFT) in the Quantum Espresso software package [5].

Analysis of the data obtained by the approach based on combination of X-ray absorption spectroscopy and DFT modelling allowed to establish the most probable models of the structure of active centers in the considered mordenite-type zeolites at different stages of the catalytic cycle.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-22-00438.

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PP-34

Features of the Kinetics of the Fischer-Tropsch Reaction on a Nanoscale Catalyst in Different Types of Slurry Reactors

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In recent decades, the need for renewable energy resources as an alternative to fossil fuels has been increasing. One of the processes for obtaining components of synthetic fuels and valuable chemical products is the Fischer–Tropsch synthesis (SFT) [1]. Various types of reactors are used for conducting SFT: with a stationary layer, with a fluidized bed, as well as three-phase slurry reactors [2]. The most important advantage of slurry reactors is the excellent mass-heat transfer characteristics [3]. Slurry reactors are divided into two types: bubbling suspension reactors (SBCR) and bubbling bed reactors (EBR) [4].

In the last decade, the above problems have been solved by using nanoscale iron and cobalt oxides (catalyst precursors requiring activation) or nanoparticles of these metals themselves as catalysts [5]. As a result of the rapid development of nanoheterogenic catalysis, it was found that nanoscale catalytic dispersions formed in situ directly in a liquid medium and forming colloidal nanosuspensions can also be used to carry out Fischer–Tropsch synthesis in the liquid phase [3].

The goal of the work is to study the behavior of nanoscale dispersions during the Fischer–Tropsch synthesis in three-phase reactors of different types: autoclave type with a stirrer and a bubbling mini-column reactor of equal volume.

Suspended Catalyst Fe/K with nanoscale particles was tested in the Fischer-Tropsch synthesis under the same conditions (temperature, pressure, volumetric velocity, reactor operating volume) in two types of bubbling reactors – an autoclave with a stirrer and a column with free bubbling. Nanoscale iron–containing catalysts for Fischer-Tropsch synthesis were prepared by thermal decomposition of a solution of a metal precursor and a promoter at 280°C while stirring in an inert gas current in a dispersion medium, which was used as molten petroleum paraffin P-2. Potassium oxide was used as a promoter.

In most experiments, a close or slightly lower value of the CO conversion achieved in a column reactor was revealed compared to a similar indicator achieved for a reactor with a stirrer (Fig. 1).

At space velocities of 25 and 100 h^{-1}, the CO conversion values in the bubbling reactor were predominantly lower or almost equal to the values for the reactor with a stirrer, although the opposite situation was systematically observed at 50 h^{-1}.

When analyzing the results obtained at different pressures in a bubbling reactor in comparison with a reactor with a stirrer, in some cases the CO conversion in the bubbling column turns out to be lower than in a reactor with a stirrer at the same temperatures and space velocity.

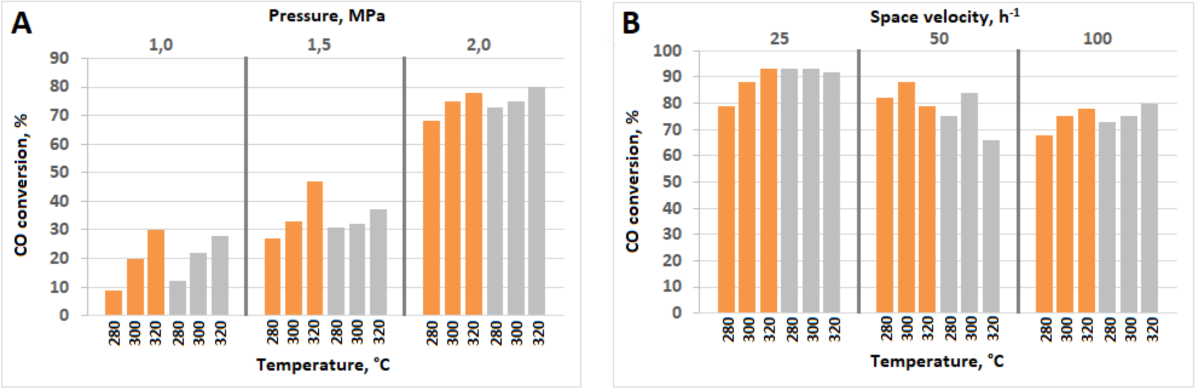

Fig. 1. Dependence of CO conversion on temperature in a bubbling reactor (🟧) and a reactor with a stirrer (⬜) at different pressures (A) and volumetric velocities (B).

This behavior contradicts both similar experimental comparisons known earlier [6-7] and theoretical ideas about the comparative efficiency of reactors with different flow structures. The kinetic estimation of the overall process speed using the 1-st order equation made it possible to cast doubt on the inhibition of the reaction in a column reactor by mass transfer at the gas/suspension interface. Kinetic estimation for both types of reactors using fractional order equations gives the values of the observed activation energies of 35-65 kJ, which indicates the reaction in the region transitioning to an external diffusion for both reactors. In combination, the results of kinetic evaluations indicate the presence of inhibition in the liquid/nanoparticle boundary region, which is hypothetically related to the dynamics of long-chain alkane molecules of the suspension medium in this area and may depend on the nature of the mechanical effect on this medium.

Acknowledgement: This work has been carried out in frames of the State Program of TIPS RAS.

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PP-35

Catalytic Destruction of Ozone in the Gas Systems ATLAS Detector Unit of the Large Hadron Collider. Argon

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The physicochemical calculations of the required amount of the GTT grade goptalum catalyst of ozone decomposition and the pressure drop on the catalyst bed under the operating conditions of the gas systems of particle accelerators were presented. The results of calculations were compared with the experimental data obtained in the gas system of the ATLAS detector unit of the Large Hadron Collider (LHC).

In the LHC, particle beams are accelerated in opposite directions and collide at special points controlled by recording units. One of them is ATLAS (A Toroidal LHC Apparatus). The internal detector consists of pixel and stripped silicon multichannel detectors (SCT) and proportional drift tubes (transition radiation trackers (TRTs)). TRT detector consists of 300 000 drift tubes (straws) [1], which are thin-walled tubes 0.004 m in diameter and 1.5 m in length. The inner surface of the tubes is covered with a conductive graphite layer and serves as a cathode. Each tube is filled with a gas mixture, which is ionized during the passage of charged particles. A gas mixture based on argon (70%) and carbon dioxide (27%) is used in the TRT drift detectors of ATLAS. With this gas filling, however, it impossible to achieve stable proportional gas multiplication without electrical breakdowns under conditions of uniquely high luminosity of LHC. To achieve stable operation of the detector without electrical discharges, a 3% electronegative addition of oxygen to the gas mixture was used.

However, ozone forms from oxygen at the detector anode under the influence of impact ionization in an avalanche of charged particles. On a test bench under laboratory conditions [1], the ozone concentration in the gas mixture of the TRT detector gradually increased to 120 ppm. It destroys the structural materials of the detector and gas system and is hazardous to the health of the personnel.

Therefore, in gas systems of this kind [1], filters with a special catalytic material must be used for ozone decomposition. The computational and experimental studies consisted in determining the amount and height of the protective layer and the pressure drop (resistance) on the catalyst bed of GTT grade goptalum based on manganese, copper and nickel oxides and high-alumina talum cement required for effective ozone decomposition in the gas system of the TRT detector of the LHC ATLAS unit.

Experiment -method 1. The gas system of the TRT detector of the ATLAS unit of LHC [1] consists of several subsystems schematically. The bulk volume of the GTT grade goptalum catalyst is 0.005 m ^{3}. The filters are located outside the irradiation zone; the gas mixture does not contain water vapor. Gas purification is controlled automatically. The ozone concentration in a real gas system was measured after the start-up of the ATLAS unit when the operating intensity of the beams from the Large Hadron Collider became 4 TeV. The gas mixture had the following compositions in experiments: 70% argon (Ar)–27% carbon dioxide (CO_2)–3% oxygen (O_2). To clarify the dynamics of ozone accumulation in the LHC gas system, the ozone concentration vs time was measured.

Experiment -method 2. The ozone decomposition on the GTT grade goptalum catalyst was studied on a laboratory catalytic flow-through unit at Moscow State University. The kinetic curves called ozonograms were obtained [1]. The dependence of the degree of ozone conversion (destruction) on the contact time of the gas mixture with the catalyst was obtained to determine the effective rate constant of ozone decomposition.

The geometrical dimensions of the ozone destructor bed determined in the theoretical calculations and laboratory studies are confirmed and effective under the real operating conditions of the TRT detector system of the LHC ATLAS unit. The physicochemical calculations of the required amount of the GTT goptalum catalyst of ozone decomposition, protective layer height, under the operating conditions of gas systems of particle accelerators are confirmed by the results of experiments for the gas system of the TRT drift detector of the LHC ATLAS unit. The GTT goptalum catalyst successfully prevents ozone damage to drift detectors, almost completely decomposing ozone in their gas systems.

The proposed computational and experimental method makes it possible to predict the characteristics of destructors with the GTT goptalum catalyst for effective ozone decomposition in the gas systems of particle accelerator detectors.

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PP-36

Heterogeneous Oxide Catalysts for Isotope Exchange between Carbon Dioxide and Water Vapor

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Due to the widespread use of products with a modified oxygen isotopic composition [1, 2], the task of separating oxygen isotopes is relevant. From a thermodynamic point of view, a promising system for separating oxygen isotopes is chemical isotope exchange (ChIE) between carbon dioxide and water. This system is characterized by almost an order of magnitude higher values of the enrichment coefficient compared to water rectification under vacuum [3].

$$H_2{}^{18}O_{(l)} + C^{16}O^{16}O_{(g)} \overset{Cat}{\Leftrightarrow} H_2{}^{16}O_{(l)} + C^{16}O^{18}O_{(g)} \qquad (1)$$

Isotope exchange between carbon dioxide and liquid water (1) has poor kinetics, which leads to large values of the height equivalent to theoretical plate (HETP) and, accordingly, large column heights. The process can be intensified by using a heterogeneous catalyst, but it is necessary to avoid wetting the active centers of the catalyst by hydrophobizing it [4] or carrying out the process in contact devices, in which contact of liquid water with the catalyst grain is excluded, such as, for example, membrane-type contact devices (MCD) [5], previously developed in D. Mendeleev University of Chemical Technology of Russia to carry out isotope exchange between molecular hydrogen and water.

The development of a highly efficient heterogeneous catalyst is one of the main tasks of research in the field of oxygen isotope separation by chemical isotope exchange between carbon dioxide and water. The paper presents the results of studies of the activity of catalysts based on oxides of rare earth metals, as well as iron group metals, deposited on a carrier – gamma alumina. All experiments were carried out in dynamic mode under the same conditions: temperature in the reactor 75 °C; carbon dioxide flow 26.6 nl/h; the molar ratio of carbon dioxide and water vapor flows is 8.2.

A comparison of the observed rate constants for the isotope exchange reaction between carbon dioxide and water vapor on catalysts based on rare earth metal oxides is presented in Figure 1. However, the most active catalysts in the reaction under study were samples based on iron group metal oxides – Fe_2O_3/Al_2O_3, CoO/Al_2O_3 and NiO/Al_2O_3. Under the same process conditions, the values of the observed rate constant were 1.50 ± 0.17 s^{-1}, 2.13 ± 0.20 s^{-1} and 5.49 ± 0.36 s^{-1}, respectively.

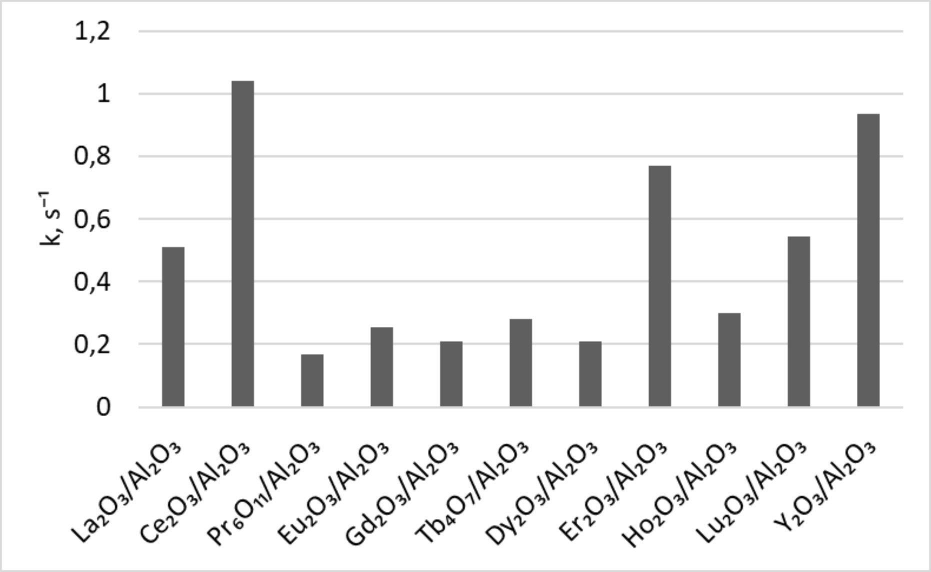

Fig. 1. Comparison of the observed rate constants of the isotope exchange reaction between carbon dioxide and water vapor on heterogeneous catalysts

The studies carried out made it possible to identify the most promising oxides for creating highly active catalysts for isotope exchange between carbon dioxide and water vapor. These include oxides of cerium, erbium, yttrium, iron, cobalt and nickel.

Acknowledgement: The work is performed in the framework of the development program "Priority-2030" of the Mendeleev University of Chemical Technology of Russia.

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PP-37

Kinetic Modeling of Fischer-Tropsch Synthesis of Liquid Hydrocarbons from CO_2

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In view of the global trend towards limiting CO_2 emissions into the atmosphere, the study of the carbon dioxide processing into valuable petrochemical products is relevant. In recent years, modified Fischer-Tropsch synthesis (CO_2 – FTS) has been actively studied. A mixture of carbon dioxide and hydrogen is used as feedstock, and CO is produced in situ in the reactor through the reverse water gas shift (RWGS) reaction. Numerous models describing the kinetics of traditional Fischer-Tropsch synthesis have been published. However, these models are not suitable for CO_2-FTS. At the moment, only a few studies out on the kinetics of the synthesis of liquid hydrocarbons from CO_2 have been carried. At the same time, a reliable CO_2-FTS kinetic model remains to be developed.

In this work, a kinetic model for the synthesis of liquid hydrocarbons from CO_2 and H_2 on the Fe/K@γ-Al_2O_3 catalyst has been developed. The synthesis was carried out in a fixed-bed reactor in the temperature range 280-320°C, pressure 10 bar, H_2/CO_2 ratio = 2-4, contact time 2-20 g(cat)*s/ml [1].

A mechanistic model is proposed to simulate hydrocarbon synthesis. The model assumes the presence of two types of active centers. At active centers of the first type, RWGS-reaction occurs according to the redox mechanism. At active sites of the second type, the hydrocarbon chain grows according to the alkyl mechanism. The reaction rate equations are compiled according to the Langmuir–Hinshelwood mechanism. This model is an adaptation of the three-center model proposed by C. Pantone [2].

The values of the rate and adsorption constants were calculated by minimizing residual sum of squares of molar flows using a genetic algorithm and the Levenberg-Marquardt method. The obtained kinetic parameters led to describe the experimental data with a relative error of less than 20% (Fig. 1).

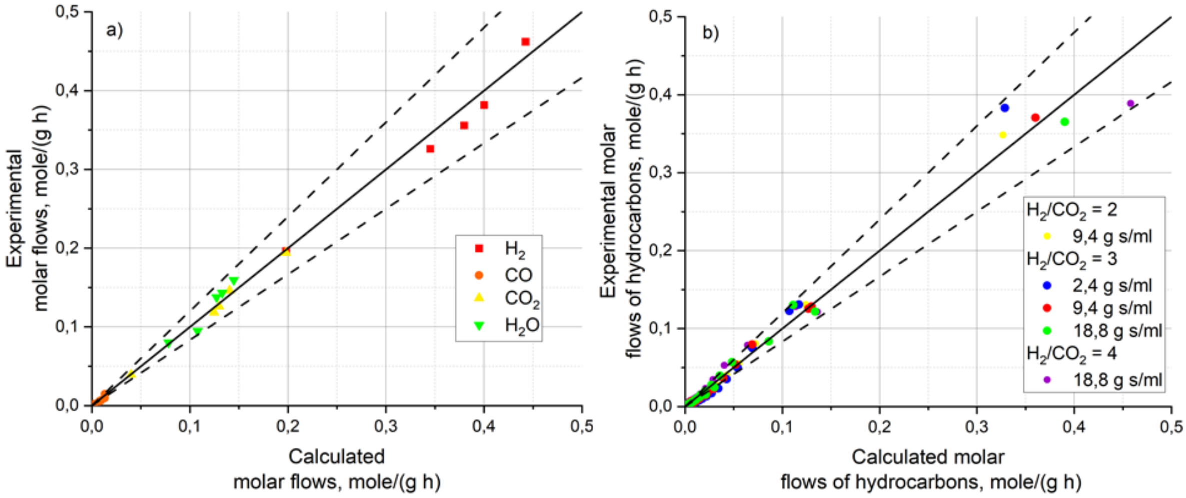

Fig. 1. Correlation of experimental and calculated molar flows of H_2, CO, CO_2, H_2O (a) and hydrocarbons C_5-C_{19} (b). Dashed lines correspond to a relative error of 20%.

Acknowledgement: This work was carried out within the State Assignment of the A.V. Topchiev Institute of Petrochemical Synthesis of the Russian Academy of Sciences.

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PP-38

Synthesis of Acetylene Alcohols in Different Catalytic Systems

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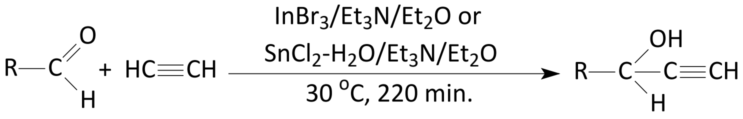
Acetylene alcohols are currently used in the production of hormones, vitamins, inhibitors, solvents and dyes [1]. One of the most common methods is the synthesis of acetylene alcohols, based on the asymmetric combination of aldehydes and ketones with alkynes [2].

In this research work, the catalytic systems $SnCl_2/Et_3N/Et_2O$ and $InBr_3/Et_3N/Et_2O$ were used based on the reactions of enantioselective ethynylation of acetylene with some aldehydes- thiophene-2-carbaldehyde (**1**), 3-methylthiophene-2-carbaldehyde (**2**), furan-2-carbaldehyde (**3**), pyridine-3-carbaldehyde (**4**), quinoline-2-carbaldehyde (**5**) and 3-bromo-4-pyridinecarbaldehyde (**6**) the synthesis reactions of the corresponding acetylene alcohols 1-(thiophenyl-2)propyn-2-ol-1 (**7**), 1-(3-methylthiophenyl-2)propyn-2-ol-1 (**8**), 1-(furanyl-2)-propyn-2-ol-1 (**9**), 1-(pyridinyl-3)propyn-2-ol-1 (**10**), 1-(quinolinyl-2)heptin-2-ol-1 (**11**), 1-(3-bromopyridinyl-4)propyn-2-ol-1 (**12**) were studied. Based on literature sources, the following reaction scheme of the process is proposed [3, 4].



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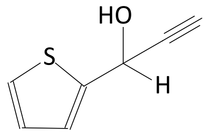

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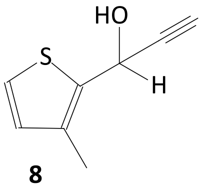

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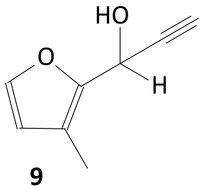

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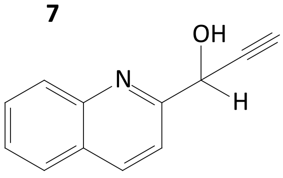

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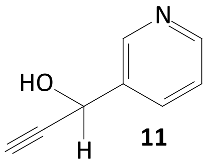

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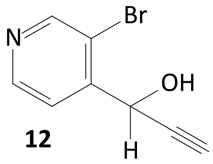

12

The influence of the complex systems used on the efficiency of the formation of acetylene alcohols is proposed. A number of factors influencing the yield of the product have been studied - temperature, reaction time, catalyst and solvents, substrates and reagents. Based on the results obtained, the most alternative conditions for the processes were found.

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INFORMATION NOTES

IN-01 ÷ IN-03

IN-01

Articles on the Thematics of Conference «Mechanisms of Catalytic Reactions» in the Journal *Russian Chemical Bulletin*

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* In 2022—2023 following articles were published: **heterogeneous catalysis** (see for example, 2022, **71**, p. 64, 70, 220, 524, 1164, 1179, 1194, 1204, 1402, 1422, 1579, 1641, 1837, 1847, 1863, 1930, 1940, 1949, 2052, 2076, 2085, 2142; 2023, **72**, p. 269, 325, 367, 393, 853, and others); **biocatalysis** (2022, **71**, p. 158, 524, 915, 1402, 2342; 2023, **72**, p. 42, 83, 617, 1612, 1618, 1932, 1648, 1661, 1673, 1680, 1688, 1701, and others).

IN-02

The *Mechanisms of Catalytic Reactions Conferences* (MCR 1974-2024) Database

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Scientific Conferences contribute much in scholarly communication. Due to this, they are under permanent discussion in the professional communities [1] including scientometric analysis. The initial information for the latter is, however, scattered over numerous sources, many of which are not easy to access. It is much suitable when the information is deposited in bibliographic databases in more or less organized form allowing its online search and further use.

During the 40 years, Boreskov Institute of Catalysis (*BIC*) serves as the permanent organizer of the *Mechanisms of Catalytic Reactions* (*MCR*) periodical Conferences. Since the first event proceeded in 1974 in Moscow, Russia, as the *All-Soviet Union Conference on Mechanisms of Heterogeneous Catalytic Reactions*, their history counts 11 Conferences *MCR-I – MCR-XI*, and the current Conference is *MCR-XII*. The 1974-2024 Conferences archives include ~ 2600 presentations (Figure 1) by *ca.* 5000 participants affiliated with more than 600 research organizations from 60 countries. Over this period numerous relevant materials are issued in both printed and electronic formats.

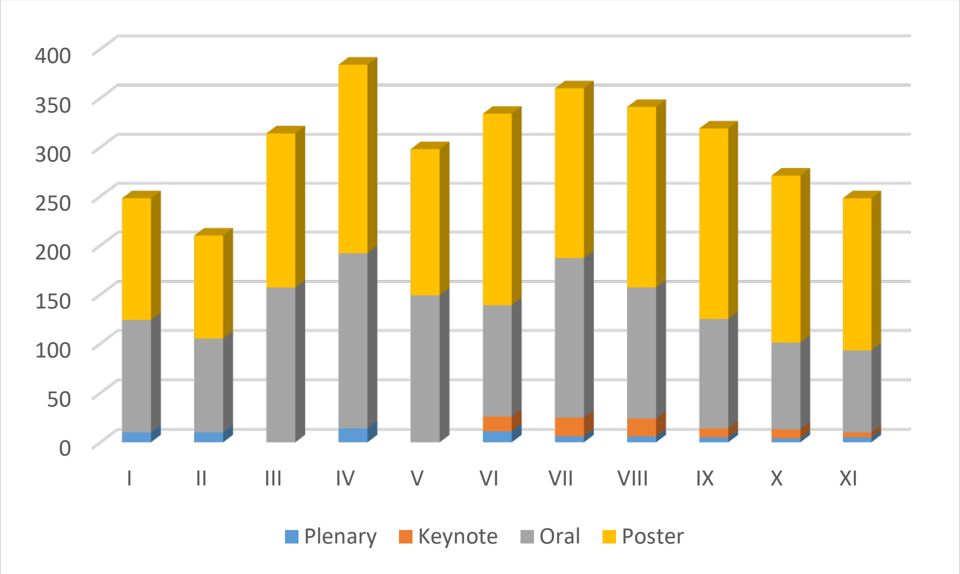

Fig. 1. Numerical distribution of presentations at MCR-I – MCR-XI

Taking into account obvious scientific value of the materials, a special *Mechanisms of Catalytic Reactions Conferences* database [2] is designed at the *BIC*. The database contains the Conferences' announces and circulars; programs; lists of contributions and participants; as well as Books of Abstracts. Overall, the Conferences' titles; chrono- and geolocations; names of organizing institutions; general and specific research themes; titles and abstracts of contributions; contributions' types (plenary, invited, key, oral, or poster); contributors' names featuring speakers; and contributors' affiliations.

In addition to documentation, particularly tracking full stories of the specific researches from Conferences' reports to eventual journal articles [1] (*cf.* the *MCR-I – MCR-XI* Books of Abstracts and selected articles in the *Kinetics and Catalysis* journal), it is important that such type databases are useful for research administration and management. Thus, they support timely identification of emerging research directions and fronts, search of new research partners, etc. Last not least, they facilitate continued organization of periodical Conferences.

Acknowledgement: The authors are grateful to M. S. Suvorova for provided materials, and the Ministry of Science and Higher Education of the Russian Federation for financial support within the State Assignment for Boreskov Institute of Catalysis (project FWUR-2024-0034).

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[2] URL: https://biblhelper.catalysis.ru/ru/public/conferences/MCR

IN-03

Scientometric Analysis of Presentations at the *Mechanisms of Catalytic Reactions* Conferences (1974-2024)

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With specially designed *Mechanisms of Catalytic Reactions Conferences* database (https://biblhelper.catalysis.ru/ru/public/conferences/MCR), a scientometric analysis of the presentations given therein has been performed. The initial status of the event as All-Soviet Union Conference than was transformed in the Russian, followed by the Russian with International Participation (*MCR-VI*, 2002), and, finally, the International Conference (*MCR-VIII*, 2009). The analysis encompasses 2600 presentations of the 50-year period 1974-2024 (*MCR-I – MCR-XI*, Figure 1) by *ca.* 5000 participants affiliated with more than 600 research organizations (Table 1) from 60 countries (Figure 2).

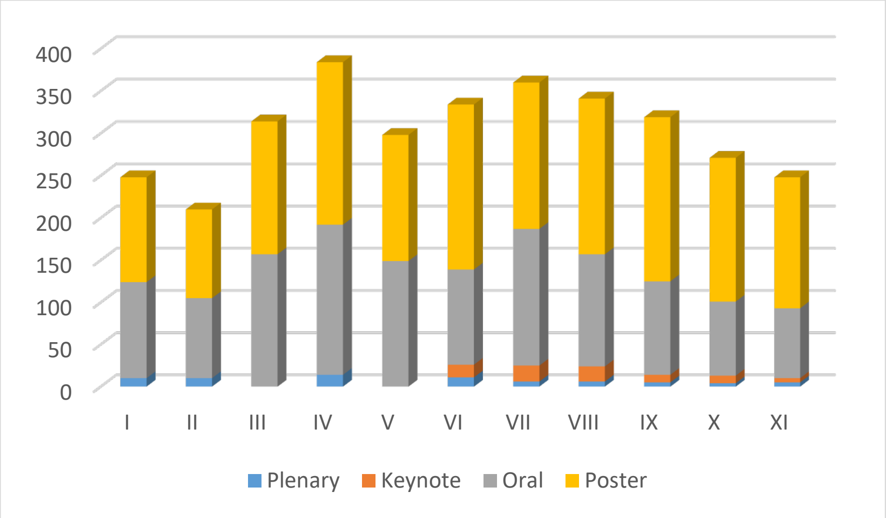

Fig. 1. Numerical distribution of presentations at MCR-I – MCR-XI

Table 1. Most active research organizations and numbers of their contributions

Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences	604
Lomonosov Moscow State University	166
National Research University – Novosibirsk State University	144
Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences	135
Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences	131
Topchiev Institute for Petrochemical Synthesis, Russian Academy of Sciences	72

Fig. 2. The Conferences Participants' Geolocation

Acknowledgement: The authors are grateful to M. S. Suvorova for provided materials, and the Ministry of Science and Higher Education of the Russian Federation for financial support within the State Assignment for Boreskov Institute of Catalysis (project FWUR-2024-0034).

VIRTUAL PRESENTATIONS

VP-01 ÷ VP-41

VP-01

Iodosulfonylation of Internal Alkynes Photoinitiated by Red Light

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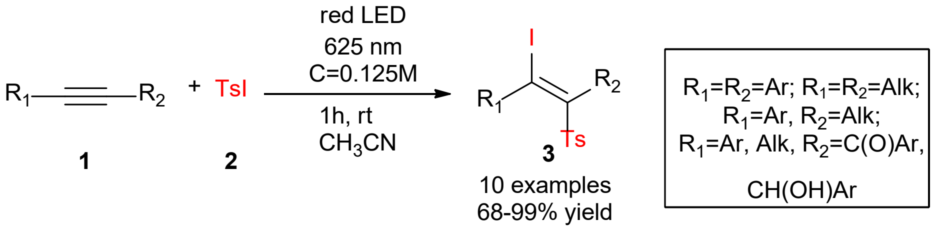
Organosulfur compounds, including sulfones of various types such as β-halogen vinyl sulfones and their derivatives, play a significant role among the diverse classes of organic compounds. They are highly valued for their extensive utilization across a wide range of human activities **[1,2]**. These compounds possess the SO_2 group and halogen atom and can be modified by substituting the halogen atom with other functional groups.

Currently, vinyl sulfones are obtained through 1,2-functionalization of the triple bond **[3,4]**. Previously, we proposed a method for radical iodosulfonylation of internal alkynes under the influence of light with λ_{max} = 400 nm and using 2 equivalents of TsI **[5]**. The process was shown to occur in high yields as well as with high regio- and stereoselectivity.

In this study, we carried out the reaction of iodosulfonylation of a number of internal alkynes under the action of arylsulfonyl iodides in a molar ratio of 1 : 1 under red light irradiation with a wavelength of 625 nm. These conditions were identical to those employed for iodosulfonylation reactions under 400 nm irradiation. The reactions at 625 nm wavelength showed comparable high yields and selectivity.



Scheme. 1. Preparation of β-iodovinyl sulfones

Acknowledgement: This work was carried out as part of the A. V. Topchiev Institute of Petrochemical Synthesis (TIPS) Russian Academy of Sciences (RAS) State Program. This work was performed using the equipment of the Shared Research Center «Analytical center of deep oil processing and petrochemistry of TIPS RAS». The work was supported by the Russian Science Foundation (project No. 19-13-00223 P).

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VP-02

$GdFeO_3$ Catalysts for the Conversion of $CO+CO_2$ to Low Molecular Weight Olefins

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The striving of sustainable development dictates the global trend towards reducing greenhouse gas emissions and preventing global warming and makes it urgent to elaborate and develop environmentally friendly chemical technology processes that should become more cost-effective, energy efficient and resource-saving than currently existing ones. The utilization of CO_2 by converting it into valuable products is one of the urgent tasks of the modern chemical industry [1-3].

In this study, we investigate the effect of the presence of carbon dioxide in the reaction medium $CO:H_2$ on the yield of reaction products and selectivity of light olefins using a complex oxide catalyst with a perovskite structure. The catalyst, GdFeO3, was synthesized using a sol-gel technique under atmospheric pressure. The prepared sample was characterized using XRF, BET, DSC/TGA.

According to the results of the experiments, it has been found that the addition of CO_2 to the reaction mixture results in an increase in the conversion of carbon monoxide while maintaining the qualitative composition of the major reaction products (C_1-C_5 hydrocarbons). Additionally, it has also been observed that even though the rites of product formation decrease in the presence of CO_2, there is an increase in selectivity towards ethylene and propylene ***(Figure 1).***

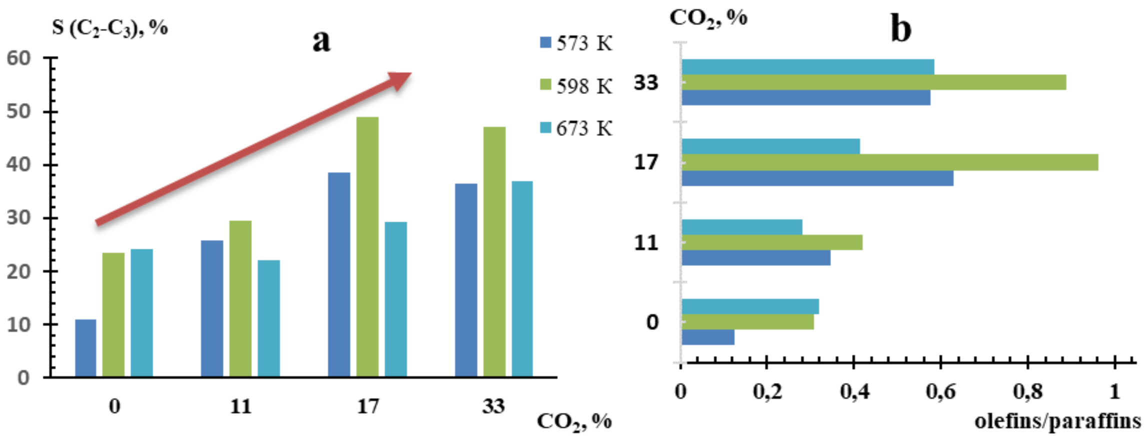

Figure 1. *Temperature dependences of selectivity for light olefins at different ratios of $CO: CO_2: H_2$ reagents (a) and the ratio of the amount of olefins to the amount of paraffins (b)*

The determination of kinetic characteristics (effective activation energies for product formation and pre-exponential multipliers) revealed that an increase in CO_2 content in the reaction mixture resulted in a decrease of Ea* and $\ln k_0$. It can therefore be concluded that the enhanced selectivity towards olefins is due to an energy-based factor.

The modified Fischer–Tropsch route of CO_2 hydrogenation could occur via redox (dissociation of CO_2 to CO and O) or via an associative mechanism, in which hydrogen reacts with CO_2 to form the intermediate HOCO [4]. This intermediate then decomposes into CO and OH, the latter being hydrogenated to H_2O. In addition, there is also evidence for the third reaction mechanism leading to the formation of stable HCOO species [5]. For example, by applying the Born–Oppenheimer molecular dynamics simulation, Lin et al. concluded that, even for low kinetic energies, both Eley–Rideal and hot atom mechanisms occur [6]. In the case of Fe-based catalysts, the formation of oxygenates and hydrocarbons is believed to occur through the CO insertion and surface carbide mechanisms, respectively. The CO_2 molecule can be initially reduced to CO by H_2 via RWGS at the Gd sites, followed by hydrogenation of CO to olefins via the FTO reaction at the Fe sites.

Acknowledgement: This work was supported by the Russian Science Foundation,
grant № 24-29-00341, https://rscf.ru/project/24-29-00341

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VP-03

Transfer Hydrogenation of Ketones Catalyzed by Manganese Complexe with Chiral Diamines Ligands

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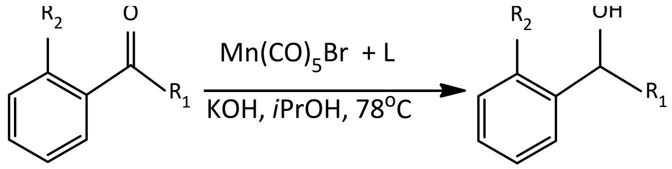
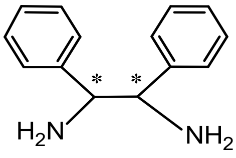
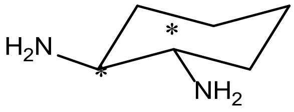
The asymmetric reduction of ketones by manganese complexes has not been fully studied [1, 2]. The reduction of ketones with 2-propanol as reductant was achieved using an in-situ generated catalytic system based on manganese pentacarbonyl bromide, as metal precursor, and several chiral diamine as ligands. The reaction proceeds in high yield at 78 °C, in 0,2-5,0 h, with a ratio substrate:catalyst of 100:1 (1 mol% of catalyst). In the presence of chiral bidendate diamines, as the ligands (see below), sterically hindered alcohols were produced with enantiomeric excess up to 75%.



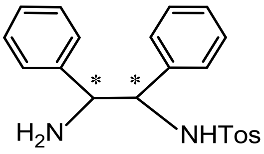
Bi- and tetradentate chiral diamines (**I-IV**) used in the reduction of ketones (**1-6**) in the presence of $Mn(CO)_5Br$ and KOH in 2-propanol:



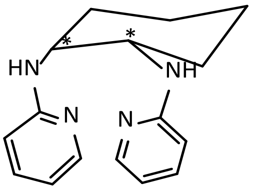
R,R-DPEN, **I**



R,R-Cydiamine, **II**

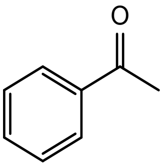


R,R-Tos-DPEN, **III**



R,R-Pyrdiamine, **IV**

Ketones:



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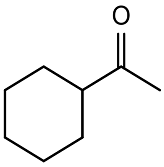

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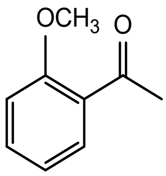

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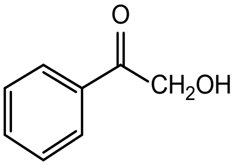

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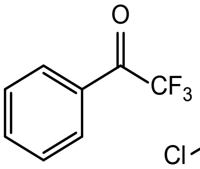

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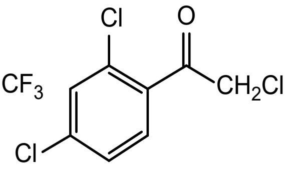

6

Table. Chiral bidentate nitrogen based ligands for the reduction of ketones in the presence of $Mn(CO)_5Br$ and KOH in 2-propanol (C_{Mn} = 1.6 mM, solvent – i-PrOH)

Entry		Ligand	Sub	Time, h	Conv., %	W_{init}, mM/h	TOF, h^{-1}
1	БН-5[1]	R,R-DPEN	APh,**1**	1	100	-	
2	БН-6	R,R-DPEN	APh,**1**	3,0	100	96,6	60,4
3	БН-10	R,R-diaminoCy	APh,**1**	1,0	100	60,6	37,9
4	БН-11	R,R-Pyrdiamine	APh,**1**		0	0	0
5	БН-7	R,R-DPEN	MeCyKetone,**2**	3,4	100	68,4	42,8
6	БН-8	R,R-Pyrdiamine	MeCyKetone,**2**	0,2	10	9,6	6,0
7	БН-9	R,R-diaminoCy	MeCyKetone,**2**	2,2	100	66,6	41,6
8	БН-14	R,R-DPEN	2’-metoxy APh,**3**	0,5	100	36,0	22,5
9	БН-15	R,R-DPEN	2’-metoxyAPh,**3**	0,4	100	60,0	37,5
10	БН-16	R,R-diaminoCy	2’-metoxyAPh,**3**	1,2	100	90,0	56,3
11	БН-12	R,R-DPEN	2-HydroxyAPh,**4**	1,5	0	0	0
12	БН-13	R,R-diaminoCy	2-HydroxyAPh,**4**		0	0	0
13	БН-17	R,R-DPEN	2,2,2-Tri-fluoro-APh,**5**	1,7	100	54,0	33,8
14	БН-19	R,R-DPEN	2,2',4'-Tri-chloroAPh,**6**	1,25	0	0	0

[1] - C_{Mn} = 0.32 mM

The reduction of acetophenone (**1**) proceeded well with in-situ generated catalysts based on (1R,2R)-N,N’-DPEN ligand **I** and (1R,2R)-N,N’-cyclohexyl-1,2-diamine **II**, as a full conversion of acetophenone into 1-phenylethanol was observed after 3 and 1 h, respectively. At the same time, R,R-Pyrdiamine as a ligand did not promote the hydrogen transfer for the reduction of acetophenone.

Methylcyclohexylketone (**2**), 2’-metoxyacetophenone (**3**) and halogenated tri-fluoro-acetophenone (**5**) were reduced with 100% yield (Table) in the presence of (1R,2R)-N,N’-DPEN ligand (**I**). The (1R,2R)-diamino-1,2-cyclohexane (**II**) as ligand in manganese system was very effective in the transfer hydrogenation of the acetophenone, methylcyclohexylketone (**2**) and 2’-metoxyacetophenone (**3**). The substrates, such as 2-Hydroxyacetophenone **(4)** and the 2,2',4'- Tri-chloroacetophenone (**6**) did not reduce with **(**1R,2R)-DPEN and (1R,2R)-diamino-1,2-cyclohexane as ligand

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VP-04

Photocatalytic Activity of $CsM_{0.25}W_{1.75}O_6$ (M = Ni, Co, Mn, Cu) β-Pyrochlores in Organic Pollutants Degradation and Kinetic Study

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Nowadays, the stable structural types of pyrochlore oxides have been actively employed as active photocatalytic materials for wastewater treatment. This study deals with the preparation of novel $CsM_{0.25}W_{1.75}O_6$ (M = Ni, Co, Mn, Cu) compounds with β-pyrochlore structure and investigation them in the photocatalytic degradation of methylene blue (MB), phenol (Ph), levofloxacin (LFX), and isoniazid (INH).

The photocatalysts were fabricated by a solid-state reaction followed by grinding in a planetary ball mill. For the preparation of the $CsM_{0.25}W_{1.75}O_6$ β-pyrochlores, nickel carbonate, cobalt nitrate, manganese carbonate, and copper carbonate were used as M precursors. Stoichiometric amounts of cesium nitrate, tungsten (VI) oxide and the M precursor were ground in an agate mortar. The obtained mixtures were annealed at 900 °C for 20 h in air at a heating rate of 5 $°C\cdot min^{-1}$. The prepared materials were denoted as CsNiWO-1, CsCoWO-1, CsMnWO-1, and CsCuWO-1. Then, these samples were grinded in a planetary ball mill for 18 h with a speed of 300 min^{-1} using ethanol as a process control agent and dried at 80 °C in air for 12 h, and labeled as CsNiWO-2, CsCoWO-2, CsMnWO-2, and CsCuWO-2.

To evaluate the efficiency of β-pyrochlores in the degradation of emerging pollutants, an aqueous solution of MB (20 $mg\cdot L^{-1}$), Ph (10 $mg\cdot L^{-1}$), LFX (20 $mg\cdot L^{-1}$), and INH (20 $mg\cdot L^{-1}$) were used. 0.03 g of a photocatalyst was suspended in 50 mL of a pollutant solution, and the system was stirred in the darkness for 60 min to achieve the adsorption-desorption equilibrium. The obtained suspension was irradiated using a 30 W domestic LED lamp for 360 min. All experiments were performed in the absence and presence of H_2O_2. As can be seen from Fig. 1(a), the materials after grinding in the planetary ball mill (CsMWO-2) are characterized by much greater photocatalytic activity in the degradation of the dye pollutant compared to the bulk powders (CsMWO-1) due to an improved specific surface area and adsorption capacity towards MB. Moreover, this investigation demonstrated that the use of Ni-containing tungstate leads to the greatest efficiency since doping with Ni^{2+} provides higher photogenerated charges lifetime and lower recombination rate of electron–hole pairs compared to other transition metals (Co, Mn, Cu, etc.) [1]. Additionally, the pseudo-first order kinetic rate constants (k) for the photodegradation reaction were calculated (Fig. 1(b)), and the rate constants were determined to be 0.00085, 0.00036, 0.00031, 0.00048, 0.00214, 0.00058, 0.00103, and 0.00073 min^{-1} for CsNiWO-1, CsCoWO-1, CsMnWO-1, CsCuWO-1, CsNiWO-2, CsCoWO-2, CsMnWO-2, and CsCuWO-2, respectively.

VP-04

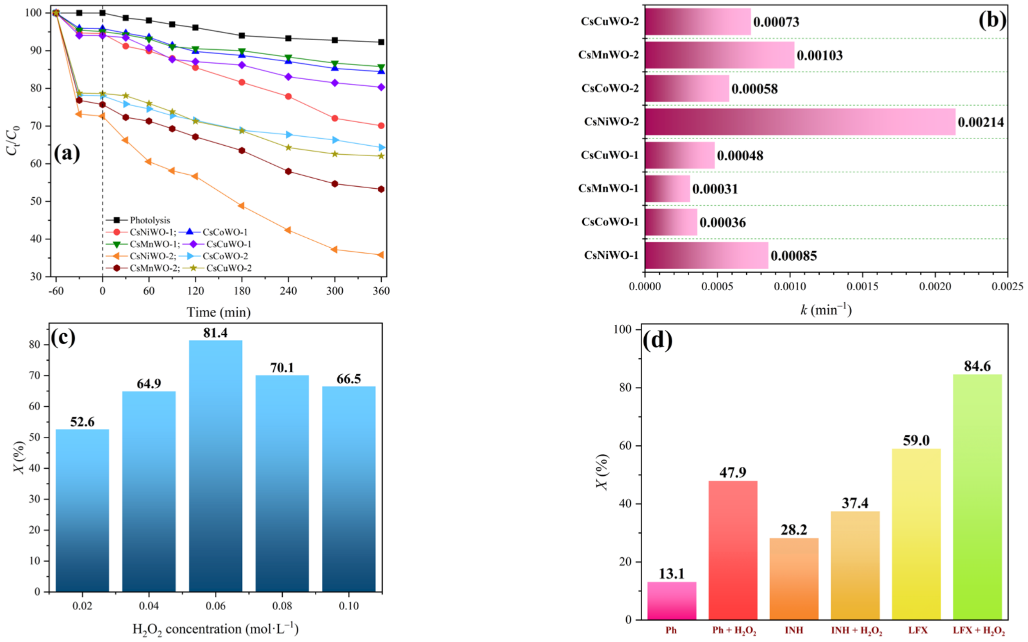

Fig. 1. (a) Photocatalytic activity and (b) pseudo-first order kinetic rate constants for MB degradation. (c) Effect of H_2O_2 concentration on conversion of MB on CsNiWO-2. (d) Conversion of Ph, INH, and LFX on CsNiWO-2 in the presence of H_2O_2 after 360 min.

Fig. 1(c) shows that the addition of small amounts of H_2O_2 had a positive effect on the conversion (X) of MB within 360 min. The highest value of MB conversion was observed at the concentration of hydrogen peroxide of 0.06 mol·L^{-1}. A decrease in the conversion at high concentrations of H_2O_2 may be associated with self-scavenging of $^{\bullet}OH$ radicals by H_2O_2 with the formation of less active hydroperoxyl radicals ($^{\bullet}OOH$) [2].

It is well-known that an ideal photocatalyst should have multifunctional properties, i.e., should be active in the degradation of pollutants with different nature [3]. As shown in Fig. 1(d), excellent and promising results were obtained for LFX degradation under visible light irradiation using H_2O_2 (0.06 mol·L^{-1}) and a cheap 30 W LED lamp.

In summary, the present study potentially contributes to designing efficient pyrochlore oxides for wastewater treatment and environmental remediation.

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation (project No. FSWR-2023-0024).

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VP-05

Substrate Structure Influence on the Micellar Effects of Cationic Gemini Surfactant in Alkaline Hydrolysis of Model Ecotoxicants

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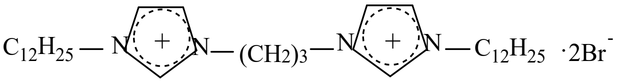
Gemini surfactants (GS) represents a unique class of compounds with abnormally low ***cmc***s, high surface activity, positive potential of micellar surface what makes these systems highly attractive for practice. Between dimeric surfactants, especially interesting are dicationic GS as a basis for organized microheterogeneous systems (OMS) for destruction of ecotoxicants, including phosphororganics. Hydrolytic reactions with hydroxide-ion pave the simplest way to construct such an OMS. In the current investigation we discuss kinetics of base catalysed hydrolysis of model compounds – analogues of ecotoxicants: 4-nitrophenyl esters of phosphonic (NPDEPN), phosphorous (NPDEP) and 4-toluenesulfonic (NPOTos) acids, in the OMS based on cationic GS of type I-III.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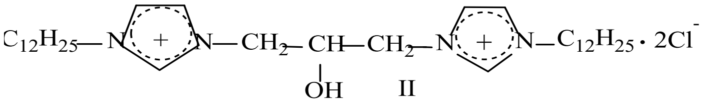
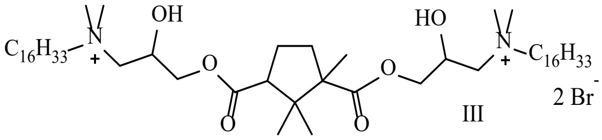

II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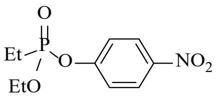
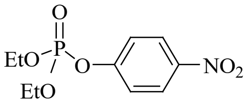
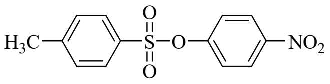
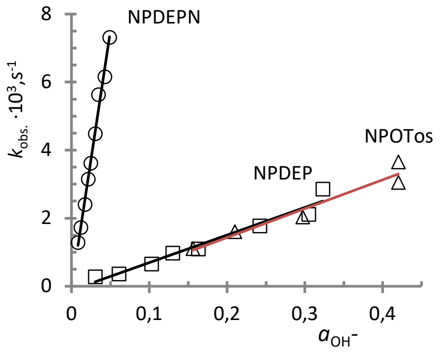

·NPDEPN


·NPDEP


·NPOTos

Micellar effects in OMS under study directly depend upon substrate structure. The set of substrates looks well-chosen. From one point, NPDEPN exceeds NPDEP and NPOTos in reactivity by approx. 10-fold. From another, NPDEPN and NPDEP both concede NPOTos in effectiveness of solubilization by approx. 10-fold. This combination of physicochemical properties makes possible to evaluate the role of substrate structural features in micellar catalysis upon transfer of base catalysed hydrolysis into micellar pseudophase. Really, a magnitude of observed acceleration depends on effectiveness of solubilization of ester, reaction centre electrophilicity, and nucleophilicity of hydroxide-ion in OMS. In water, substrates under study make a sequence NPDEPN > NPDEP ~ NPOTos (Fig.1). For OMS based on GS and monomeric surfactants, the maximal catalytic effects were found for NPDEPN as a rule, whereas for NPDEP and NPOTos values of $k_{\mathrm{obs}}^{\mathrm{m}}$ usually are comparable (Fig.2).



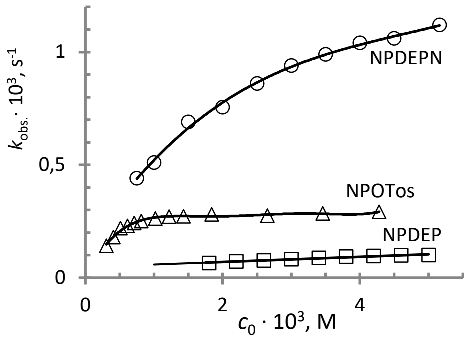


Fig.1.First order rate constants $k_{obs.}$, s^{-1} vs hydroxide concentration a_{OH^-} for base catalysed hydrolysis of some esters; water, 25°C

Fig.2.First order rate constants $k_{obs.}$, s^{-1} vs initial concentration c_0 of GS I for base catalysed hydrolysis of some esters; water, pH 11.0, 25°C

Kinetics of base catalysed hydrolysis were analysed in a frame of pseudophase partitioning . model (PPM). It was found that catalytic effects of transferring process from water to GS micelles can achieve (10-100)-fold. Not only reagents concentration but changes in nucleophilicity of hydroxide governed by its microarrangement contribute to rate enhancement. It is possible quantitatively evaluate contributions of these effects to observed rate enhancement by equation

$\left(\frac{k_{obs.}^{m}}{k_{obs.}^{w}}\right)_{max}=\frac{k_2^{m}}{k_2^{w}}\cdot\frac{K_S\cdot K_{HO^-}}{V_m(\sqrt{K_{HO^-}}\sqrt{K_S})^2}$, where k_2^{W} и k_2^{m}, $M^{-1}\cdot s^{-1}$ – second order rate constants for HO^- reaction in water and micellar pseudophase; K_S and K_{OH^-}, M^{-1} – equilibrium constants for binding of substrate and nucleophile. Usually, concentrating of reagents play determining role in micellar effects. It is glaringly seen in a case of GS II and III (Fig. 3a,b) where maximal micellar effects are noted for NPOTos. Introduced hydroxyl group (GS II) or ester spacer (GS III) open additional possibilities for intermolecular interactions, facilitating saturation of micellar pseudophase with water molecules.

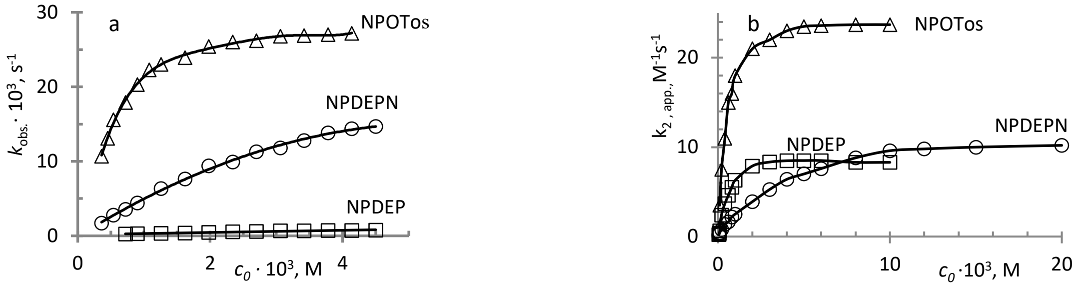


Fig.3 Rate constants (observed first order (a) and apparent second order (b)) vs initial concentrations of GS II (a) and GS III (b) for base catalysed hydrolysis of esters, pH 11.0, 25°C

It looks dubious that further intensification of GS based micellar catalysis could be achieved by simple variation of polar group spacer or alkyl tail lengths. Functionalization of surfactant molecule may be a promising way.

VP-06

Influence of the Nature of Transition Metals on the Electrocatalytic Activity in ORR CNTs Doped with Phthalocyanines of Metals and Modified with Silver

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Fuel cells are one of the most promising sources of environmentally friendly electricity, using hydrogen as fuel. They are widely used in various fields such as the automotive industry, energy, aerospace and in everyday life. FC have a number of advantages and disadvantages. FC have a high energy conversion coefficient, which makes them more efficient than traditional energy sources, do not emit harmful emissions such as carbon dioxide or other pollutants, which makes them promising for use in various fields.[1] The main disadvantage of FC, which limits their widespread use, is expensive materials, in particular, platinum, which are part of the catalysts, in particular, the use of platinum. Recently, scientists have been conducting research to find effective inexpensive non-platinum catalysts for thermal power plants. The most promising oxygen reduction catalysts (ORR), as studies show, are carbon nanotubes (CNT) modified with various metals. The purpose of this study was to study the influence of the nature of the transition metal on the electrocatalytic activity in the oxygen reduction reaction.

For this purpose, samples of catalysts based on carbon nanotubes were synthesized, which were doped with phthalocyanines (Pc) of cobalt(II), copper(II) and nickel(II) and modified with silver atoms[2]. The pyrolysis of the catalysts was carried out in an inert nitrogen atmosphere at a temperature of 900 °C. The resulting catalysts were designated MWCNT_CoPc_Ag, MWCNT_CuPc_Ag and MWCNT_NiPc_Ag.

The activity of the obtained catalysts in the reaction of electrical oxygen reduction was studied by the voltammetric method. A potentiostat was used-a galvanostat with a three-electrode electrochemical cell. A disk rotating glass-carbon electrode with the catalyst under study served as a working electrode. The reference electrode was a mercury oxide electrode. It can be seen from the graphs that MWCNT_CoPc_Ag is closest to the platinum catalyst in terms of its properties. In relation to other synthesized samples, the MWCNT_CoPc_Ag potentiometric curve has a narrower region of mixed kinetics and a more pronounced region of limiting current (Fig. 1). The kinetic and thermodynamic parameters of the studied catalysts are shown in Table 1.

SEM analysis of the synthesized catalysts showed the preservation of the structure of carbon nanotubes, as well as the formation of spherical metal particles with a diameter from 100 nm to 3 microns on their surface. Raman analysis showed the appearance of defects in the MWCNT structure, the largest number of them was observed in the MWCNT_CoPc_Ag catalyst. Defects in carbon nanotubes are presumably associated with the formation of additional active centers on the surface due to the formation of pyrolyzates formed during high-temperature synthesis.

Table 1.

Parameters of synthesized samples in ORR

Catalyst	**E_{onset},V**	**E½,V**	**J_{dif}, mA/cm^2**
Pt/C	0.05	-0.10	2.634
MWCNT_NiPc_Ag	-0.22	-0.39	1.741
MWCNT_CuPc_Ag	-0.16	-0.31	1.673
MWCNT_CoPc_Ag	-0.10	-0.20	2.075

Based on the research results, it can be concluded that the most effective catalyst is MWCNT_CoPc_Ag. This is probably due to the electronic structure of the metal, which determines the most optimal shape of the activated complex, as well as the largest number of defects on the surface of the carrier. The activity of this catalyst is closest in terms of electrocatalytic properties to platinum.

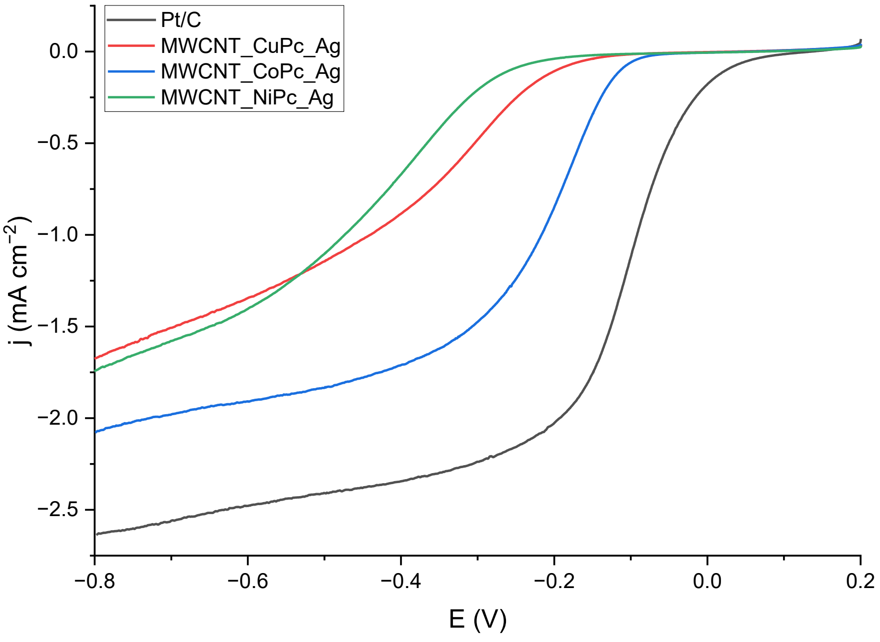

Fig. 1. Linear voltammograms of the studied catalysts.

Acknowledgement: The research was carried out at the expense of a grant from the Russian Science Foundation No. 23-73-00063, https://rscf.ru/en/project/23-73-00063.

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VP-07

DFT Modeling of the Mechanisms of Catalytic Allylation of Norbornadiene in the Presence of Palladium Complexes

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Recently, papers [1] devoted to the catalytic allylation of norbornadiene (NBD) with allyl formate (AF) in the presence of Pd complexes are regularly published. The reaction in one technological stage leads to a number of diverse polycyclic compounds, among which there are monomers that are difficult to obtain for the polymer industry, figure. 1. Methods of density functional theory (DFT-PBE/L11) were used to simulate the mechanisms of interaction between NBD and AF in the presence of Pd complexes of various compositions [2, 3].

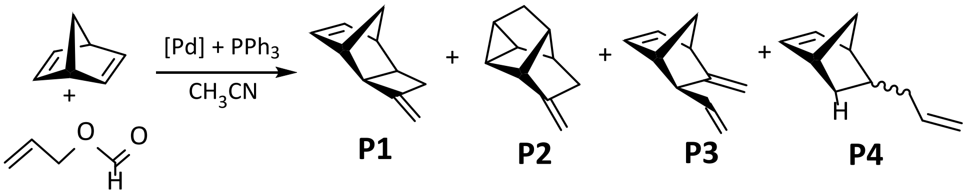

Fig. 1. The main products of allylation of NBD with allylformate in the presence of palladium phosphine complexes.

It has been established that the rate-determining step for all routes of allylation of NBD is the formation of the first C-C bond, since the step is characterized by the maximum activation barrier. The predominant formation of *exo*-structure products in the presence of phosphines is associated with a lower transition state energy of this step, because it is also responsible for the stereostructure of the product.

It was shown that the formation of the hydroallylation product (**P4**) proceeds along two routes with similar activation energies, which differ in the order of the steps of C–C bond formation and β-hydride elimination. In the absence of phosphine ligands, the regioselectivity of obtaining the **P4** product is mainly due to the large activation barriers of the step of formation of second C-C bonds in the routes of oxidative allylation products (**P1**-**P3**) formation. The introduction of PPh_3 ligands reduces the Gibbs energy of activation of this step, thereby opening the way to other products.

Representations about the course of key steps were detailed. Thus, for example, the formation of η^3-allyl complexes of Pd occurs through the formation of a five-center transition state. The cleavage of the C–C bond, leading to the product **P3**, proceeds in the methylenecyclobutane fragment by the type of β-carbon elimination. The cleavage of C–H bonds during β-hydride elimination is possible with the participation of β-agostic Pd complexes.

Based on calculations [4] using the DFT-ωB97X-D3(BJ)/ZORA-def2-TZVP/SARC-ZORA-$TZVP_{Pd}$ method, it was shown that it is possible in principle to obtain a noticeable enantiomeric excess in the reaction using chiral alkylarylphosphine ligands. In this case, the most optimal is the presence of one aryl substituent in the phosphine. In addition, chiral phosphines can affect the regioselectivity of the reaction for products of the same stereostructure (*exo* or *endo*).

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-73-00123.

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VP-08

Kinetics of Hydrogen Evolution during Sodium Borohydride and Ammonia Borane Hydrolysis using Cobalt Catalysts

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Among the numerous hydrogen storage systems, the predominant materials are sodium borohydride $NaBH_4$ (SB) and ammonia borane NH_3BH_3 (AB). Hydrolysis is a convenient way to produce hydrogen from borohydrides, since this reaction can start at room temperature, proceed quickly using various catalysts, and it can be controlled or stopped by removing the catalyst from the solution.

There is a need for active and stable catalysts to accelerate the hydrolysis reaction by reducing the activation energy of this reaction. Cobalt-based catalysts, due to their high catalytic activity and low cost, are an alternative to noble metals for hydrogen production.

A better understanding of the kinetics of the hydrolysis reaction and the development of a reliable kinetic model is an area of great importance in the study of a borohydride-based hydrogen production system.

The kinetics of the catalytic hydrolysis of ammonia borane [1] and sodium borohydride with cobalt catalysts: metallic cobalt and cobalt oxide Co_3O_4 on zeolite and zinc oxide substrates, as well as $Co(OH)_2$, Co_3O_4 and mixed catalysts with the active part of cobalt borides of variable composition Co-B has been investigated. The reaction order, rate constants and apparent activation energy of the reaction, the rate of hydrogen release during hydrolysis in the temperature range of 35-80 °C have been determined. The concentrations of ammonia borane, sodium borohydride and NaOH in aqueous solution have been 0.078 M, 0.064 M and 0.06 M, respectively. The amount of the active part of the catalysts on the carriers (ZnO, zeolite) have been determined by chemical method and amounted to 7.5–10% of the total mass of the catalyst (0.04 g).

The kinetic data processing has been carried out using the first-order, zero-order and Langmuir-Hinshelwood reaction models. A comparison of the values of the apparent activation energy in the hydrolysis process (SB) and (AB) is shown in Fig.1.

The values of the apparent activation energy during the hydrolysis of sodium borohydride are in the range from 37.0 for Co_3O_4 to 72.6 kJ/mol for Co_3O_4/ZnO. These values exceed similar values during the hydrolysis of ammonia borane [1], which are in the range of 26.0 – 47.4 kJ/mol.

VP-08

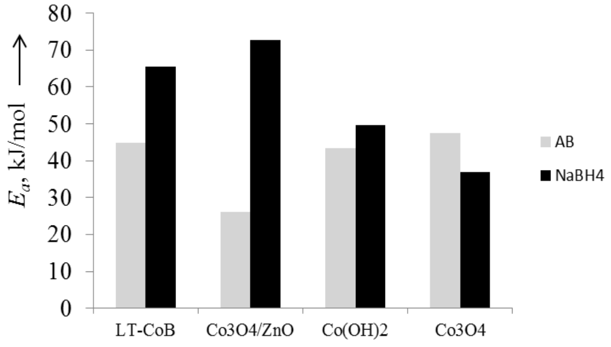

Fig. 1. The activation energy comparison of sodium borohydride and ammonia borane the hydrolysis reaction using cobalt catalysts

The dependences of hydrogen evolution on time can be approximated by a polynomial, and the rates of hydrogen evolution at the initial moment are calculated from the derivative of these functions (Fig.2).

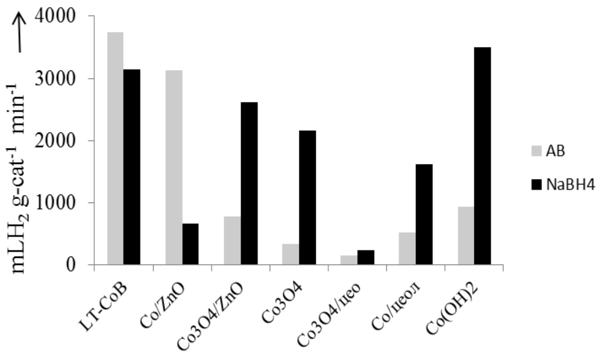

Fig. 2. Hydrogen release rates in the hydrolysis reaction of sodium borohydride and ammonia borane using cobalt catalysts

A high rate of water release is observed during the hydrolysis of sodium borohydride in combination with ammonia borane using catalysts, with the exception of Co-B and Co/ZnO catalysts. The maximum rate of water release is gained by using $Co(OH)_2$catalysts and Co-B and amounts to 3510 and 3750 mL H_2·(g-cat)$^{-1}$·min^{-1}, respectively.

The studied cobalt catalysts are quite effective and can be used in the production of hydrogen by hydrolysis of sodium borohydride and ammonia borane to power fuel cells in low- and medium-power plants.

Acknowledgement: The work was performed according to the state task No. 075-01304-23-00.

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VP-09

Supercomputer Simulation of Coke Sedimentation Burning from a Cylindrical Grain of a Hydrotreating Catalyst

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The volume of production of domestic catalysts is growing against the background of import substitution. Obviously, the question arises about the deactivation of catalysts and methods of restoring catalytic activity (regeneration). The regeneration time becomes an essential factor for the stable operation of many chemical and technological processes. The great capabilities of modern computing complexes and the increased role of big data methods, the development of new parallel computing technologies and their effective adaptation to the needs of mathematical modeling can significantly reduce the time spent on study of catalyst regeneration. If a lot of modeling experience has been accumulated for spherical catalysts, then little attention is paid to other geometric grain shapes. Supercomputer modeling of heat and mass transfer processes in cylindrical catalyst grains is becoming relevant given the scale of the increase in the use of cylindrical catalysts. On the one hand, supercomputer modeling methods are becoming crucial in creating simulators for operators and students of the chemical technology field, on the other hand, they allow them to quickly solve industrially significant scientific problems at the nanoscale. For example, it make it possible to accurately predict the course of an industrial process, reactor heats, the accumulation of explosive substances or the production of substances harmful to the environment. As is known, any software of this purpose is based on a mathematical model [1]. Modeling grains of a shape other than spherical is currently an interesting task due to the abundance of catalyst types [2, 3].

The report is devoted to the numerical study of a mathematical model for burning sulfur sedimentation from a cylindrical catalyst grain [4]. A parallel algorithm for calculating the main characteristics of the process has been developed for the computer implementation of the model. The model is described by a system of nonstationary equations of mathematical physics. The splitting by physical processes is used to build a computational algorithm. Separately, calculations of concentration changes during chemical reactions, forced convection and diffusion flows were carried out [5].

The constructed model corresponds to the law of mass conservation: the material balance of the solid and gas phases is maintained in dynamics. The developed software meets an important task of the chemical industry – the need for a detailed study of the chemical process at the micro level. The implemented parallel algorithm has shown good efficiency even on a small number of calculation nodes, which will allow calculations to be performed without the use of complex computing complexes – as a rule, any computer now has two or more processors.

The result of the program is the concentrations' distribution across the catalyst grain, as well as the dynamics of concentrations over time. The efficiency of the algorithm allows for multiple calculations in order to establish optimal values of the catalyst pore diameter, gas temperature, reagent concentrations, etc.

The development and software implementation of adequate multi-level, multi-scale mathematical models of grain and catalyst layer in the form of systems of ordinary nonlinear differential equations and partial differential equations will allow for a deep system analysis of chemical reactors with a fixed catalyst layer, which consists of numerous grains of different designs (spherical, cylindrical, etc.), where multi-scale hydrodynamic processes with complex physical properties take place (chemical and thermal phenomena) [6]. The efficiency and scalability of the parallel implementation of numerical methods shows the possibility of using the results of this work to create a computer analogue of existing industrial reactors and chemical technology devices. Computer simulators, on the one hand, allow to increase the profitability of industrial chemical plants, on the other hand, to train highly engineering specialists for the oil refining and petrochemical industries.

Acknowledgement: The work of Gubaydullin I.M. was funded by the Institute of Petrochemistry and Catalysis of the Russian Academy of Sciences (theme No. FMRS-2022-0078). The work of Yazovtseva O.S. was supported by the grant of the Russian Science Foundation No. 19-71-30012, https://rscf.ru/en/project/23-71-33002/.

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VP-10

Tungsten Oxide and Al-SBA-15 Based Catalysts for Oxidation of Sulfur Compounds of Petroleum Origin

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The rapid industrialisation of cities is currently increasing global energy demand. Energy production and transport cause significant emissions of hazardous gases, including sulphur oxides (SO_x), nitrogen oxides (NO_x) and carbon monoxides, into the atmosphere. SOx emissions are a serious problem for the environment as they contribute to acid rain and air pollution, which adversely affects the ecosystem and human health. The presence of pollutants in fuels also leads to the deactivation of valuable metal catalysts such as nickel and palladium, which are commonly used in car exhaust treatment [1].

There are various methods for removing sulphur compounds such as hydrotreating, oxidative desulphurisation, extractive desulphurisation and adsorptive desulphurisation. The cost of hydrotreating is high because high reaction temperature and pressure are required to effectively remove inactive sulfides. Compared to other methods, oxidative desulphurisation has attracted the most attention due to the simplicity of the process and mild reaction conditions [2].

It is known that heterogeneous systems including transition metal oxides and carrier are used as promising catalysts for oxidative desulphurisation. Studies show that the oxidation process of sulphur compounds is more active in acidic medium. One of the simplest and most effective ways to increase the acidity of the catalyst is to modify the SBA-15 type carrier with aluminium. The inclusion of aluminium in the structure of mesoporous carrier leads to the formation of a large number of Brønsted and Lewis acid centres on the carrier surface, which in turn promote more active oxidative desulphurisation reactions [3].

In the report W/Al-SBA-15 catalysts containing aluminium from 1 to 5 wt.% and tungsten from 2.5 to 10 wt.% were synthesized. The effect of aluminium on the acidity of the catalyst was studied by the method of thermo-programmed ammonia desorption. It was experimentally confirmed that incorporation of aluminium into the structure of SBA-15 carrier leads to the increase of acidity and to the increase of DBT conversion efficiency. The effects of the main oxidation parameters such as reaction time, temperature, catalyst composition and amount, and amount of oxidant on the conversion of DBT were investigated. The catalyst 5%W/5%Al-SBA-15 provides complete conversion of DBT to sulfone in 20 min at 60°C and four times excess of hydrogen peroxide. The optimum conditions for the oxidation of a DBT-based model mixture with 10000 ppm sulphur content are 80°C, 3 wt% catalyst, 3 mL acetonitrile and 60 minutes. The 5%W/5%Al-SBA-15 catalyst can be used for at least five cycles without significant loss of activity.

VP-10

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VP-11

Modeling of Alkene Insertion into Complexes of $Cp_2ZrMeCl$ with Chain-Type Methylalumoxane

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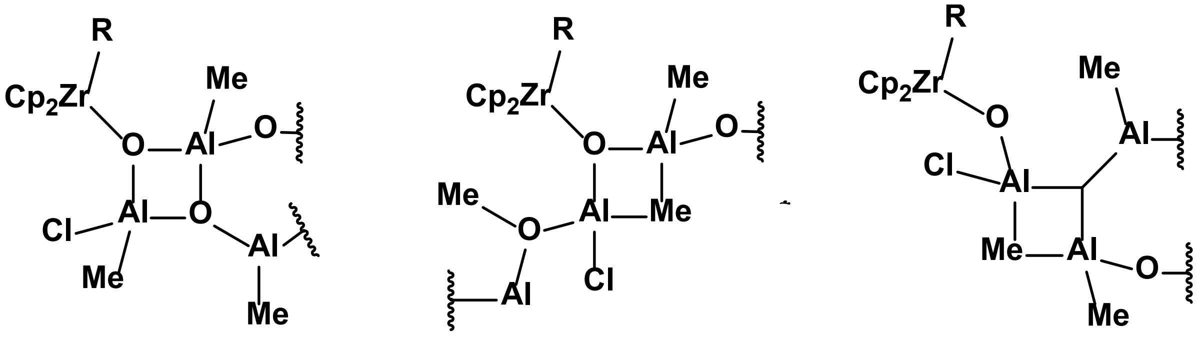
The discovery of the Ziegler-Natta polymerisation in the 1950s marks a significant milestone in the history of organic chemistry. This catalytic process, based on active organometallic complexes, became an effective tool for the synthesis of polymers with high stereospecificity. In Ziegler-Natta catalysis, the role of activators, particularly methylaluminoxane (MAO), cannot be overstated. MAO, despite its structurally undefined nature, serves as a crucial cocatalyst, enhancing the activity of the transition metal catalysts by forming highly reactive species. Understanding the intricate interplay between transition metal catalysts and MAO is paramount for advancing polymerization methodologies. Particularly little is known about the initial stage of the Ziegler-Natta polymerisation at which catalyst activation occurs.

In our previous work, the structural patterns of a number of complexes of zirconocene compounds with chain-type MAO were proposed (Fig. 1) [1]. Further study of the features of the interconversion of these patterns, as well as their catalytic activity in the olefin addition reaction, can shed light on the mechanism of activation of Ziegler-Natta catalysts under the influence of MAO activator.



P1 **P2** **P3**

Fig. 1. Structural patterns of Cp_2ZrRCl complexes with chain MAO ($Me_{11}Al_{11}O_{10}$)

All calculations were carried out at the DFT level in the Priroda 9 [2] program using the PBE/3ζ method [3]. Thermodynamic parameters and activation energies were determined at 298.15 K. Equilibrium geometries and energetic parameters of all intermediates and transition states were recalculated using Gaussian 09 [4] at the PBE0 level of theory [5] employing the def2-TZVP basis set [6,7]

In the course of the work, modeling of possible pathways for the formation and interconversion of $Cp_2ZrMeCl$ complexes with chain MAO structure, corresponding to patterns

P1, P2, and P3, was carried out. It has been shown that only the formation of the P3 pattern from the P2 pattern is thermodynamically unfavorable (ΔG_r = 16.3 kcal/mol) and requires overcoming a relatively high activation barrier ($\Delta G^{\ddagger}$ = 24.1 kcal/mol). The potential energy surface of the process of 1,2-insertion of propene into the Zr-Me bond of these complexes, which can be considered as the first stage of the polymerization reaction, was also studied. The calculated values of the thermodynamic and activation parameters of these transformations indicate the low potential catalytic activity of the studied complexes (Fig. 2). However, the energy costs for the addition of one olefin molecule still do not exceed those necessary for the formation of a cationic catalytically active center. The $Cp_2ZrMeCl$-MAO complex, corresponding to the P3 pattern, demonstrated the highest catalytic activity and can be considered as a potential catalytically active site acting in the initial stages of the Ziegler-Natta polymerization.

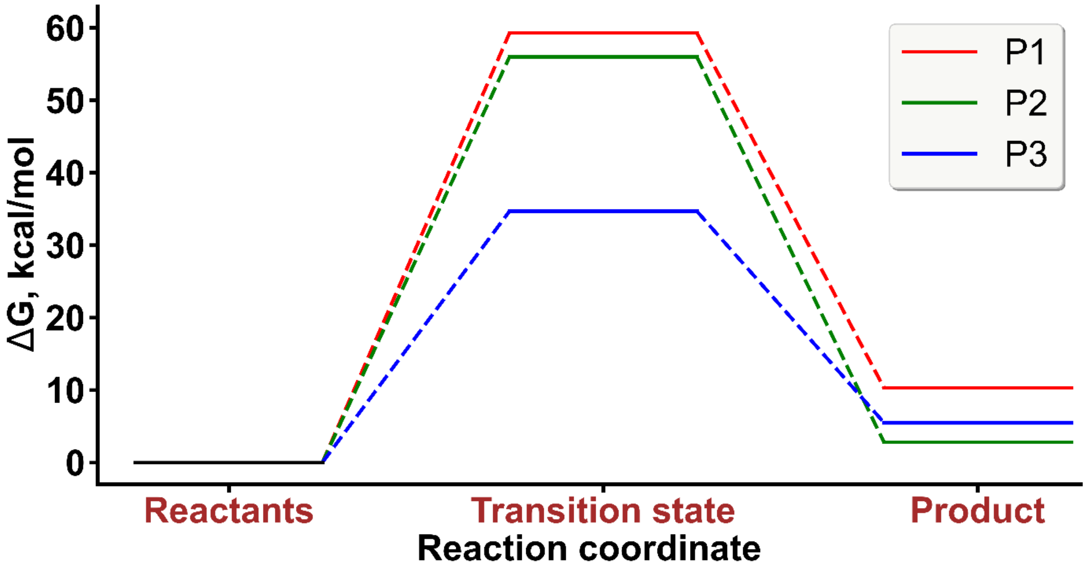


Fig. 1. Energy profile of the reaction of 1,2-insertion of propene at the Zr-C bond of various $Cp_2ZrMeCl$–MAO complexes

Further study on the influence of different MAO structures on the stages of chain growth and termination within zirconium species is in progress.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 22-73-00280.

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VP-12

Purification of Gas Emissions of Srednebotuobinsky Oil and Gas Condensate Field on a Heterogeneous Catalyst

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The carbon dioxide produced as a result of complete combustion of hydrocarbon fuels can be captured in several ways. But the most interesting and effective method is the catalytic one [1-3].

The purpose of this work is to study the process of catalytic purification from carbon dioxide of combustion gases of associated petroleum gas of the Srednebotuobinskoye oil and gas condensate field in fluorine-containing media, such as suspensions of calcium fluoride with different concentrations, and to determine the optimal parameters for the purification process from carbon dioxide in the suspensions under consideration. The goal set in the work is achieved by solving problems related to the study of the sorption abilities of calcium fluoride suspensions at various concentrations and carbon dioxide supply rates, and the catalytic ability of the fluorides under study is determined [4-5].

The study of the catalytic purification of carbon dioxide in the medium of calcium fluoride suspensions was carried out at atmospheric pressure and a temperature of 25^0C. To restore the catalytic ability of the spent calcium fluoride suspension, atmospheric oxygen was passed through the system for one hour.

As a result of the regeneration, the catalytic system completely restored its oxidizing abilities.

The work shows the fundamental possibility of carrying out catalytic purification of combustion gases using the example of associated petroleum gas from the Srednebotuobinsky oil and gas condensate field in a calcium fluoride environment from CO_2.

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VP-13

Kinetics and Mechanism of Liquid-Phase Aerobic Oxidation *sec*-Butylbenzene in the Presence of *N*-Hydroxyphthalimide

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Phenol and methyl ethyl ketone are valuable large-scale products of basic organic and petrochemical synthesis and are widely used in various branches of science and technology. Phenol is used in the production of plastics, synthetic fibers, and in the purification of oils in the oil refining industry [1]. Methyl ethyl ketone is used in the production of polymers and paints and coatings, polyurethane suspension for synthetic leather, glue, printing inks and magnetic tapes [2].

A promising direction for the production of these compounds is the hydroperoxide method for their preparation, based on the hydroperoxide oxidation of *sec*-butylbenzene followed by the acid decomposition of the hydroperoxide to the target products:

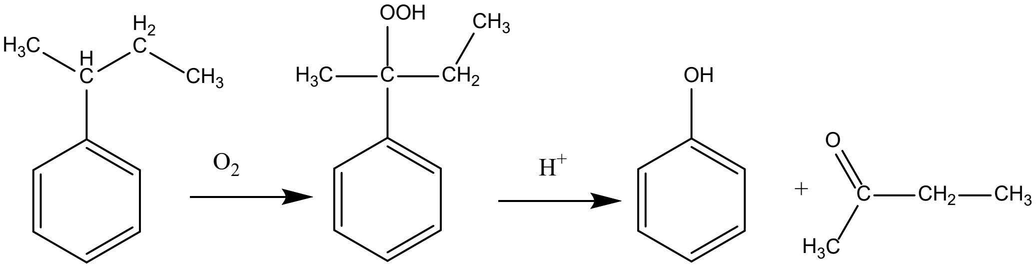

Fig. 1. Scheme for the production of phenol and methyl ethyl ketone.

The key stage of the method being developed is the liquid-phase aerobic oxidation of *sec*-butylbenzene to the hydroperoxide: the economics of the entire process depends on the efficiency of this stage. In this regard, an urgent task is to find ways to improve the oxidation process of *sec*-butylbenzene.

It is known that the process of *sec*-butylbenzene oxidation to hydroperoxide in the presence of hydroperoxide initiators has low hydrocarbon conversion and hydroperoxide accumulation rates, which is not acceptable from the point of view of industrial implementation of the process [3].

The intensification of the process under study was made possible by the use of organic phthalimide catalysts, such as *N*-hydroxyphthalimide (NHPI) and its derivatives.

During the work, the kinetic laws of the reaction of liquid-phase aerobic oxidation of *sec*-butylbenzene to its tertiary hydroperoxide in the presence of *N*-hydroxyphthamylide as a catalyst were studied. The influence of temperature, reaction duration, and catalyst content on the rate of *sec*-butylbenzene oxidation and the selectivity of the formation of its hydroperoxide was studied.

VP-13

It has been established that the use of *N*-hydroxyphthalimide allows the oxidation of *sec*-butylbenzene to its conversion of 35-40 % with a selectivity of hydroperoxide formation above 95 %.

When *N*-hydroxyphthalimide reacts with the peroxyl radical ($ROO^\bullet$) of a hydrocarbon, the *N*-oxyl radical of phthalimide ($PINO^\bullet$) is formed, which has high selectivity at the stage of abstraction of a hydrogen atom from the C–H bond of the alkyl derivative of the aromatic hydrocarbon (RH). In the presence of oxygen, the resulting alkyl radical ($R^\bullet$) undergoes transformation into a peroxide radical, which reacts with *N*-hydroxyphthalimide to form $PINO^\bullet$ and hydroperoxide (ROOH):

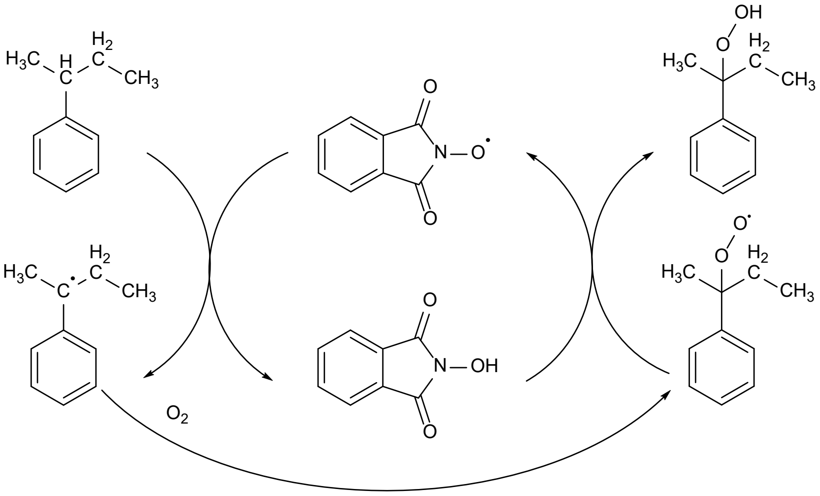

Fig. 2. Oxidative transformations of sec-butylbenzene and N-hydroxyphthalimide.

Based on the experimental data obtained, a kinetic (mathematical) model of the process under study was compiled, which adequately describes the change in the concentration of the main components during the reaction. The numerical values of the rate constants of the main stages of the process are calculated.

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VP-14

Catalysts for Hydrodeoxygenation of Bio-Oil Components Based on MFI Zeolite Synthesized from Natural Halloysite Nanotubes

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The depletion of traditional reserves of liquid hydrocarbons has led to the need to search for alternative sources of carbon-containing raw materials. Bio-oil obtained from biomass is a cheap renewable source of energy and in the future may act as an alternative to fossil oil. However, due to the high oxygen content, bio-oil is not suitable for direct use as fuel components. Reducing the oxygen content by hydrodeoxygenation (HDO) makes it possible to obtain motor fuel components and intermediate products for the petrochemical industry from bio-oil.

Promising catalysts for the hydroprocessing of biomass thermal degradation products are systems based on noble metals [1]. Zeolite-containing catalysts based on pentasil ZSM-5 exhibit the greatest activity. However, their high acidity provokes side reactions of cracking, alkylation and isomerization, which leads to a decrease in selectivity for the target products. In addition, the microporous structure complicates the diffusion of branched organic substrates to the active sites of the catalyst, which leads to rapid deactivation. The use of natural aluminosilicates, in particular halloysite nanotubes, as a precursor to silicon and aluminum oxides allows not only to reduce the cost of producing MFI-type zeolite, but also to optimize its textural and acidic characteristics, as well as to form meso-pores to improve the mass transfer of molecules included in the composition bio-oil [2].

In this work, Ru-containing catalysts (ruthenium content 2% wt) were obtained based on MFI zeolite, synthesized using template and template-free methods. The resulting samples were designated Ru/MFI:HNT-t and Ru/MFI:HNT-bt, respectively. In the case of template-free synthesis, halloysite aluminosilicate nanotubes acted as a precursor of silicon and aluminum oxides, and LUDOX HS-40 as an additional source of SiO_2. The activity of the synthesized catalysts in the HDO of a model bio-oil compound, guaiacol, was studied. The activity study was carried out in the temperature range 120-180°C in autoclaves at a pressure of H2 = 3.0 MPa and a molar ratio of substrate/metal = 200

VP-14

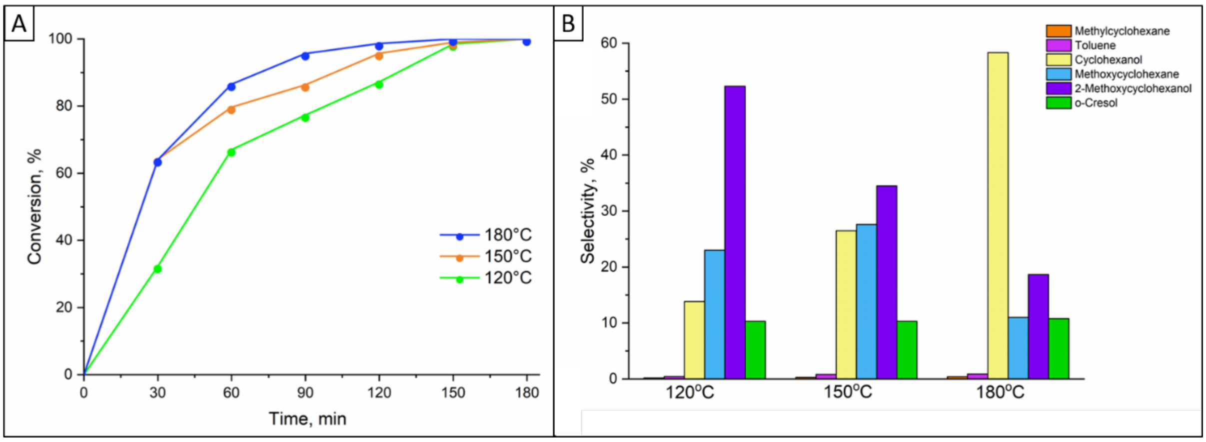

Fig. 1. Kinetic curves (A) and product selectivity (B) of guaiacol HDO in the presence of the Ru/MFI:HNT-t catalyst. Reaction conditions: molar ratio guaiacol/Ru=200, pressure 3 MPa, solvent – water

It was found that samples of catalysts showed high activity in the HDO of guaiacol over the temperature range for 180 minutes. In the case of the Ru/MFI:HNT-t catalyst, the distribution of reaction products indicated that the process proceeded along the route of saturation of the aromatic ring with retention of the polar hydroxy group. At the same time, hydrogenolysis of the O-CH3 bond, which has the lowest dissociation energy in the molecule – 205 kJ/mol, actively occurred. The main product at 120 °C was 2-methoxycyclohexanol, the selectivity of which was 52%. Increasing the process temperature to 180 °C significantly affected the distribution of hydrodeoxygenation products. At 180 °C, 2-methoxycyclohexanol underwent demethoxylation to form cyclohexanol (selectivity 58%).

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-29-00589.

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VP-15

Metals Deposited on Graphite in the Electrocatalytic Reaction of Reducing Nitrates to Ammonia

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Along with classical catalytic methods, photo- and electro-catalytic methods can also be used for the same reactions [1]. The group of reactions under the general "aegis" of the nitrogen reduction reaction (NRR) is currently studied almost exclusively in electrocatalytic design [2]. Their reactions have great prospects for replacing the Haber-Bosch ammonia synthesis process and are eco-friendly. The main challenge is to find conditions and catalysts to increase the product yield and Faraday efficiency (FE) selectivity. The reaction of electrocatalytic reduction of nitrates is a complex process that can occur via several pathways (Fig. 1). Determining the mechanism is not only an exciting scientific task, but also an urgent modern problem of great practical importance.

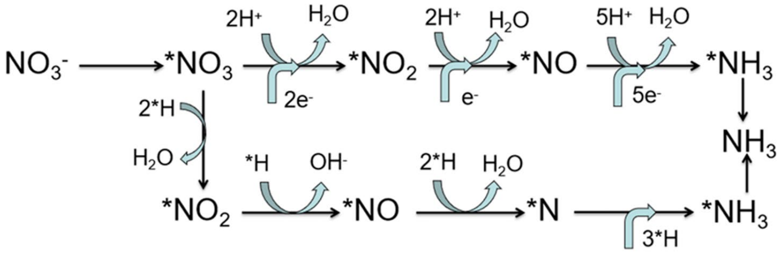

Fig. 1. Electrochemical NO_3 -RR mechanism mediated by electron transfer and atomic hydrogen. Reproduced from [2].

The objectives of the work were:

i -to create a test facility for testing samples of electrode-catalysts of some metals deposited on a graphite substrate.

ii -to develop a synthesis procedure of deposition of metal nanoparticles on a substrate.

iii -to screen synthesized nanocatalysts in a model reaction.

iiii -to obtain experimental results that allow one to suggest the mechanism of the reaction under study.

Nanoparticle deposition and electrochemical research methods were carried out according to the methods given in [3,4]. Quantitative determination of ammonia is based on the indophenol reaction, the methodology of which is given in [4]. The main result of the reaction was the value of the FE, that is, the output of the electric current spent on the reaction (%), which was calculated using the formula [4]:

$$\mathrm{FE(NH_3)} = \frac{8 \times 96500 \times m(\mathrm{NH_3})}{17 \times Q}$$

, where Q is the total spent charge and m is the mass of the released target product (ammonia).

The obtained metal nanoparticles were characterized by means of scanning electron microscopy. Among the studied nanocatalysts (on the basis of cobalt, iron and copper), the best activity and selectivity were shown by samples containing electrochemically deposited cobalt nanoparticles. Dense layers (deposition 30 min) had FE of more than 60% (Fig.2). Even samples containing trace amounts of cobalt by weight (precipitation for only 5 minutes) have already shown FE of almost 40%.

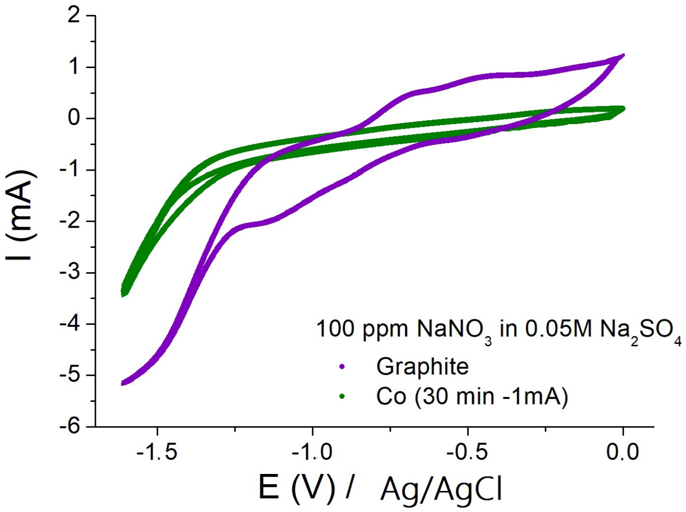

Fig. 2. Typical CV curves illustrating significant progress in ammonia synthesis at the reaction potential E=(-1.3)-(-1.4) V vs Ag/AgCl for graphite substrate and deposited catalyst (nanocobalt, 30 min deposition) in a pH-neutral nitrate-sulfate electrolyte.

Thus, using the created installation, electrochemically precipitated catalysts containing cobalt, iron and copper nanoparticles on a graphite substrate were obtained and tested in the electrocatalytic reaction of reduction of nitrates to ammonia. It should be noted that the tasks and formulation of the experiment fully comply with the targets and necessary requirements specified in a very recent work (December 2023) by scientists who are the world leaders in this field [5].

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VP-16

Multifactorial Computer Analysis of the Octane Number of the Industrial Gasoline Reforming Process

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In oil refining, one of the basic processes is catalytic reforming. The main products of catalytic reforming are: high-octane gasoline components, hydrogen and benzene, toluene and xylenes used for petrochemical needs [1]. Improving the catalytic reforming process is a very important task, since half of all commercial gasoline in Russia is produced with its help.

It is also necessary to optimize the process due to the constant tightening of requirements for the composition of gasoline and their quality.

The optimization of the catalytic reforming process can be carried out in various ways – by changing the process conditions, its parameters, improving existing catalysts, using additives for them, synthesizing new catalysts, additional preparation of raw materials, etc. [2]. With the help of computer modeling, it is much easier to optimize the process by selecting optimal parameters (temperature, pressure, volumetric feed rate, etc.) to obtain the best results.

Multi–criteria optimization is the improvement of the process in several output parameters. In the case of catalytic reforming, such parameters can be: the octane number obtained by the research method, the yield of the reformate, the benzene content in the reformate, the content of aromatic compounds in the reformate, etc. [3].

Multi–criteria optimization can be carried out by constructing a Pareto set – this is a set of values that correspond to the Pareto principle - there is no result in which all the specified goals will have the best value, at least one value will have the worst result. The Pareto set allows you to see all the compromises between the output parameters and find their optimal values [4].

To construct the set of Pareto catalytic reforming process, the following parameters were selected, such as the octane number obtained by the research method and the output of the reformat. The analysis of the data of the technological mode of operation of the installation obtained over 1 year has been carried out. The Pareto front is constructed for the selected parameters, the result is shown in Figure 1.

VP-16

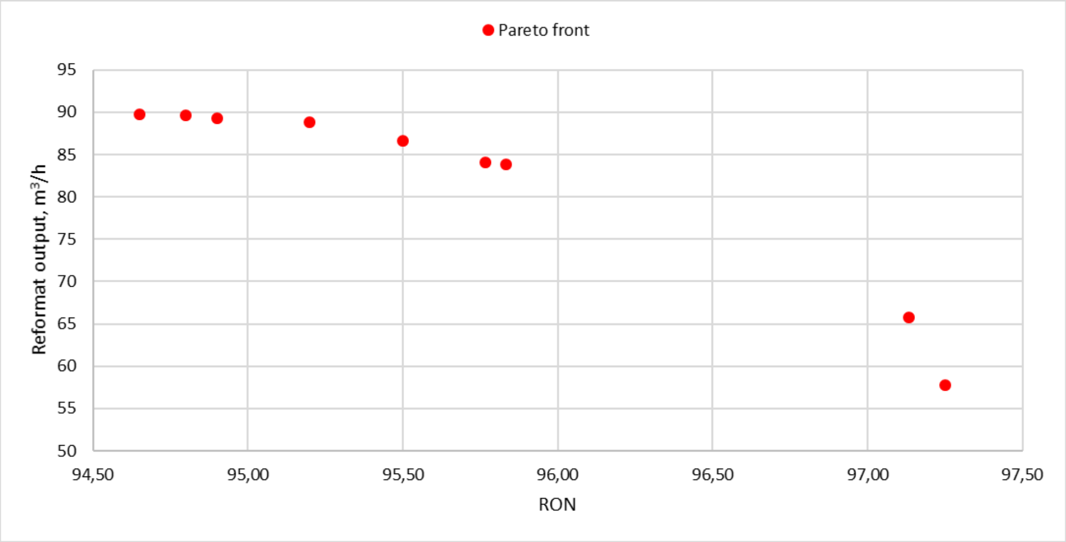

Fig. 1. Pareto front

According to the constructed Pareto front (Figure 1), we observe that at the highest value of the octane number, 97,25, the output of the reformat is 57,8 m^3/h. Conversely, at the highest output of the reformat, 89,7 m^3/h, the octane number is 94,65.

Depending on the purpose of the catalytic reforming unit (production of high-octane gasoline components or raw materials for petrochemicals), you can choose the most optimal values of the output parameters and the operating modes of the unit with them. Also, the results obtained allow us to choose the optimal technological mode of the process, with the maximum yield of the high-octane component, without violating the requirements for the octane number.

Acknowledgement: The work was carried out as part of the implementation of the state assignment of the Institute of Petrochemistry and Catalysis of the Russian Academy of Sciences (topic No. FMRS-2022-0078).

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Study of the Heterocatalytic Oxidation of the Saturated Chlorohydrocarbons C_1–C_4

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Over the past decade, the heterogeneous catalytic oxidation of hydrocarbons takes one of the central places in modern chemical and petrochemical science. The study of the kinetic laws and mechanisms of catalytic reactions has allowed us to accumulate a lot of experimental material for theoretical generalizations, which promotes general concepts and theories of catalysis [1].

After selecting an active catalytic system according to the method of mathematical statistics, the validity of these systems was tested by direct study of their activity and selectivity in the oxidation reactions of various chlorohydrocarbons [2].

First, the influence of various variable parameters on the oxidation reaction of saturated chlorohydrocarbons, carbon tetrachloride, 1,2-dichloroethane, 1-chloropropane, 1,2,3,3,-tetrachlorobutane, 1,2,2,3-pentachlorobutane, 1,1,2,2,3,4-hexachlorobutane formed as by-products in the production of chlorinated hydrocarbons was studied.

These compounds were individually subjected to an oxidation reaction. The main goal of studying possible ways of selective oxidation of these chlorohydrocarbons on oxide catalysts is related to solving the problem of their utilization. Based on the results the catalytic systems Co–Mo, V_2O_5–MoO_3/Al_2O_3, V–P–O/$SiO_2$with the Mg and Mn-additives or without additives were studied in the oxidation reaction of the above mentioned chlorohydrocarbons.

First, we studied the influence of variable parameters on the oxidation reactions of some chlorohydrocarbons in a reactor with a stationary (fixed) bed, and then with a “fluidized” bed of different catalytic systems, the results of which are presented in the figure.

As is seen from the results, the activity of catalysts in a fixed bed of catalysts is 8–10% higher than in a fluidized bed. However, the yield of products and the selectivity of the process are inferior to the “fluidized” bed. In reactors with a stationary catalyst bed, mainly the deep oxidation reaction of chlorohydrocarbons (CHCs) occurs at relatively high contact times. Therefore, further researches were pursued in reactors with a “fluidized” catalyst bed.

VP-17

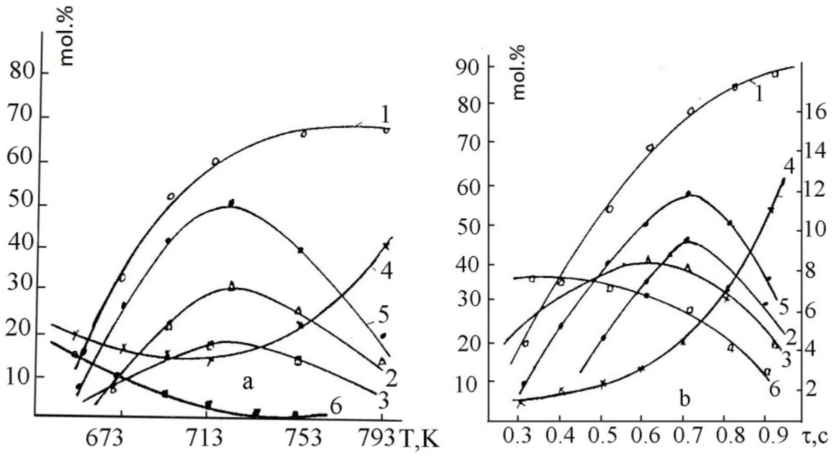

Fig.1. The effect of reaction temperature (a) and contact time (b) on the oxidation reaction of chlorohydrocarbonson V–P–O/SiO$_2$+Mg (a) and Co–Mo (b) catalysts. 1—degree of conversion, 2—yield of targeted products, 3—yield of total chloro-substituted acids, 4—yield of CO+CO$_2$, 5—selectivity of the process, 6—yield of by-products of chlorine derivatives.

A study of the temperature effect in the range of 653–773 K on the degree of conversion and selectivity of C$_1$–C$_4$chloroalkanes in a fluidized bed of various catalytic systems on different substrates and with additives showed that all of these catalysts are active in the oxidation reaction. The degree of conversion of XY reaches 90–95% mol (Fig. 8 a, b). However, the yield of targeted products and the selectivity of the process do not always increase. Only in some cases the product yields are 15–30 mol.% with a selectivity of 25–50 mol.%. Only deep oxidation products and only traces of some unstable products (Cl$_2$C=O) are formed during the oxidation of CCl$_4$.

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VP-18

Mechanism of the H_2O_2 Autocatalytic Decomposition onto the Surface of the Potassium Polytitanates

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The dispersions containing H_2O_2 aqueous solutions and potassium polytitanate (PPT) powders represents a promising system to generate molecular oxygen and support redox reactions in the soft conditions of “green” chemistry, i.e. for water purification [1-4]. Varied content of the components allows obtaining these systems characterized with controlled release of O_2 and stable conditions of the oxidation process [4].

The series of experiments were done to specify the mechanism of the oxygen generation taking place in this system. Taking into account the data of FT-IR spectroscopy, DSC, PEM and SEM as well as kinetic data it was recognized that the O_2 generation takes place as a result of the autocatalytic process confirming with S-shaped kinetic curves of the oxygen generation. It was established that the catalytic activity of the PPT’s synthesized in the system of TiO_2-KOH-KNO_3 at different experimental conditions depends on some structural features of the obtained parent PPT powders, in spite of the same chemical composition.

The proposed mechanism of the PPT powder interaction with H_2O_2-H_2O solutions includes the following stages similar to the process described in [5] for the titan-silicate catalysts.

1) Transformation of the surface Ti-O-H groups into the Ti-O-O-H groups

$$\text{Ti-O-H \{Ti-O(H)-Ti\}} + H_2O_2 \rightarrow \text{Ti-O-O-H \{Ti-O(OH)-Ti\}} + H_2O$$

2) Interaction of the surface peroxo-groups with the H_2O_2 [5]:

$$\text{Ti-O-O-H \{Ti-O(OH)-Ti\}} + H_2O_2 \rightarrow \text{Ti-O-H \{Ti-O(H)-Ti\}} + O_2\uparrow + H_2O$$

High catalytic activity of the PPT powders is determined by well-developed internal surface of the quasi-amorphous layered PPT particles (S_{sp}= 130-150 m^2/g) and large interlayer distance (from 0.1 to 1.1 nm). A generation of the peroxo-groups on the internal surface of the PPT powder (stage 1) requires any time and determines the duration of the induction period of the autocatalytic process. Various kinds of the PPT powders, synthesized in different experimental conditions, are characterized with different average interlayer distance and, therefore, have various duration of the induction period depending on a rate of the H_2O_2 interlayer diffusion.

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VP-18

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VP-19

Regression Analysis of Industrial Data of Catalytic Gasoline Isomerization Process

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Any petrochemical process is subject to optimization, the main reasons for which are tightening requirements for commercial gasoline, low product yields, and high energy consumption.

The key process in oil refining is isomerization, the purpose of which is to produce high-octane components of gasoline or petrochemical feedstock. In order to maximize its yield, it is necessary to optimize this process. Knowing the process parameters and the component composition of the raw materials, it is posьsible to perform regression analysis and identify strongly dependent parameters that contribute to the quality of the resulting product.

Process data on feedstock composition and operating conditions were collected from the Midor isomerization unit (Alexandria, Egypt) over a 4-year period based on catalyst lifetime [1]. A total of 26 values were selected for 6 parameters, presented in Table 1.

Table 1 – Technological data

№ / Parameter	1	2	3	4	…	26
Benzene content, % wt.	10	6	12	5	…	34
Naphthene content, % wt.	0,31	0,64	0,76	0,75	…	3,03
Reactor temperature, ℃	168,81	167,65	163	170	…	156
LHSV, h^{-1}	0,87	1,3	0,93	0,82	…	2,81
Hydrogen consumption, kmol/h	102,6	102,8	103	103	…	124
RON	88,47	88,18	88,07	88	…	86

To analyze a large number of data and automate the regression analysis, a Python program code was written with parallel calculations in Microsoft Excel.

To identify dependencies between two or several variables, values such as the coefficient of determination R^2, Fisher's criterion F, standard deviation and adequacy variance σ^2 for both linear and polynomial regressions were determined.

The above values calculated in the Python program for several dependencies are presented in Table 2.

Table 2 – Calculated parameters for one-factor analysis

RON - Benzene content dependence				
	Parameteres			
Degree of the equation	R^2	σ^2	S	F
1	0,927	0,041	0,704	159,872
2	0,929	0,040	0,705	164,512
3	0,938	0,035	0,708	188,560
…	…	…	…	…
25	0,942	0,034	0,709	97,123
RON - Hydrogen consumption dependence				
1	0,791	0,120	0,650	50,914
2	0,896	0,059	0,692	110,149
3	0,905	0,054	0,695	121,176
…	…	…	…	…
25	0,942	0,034	0,709	97,123
RON – LHSV dependence				
1	0,742	0,149	0,629	39,660
2	0,742	0,149	0,630	39,690
3	0,743	0,148	0,630	39,815
…	…	…	…	…
25	0,819	0,104	0,691	59,718

In the regression analysis, a multivariate analysis consisting of two dependent and one independent parameter was calculated and the results are presented in Table 3.

Table 3 – Calculated parameters for multivariate analysis

Dependence	Parameteres			
	R^2	σ^2	S	F
RON – (Benzene content + LHSV)	0,944	0,033	0,710	101,329
RON – (Benzene content + Hydrogen consumption)	0,942	0,034	0,709	97,123
RON – (Benzene content + Reactor temperature)	0,948	0,031	0,711	107,718

The best results were obtained for the two-factor regression equation with the factors benzene:temperature, benzene:volume feed rate and benzene:hydrogen consumption. In this case, the values of adequacy variance are lower than those of the one-factor regression and the coefficients of determination are higher. The obtained values of Fisher's criterion are higher than the tabulated value, which indicates that the dependencies are significant; the standard deviation ranges from 0.709 to 0.712.

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VP-20

Hydroconversion of Aromatic and Organosulfur Compounds over Dispersed Ni-Mo-Sulfide Catalysts under Water Gas Shift Reaction Conditions

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Nowadays the quality of crude oil is decreasing, which it caused by the depth of its recovery. Meanwhile, the environmental standards become stricter, and the development of more energy efficient and effective technologies and catalysts for production of fuels are required. Aimed at reducing of sulfur and aromatic content, hydrotreating is considered as the domain process for production of fuel with satisfied specification from ecological standpoint. However, existing technologies and catalysts are not adapted for processing of low-quality high-viscosity feed with high content of polyaromatics and sterically hindered compounds, including heteroatomic ones. To achieve the quality requirements, the tightening of conditions is usually applied, which leads to increased hydrogen consumption, deterioration of technological equipment, shortens catalysts life-time, increases the cost of their regeneration. The last few decades the dispersed catalysts based on transition metals, such as Ni, Co, Mo, W, are considered as a promising alternative for zeolite-based ones [1]. Among their advantages are high dispersity of active component, nanoscale particle size, a large specific surface area (up to 300 m^2/g), resistance to deactivation due to low acidity and the ability to transfer “active” hydrogen, which ensures the binding of free radicals and prevents polymerization. The active component of those catalysts can be obtained by high-temperature decomposition of water- or oil-soluble precursors *in situ*. Being the major component of hydrotreatment catalysts, the molybdenum-based ones are active in the water gas shift reaction [2,3]. Therefore, it allows to consider the water as a source for *in situ* hydrogen production, followed by its involvement into hydrogenation of heavy components of water-containing feed during hydrotreatment.

In this work, we examined the catalytic properties of dispersed Ni-Mo sulfide systems forming *in situ* during the decomposition-sulfidation of oil-soluble precursors using elemental sulfur as a source of sulfiding agent in the hydrogenation of model feed containing difficult-to-remove aromatics (naphthalene derivatives) and organosulfur (benzo- and dibenzothiophenes) compounds under water gas shift reaction conditions. The fundamental chemistry and the reaction route for hydrotransformation of model compounds, their mutual influence when the joint presence in the model feed depending on the source of hydrogen, the mass content of water, pressure of carbon monoxide at the temperature range of 340-420 ºC, were studied. The influence of the molar aromatics and organosulfur component ratio on regularities of joint transformation were estimated. The optimal conditions to achieve a high conversion of model feed into naphthenic and naphthenic-aromatic ones were defined.

VP-20

Acknowledgement: the study was financially supported by the Russian Science Foundation (project no. 21-79-10140, https://rscf.ru/ project/21-79-10140/).

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VP-21

Oxidation of Isopropylbenzene under the Influence of Potassium 2-Ethylhexanoate

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Hydrocarbon oxidation processes are widely used in the production of various oxygen-containing compounds (ketones, aldehydes, acids, epoxides, phenols). Effective catalysts for the liquid-phase oxidation of alkyl aromatic hydrocarbons into hydroperoxides (primary products) are compounds of non-transition metals [1].

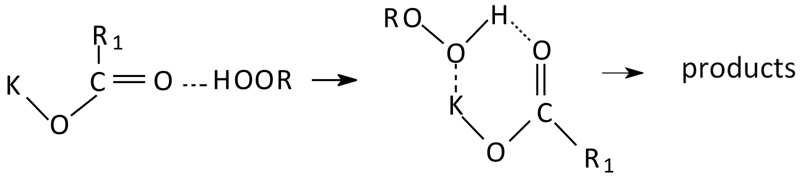
Potassium 2-ethylhexanoate (KEH) catalyzes the oxidation of isopropylbenzene by molecular oxygen into isopropylbenzene hydroperoxide (110–130°C, atmospheric pressure, [Cat]0 = 5 mmol/L). In the absence of a catalyst, the oxidation of isopropylbenzene occurs with a pronounced induction period (8 – 9 hours) [2]. KEH reduces the time to achieve the required conversion of isopropylbenzene (~20%) to 3 hours. In the presence of KEH, high selectivity for isopropylbenzene hydroperoxide (93%) is achieved. According to gas-liquid chromatography (Chromatec Crystal 5000 chromatograph, the manufacturer is JSC SDO "CHROMATEC", Yoshkar-Ola, Russia; capillary column: sol-gel wax, l = 30 m, d = 0.53 mm) in the process of oxidation of isopropylbenzene, dimethylphenylcarbinol, acetophenone, α-methylstyrene, methanol, benzaldehyde, and phenol are formed.

Oxidation occurs by a radical chain mechanism. By decomposing some isopropylbenzene hydroperoxide (ROOH), KEH initiates oxidation. The decomposition of isopropylbenzene hydroperoxide is preceded by the formation of the intermediate compound ROOH·Cat.

$$\mathrm{ROOH + Cat \rightleftharpoons ROOH{\cdot}Cat}$$

$$\mathrm{ROOH{\cdot}Cat \longrightarrow RO^{\bullet} + {}^{\bullet}OH + Cat}$$

When the intermediate compound ROOH·Cat is formed, a hydrogen bond of isopropylbenzene hydroperoxide is first formed with the oxygen of the acidic residue of the salt, and then the cycle is closed with the formation of a metal–oxygen bond.



The formation of the ROOH·Cat intermediate was determined by kinetic and quantum chemical methods. The enthalpy of formation of the intermediate compound ROOH·Cat is ΔH^{o}_{298} = – 105.3 kJ/mol and significantly exceeds the strength of hydrogen bonds in hydroperoxides (8 – 13 kJ/mol). Consequently, one of the oxygen atoms of the O–O group of isopropylbenzene hydroperoxide is also coordinated with the central metal atom. The formation of intermolecular bonds is accompanied by a change in the initial structure (bond lengths and angles) of the molecules involved in the formation of ROOH·Cat, as well as a redistribution of electron density in them. In the ROOH·Cat intermediate, the electron density on the oxygen atoms of cumene hydroperoxide decreases, and the charge on the metal ion is almost halved. The formation of hydrogen bonds loosens the O–O bond in ROOH and facilitates its homolytic cleavage. The value of the Gibbs free energy ($\Delta G^{o}_{298} = -56.9$ kJ/mol) shows that the formation of the intermediate compound ROOH·Cat is thermodynamically possible and favorable.

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VP-22

Synthesis of Complex Oxides from Nitrate-Organic Precursors via Solution Combustion Synthesis and Related Catalytic Phenomena

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The synthesis of various polyfunctional materials based on complex oxides via combustion reactions of organo-nitrate precursors is associated with the manifestation of catalytic properties of the metal ions constituting these materials, capable of reversible changes in oxidation degree [1]. Magnetic and luminescent materials, solid oxide fuel cell components, catalysts, materials for biomedical applications, etc. could be produced by solution combustion synthesis.

Redox reactions of interaction between nitrate and organic parts of precursors (glycine, glycerol, polyvinyl alcohol, polyvinyl pyrrolidone, urea, etc.) occur more actively during combustion, more often with the development of higher temperatures, in systems containing metal ions with catalytic activity (copper, cobalt, nickel, cerium, silver, vanadium, molybdenum, etc.). The combustion of such precursors is usually accompanied by the formation of high-density charges in them [2, 3]. The potential difference between the precursor and the ground ranges from units to hundreds of volts, as measured by the IPEP-1 electrostatic field meter (manufactured in the Republic of Belarus). On the other hand, when burning organonitrate compositions containing metal ions with a stable oxidation state (aluminium, zirconium, etc.), the charges in the precursors are practically not fixed and combustion is not intense [1, 3]. This confirms the link between the charge generation process and the presence of catalytic centres on the nanoparticles obtained in the form of metal ions with a variable degree of oxidation and, apparently, active oxygen. Charges are generated by the release of negatively or positively charged molecular groups (negatively ionised water molecules or carbonate-like particles [4], positively charged NO^+ groups, etc.) into the environment. The generation of charges leads to mutual electrostatic repulsion of the particles, allowing to obtain powders with a higher surface energy reserve, which leads to a reduction of their intensive sintering temperature by 250-300°. It is possible to 'fit' dilatometric shrinkage curves [5] for different materials in order to sinter layered composites in a single cycle, for example in the manufacture of solid oxide fuel cells. The control of charge generation processes, morphology of obtained materials is possible under the influence of external electromagnetic fields. The superposition of external fields, electrostatic repulsion potentials of particles and magnetic interaction between them (in the case of production of magnetic media) [6, 7] allows, for example, to select conditions for production of extended chain aggregates of particles and to achieve higher coercivity properties of the material.

The catalytic effect is also useful in reducing energy consumption and emissions of pollutants (carbon monoxide, nitrogen oxides) in solution combustion synthesis processes. For example, the introduction of a relatively small amount of the synthesising complex oxide powder (from 10 wt%) into the organo-nitrate precursor leads to a multiple reduction of the abovementioned emissions by catalytic neutralisation [8].

It should be noted that the manifestations of the catalytic effect of metal ions with a variable degree of oxidation can be observed and should be taken into account in the initial stages of precursor preparation for the synthesis of complex oxides. The interaction between the oxidant (nitrate ion) and the organic part of the precursor is already observed in concentrated solutions containing iron nitrate and polyvinyl alcohol, with the release of gases and self-heating. Such precursors in film form undergo "cold" combustion [7], essentially at room temperature, as do compositions containing ammonium heptamolybdate [1]. On the other hand, in glycine-containing precursors for the preparation of magnetic materials based on strontium or barium hexaferrites, there is no degradation of the composition at room temperature due to iron-glycine complexation, which reduces the potential difference of the Fe^{2+}/Fe^{3+} ion pair. Moreover, it is possible to obtain centimetre-long magnetic fibres [7] during the combustion of such compositions.

Acknowledgement: This work was financially supported by the State Assignment of the Ministry of Science and Higher Education of the Russian Federation, project FEUZ-2023-0016.

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VP-23

Activation of Nitration of Aliphatic Oligomers from Polyamide in the Presence of Silver Ions

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The material for nitration aliphatic polyamide oligomers was metallized fabric, which did not meet the operating requirements for electrical resistivity. The basis of the metallized electrically conductive fabric was a polyamide textile thread, on which a tinsel metal thread made of copper 0.1 mm thick with a silver coating of up to 5 micrometers was located. Table 1 shows the material balance of the composition of metallized tinsel thread with a polyamide core.

Table 1. Material balance of the composition of metallized tinsel thread with a polyamide core.

No./No.	Name of components of metallized tinsel thread	% mass
1	Metallized tinsel thread	100
2	Copper tinsel thread	75,3
3	Silver plating	4,7
4	Polyamide core	20,0

Metallized fabric that did not meet the operating requirements for electrical resistivity was immersed in concentrated nitric acid for the time required to dissolve the silver coating (5-10 seconds). During this period of time, due to the exothermic effect, destruction of the polyamide thread and exothermic nitration of the resulting aliphatic oligomers occurs in the presence of monovalent silver ions. Industrial nitration of aliphatic linear compounds in concentrated nitric and sulfuric acids is carried out within several hours.

The degraded polyamide thread and nitrated aliphatic oligomers were collected and removed from nitric acid, after which the collected products were washed with distilled water to remove the acid and Ag^+ silver ions.

The destruction products of the polyamide thread were nitrated aliphatic oligomers - 6-[(6-aminohexyl)amino]-6-(nitrooxy)hexanoates, which is consistent with the infrared spectroscopy data of the original and degraded polyamide thread. IR spectra of polyamide and nitrated polyamide degradation products were obtained on a PerkinElmer RX-1 IR-Fourier spectrophotometer. In the IR spectra of polyamide and nitrated polyamide degradation products, absorption bands at 3295 and 3327 cm^{-1}, characteristic of the NH group, and absorption bands at 2930 and 2937cm^{-1}, characteristic of CH_2, were detected. The presence of the absorption band 1708 - 1733 cm^{-1} in both spectra indicates the presence of a C=O group. The difference in the IR spectra is that the nitrated polyamide degradation products have absorption bands of 1616 cm^{-1}, characteristic of asymmetric vibrations of NO_2 and absorption bands of 1277 cm^{-1}, characteristic of symmetric vibrations of NO_2 .

Spectra obtained by proton nuclear magnetic resonance (H1 NMR) confirm nitration, signal at 4.5 ppm. (chemical shift) is identical to the hydrogen located next to the nitro group.

Thus, due to the activation of nitration of aliphatic polyamide oligomers in the presence of silver ions, the kinetic parameters of nitration are improved.

VP-24

Oxidation of the Styrene Epoxide – Hydroquinone – Cu(II) Chloride System in a Methanol Solution

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It was established for the first time, that in joint solution of styrene epoxide (SE), hydroquinone (HQ) and $CuCl_2 \cdot 2H_2O$ (Cu(II)) in methanol triple complex, ternary synergistic system (TrS) appears, which absorbs molecular oxygen (Fig. 1).

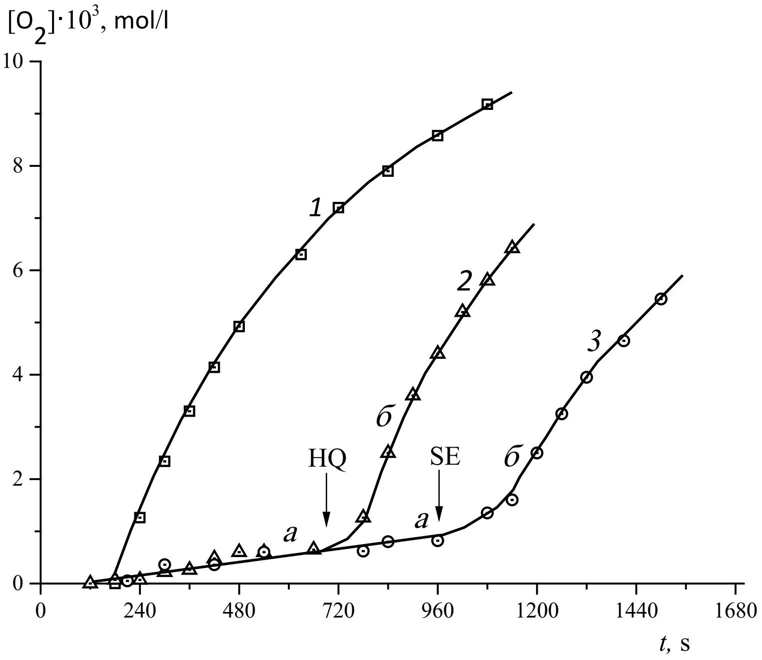
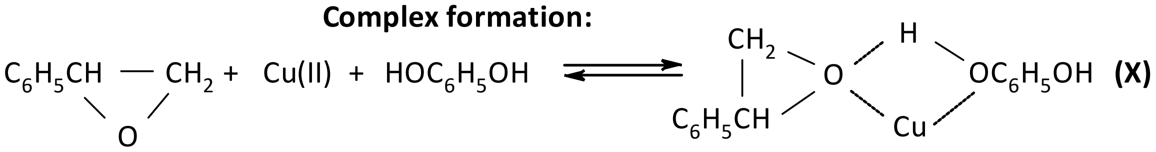


Fig. 1. Kinetic curves for oxygen absorption by (1) TrS (SE – HQ – $CuCl_2$); 2a – binary system (BiS) (SE – $CuCl_2$); 2b – after introduction into BiS HQ (marked by arrow); 3a – BiS (HQ – $CuCl_2$); 3b – after addition SE into this BiS. Bubbling O_2, $[SE]_0 = 0.35$, $[HQ]_0 = 0.031$, $[CuCl_2] = 5.8 \times 10^{-4}$ mol/L, methanol, 323 K.

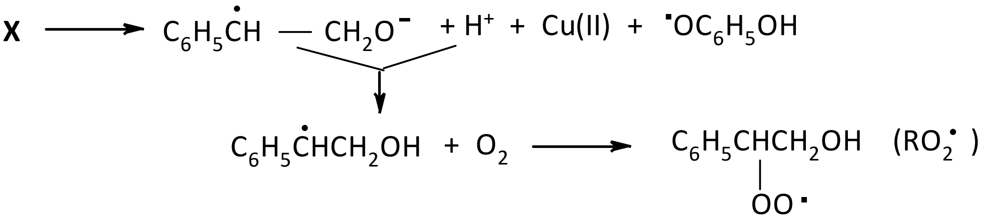
The standard technique for measuring oxygen absorption rates using a constant-pressure manometric installation was used [1]. Volumetric investigation of oxygen absorption in TrS gives TrS rate oxidation expression $V = k\,[\mathrm{Cu(II)}]^1[\mathrm{HQ}]^0[\mathrm{SE}]^0$, effective pseudomonomolecular rate constant $k = 1.82\times10^5\exp(-40.0\ \mathrm{kJ.mol^{-1}}/\ RT)\ \mathrm{s^{-1}}$, (308 – 323) K. The mechanism scheme of complex TrS reaction in oxygen atmosphere is proposed on the experimental date of oxygen uptake, SE and HQ consumption and accumulation of benzoquinone.

VP-24

Complex formation:

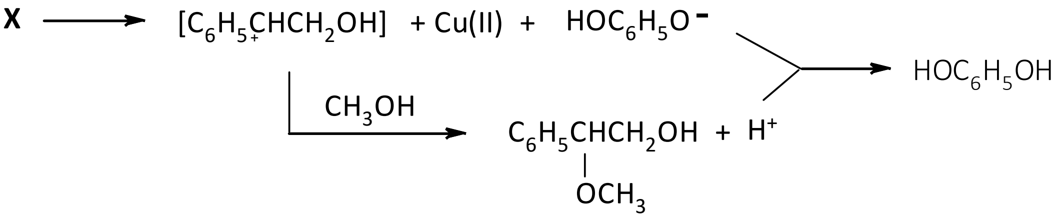


Oxidative canal:



Benzoquinone accumulation:

Heterolysis of Epoxide:



This mechanism represents the combination of two competitive nonradical and radical routes; oxygen uptake is consequence of radicals appearing in TrS. The ratio of two those reaction canals $(V_{O2}/V_{SE})\times100 \approx 18\%$; V_{O2} – the rate of O_2 absorption, V_{SE} – the rate of epoxide consumption.

Acknowledgement: This work was done on the topic of the state assignment, the state registration number AAA – 19-119071890015-6.

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VP-25

Peculiarities of Ethylene Polymerization Reactions with Bis(imino)pyridyl Complexes of $CoCl_2$ and $FeCl_2$

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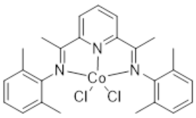
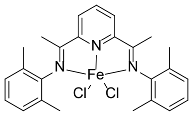
Here we report an examination of ethylene polymerization reactions using as catalyst precursors complexes of $CoCl_2$ and $FeCl_2$ with a N,N,N-tridentate ligand, 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridine ($LMCl_2$).



LCoCl₂



LFeCl₂

Two organometallic activators were used to convert the complexes into polymerization catalysts, polymethylalumoxane (MAO) and a combination of $Al(C_2H_5)_2Cl$ and $Mg(C_4H_9)_2$ at a [Al]:[Mg] molar ratio of ~3. As we demonstrated earlier, combinations of AlR_2Cl (R = CH_3, C_2H_5, i-C_4H_9) and MgR'_2 (R' = n-C_4H_9 and i-C_4H_9), when used at an [Al]:[Mg] molar ratio of >2, are universal activators for various types of transition-metal polymerization catalysts [1].

Catalytic systems based on $LCoCl_2$ and both activators readily polymerize ethylene in the 25-50 °C range. The PE yield with $LCoCl_2$ was 9900 and 5270 kg/($mol_{Co}\cdot C_E^{mon}\cdot h)^{-1}$ with MAO and $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$, respectively (toluene, T=35 °C, P_E ~4 atm). The reaction product is a highly crystalline (crystalline degree 65%) low-molecular weight PE (M_w =1500 - 2000) with vinyl end-groups.

The activity of systems based on $LFeCl_2$ under similar conditions is significantly lower, 2000 and 400 kg/($mol_{Fe}\cdot C_E^{mon}\cdot h)^{-1}$ with MAO and $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$, respectively. The polymer obtained using MAO is also a linear crystalline PE with low MW (M_w = 3500). The molecular weight of PE synthesized with the $LFeCl_2$ complex activated with $Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ is much higher, M_w = 140000-270000.

Systems based on $LCoCl_2$ and $LFeCl_2$ complexes with MAO as an activator are typical homogeneous catalysts. They produce one type ($LFeCl_2$) or two types ($LCoCl_2$) of active centers with similar kinetic characteristics. The polymers products produced with them have a narrow MWR (M_w/M_n ≈2) consisting of one or two closely spaced Flory components [2], which are produced by one type of active centers (Fig. 1).

VP-25

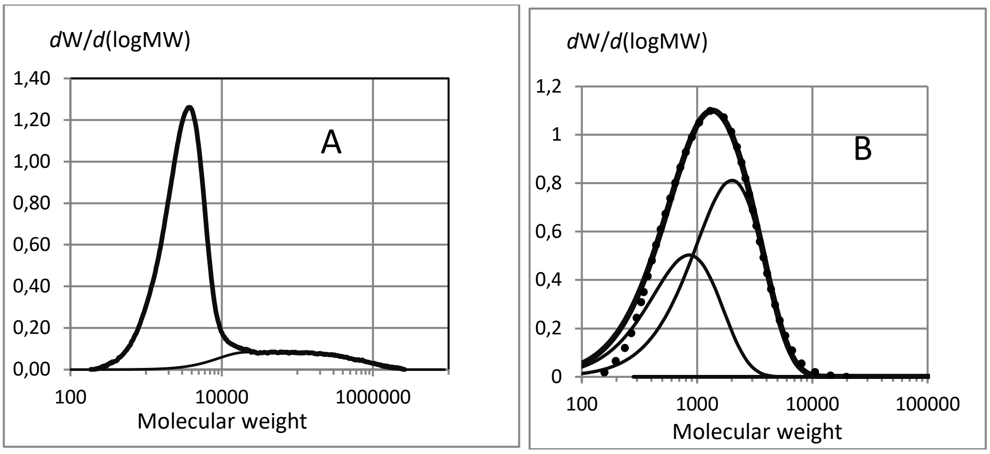


Fig. 1. A. GPC curve of PE produced with $LFeCl_2$-MAO catalyst B. GPC curve of PE produced with $LCoCl_2$-MAO catalyst (points), its resolution onto Flory components (thin lines) and the combined calculated GPC curve (thick line).

The same complexes, when activated with the $Al(C_2H_5)_2Cl$ - $Mg(C_4H_9)_2$ cocatalyst, form multi-center catalysts. They produce PE with a wide MWR (M_w/M_n ≈3-4 in the case of *L*$CoCl_2$ and 6-11 in the case of *L*$FeCl_2$) and consist of 4 and 5 Flory components with different average MW (Fig. 2).

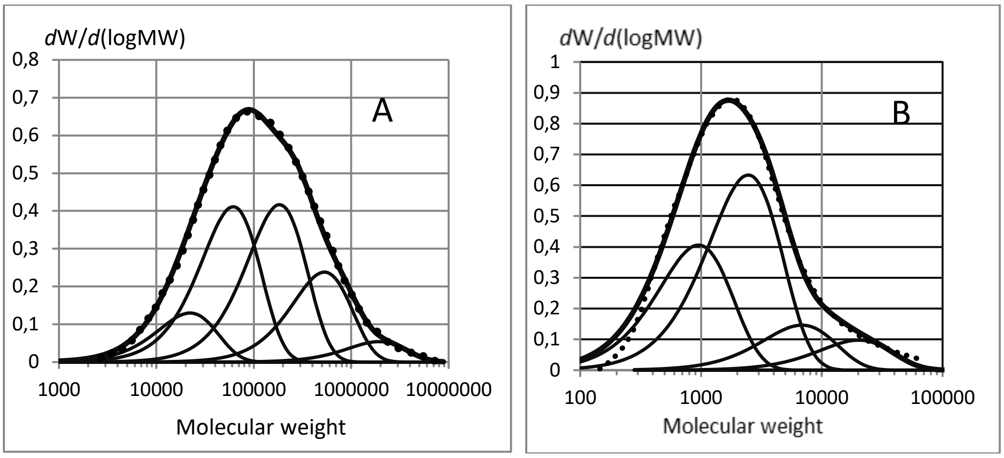


Fig. 2. GPC curve of PE (points), their resolution onto Flory components (thin lines), and the combined calculated GPC curves (thick line). A: $LFeCl_2$-$Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ catalyst, B: $LCoCl_2$-$Al(C_2H_5)_2Cl/Mg(C_4H_9)_2$ catalyst.

Acknowledgements: We are grateful to Dr. Dr. M.A. Matsko (Boreskov Institute of Catalysis, Novosibirsk, Russia) for GPC analysis of polymers. The work was carried out according to the program of Fundamental Scientific Research of the Russian Federation.

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VP-26

Plausible Mechanism of C-H/C-H Oxidative Coupling of Arenes in the Presence of Trinuclear Palladium Nitrosyl Carboxylate Complexes $Pd_3(NO)_2(RCO_2)_4(ArH)_2$

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Palladium carboxylate complexes are well-known catalysts for both classical and direct C–H/C–H arene coupling reactions. Corresponding catalyst systems exhibit low catalyst loading (<10 mol% Pd, typically 1-5 mol%), moderate to high yields (30-95%) and high selectivity (>80%) for a wide range of substrates in relatively mild conditions. Herein we describe a catalytic system for an effective oxidative C–H/C–H coupling of arenes based on palladium nitrosyl carboxylates (NCCs) $Pd_3(NO)_2(\mu\text{-}CX_3CO_2)_4(ArH)_2$ (Fig. 1a; I: R = Cl, Ar = Ph; II: R = F, Ar = Tol; synthesis, structure and properties of complexes see [1,2]). The optimal conditions were found to include the catalyst loading of 5 mol. % by Pd, temperature 110°C, O_2 as an oxidiser (1-5 atm.), carboxylate anion as an external base ($CCl_3CO_2^-$ or $CF_3CO_2^-$) and reaction time 12-24 hours. It was also shown that the overall activity of complex II exceeds that for complex I. In the heterocoupling of benzene and PhR (R = Me, 1,2-Me2, 1,3,5-Me_3, OMe, Cl, F, 1,4-F_2, 1,2,3,4,5-F_5) complex II provided moderate yields (56-77%) and high selectivity (90-100%) for all substrates tested.

The plausible mechanism for C–H/C–H oxidative coupling of arenes in the presence of trinuclear palladium nitrosyl carboxylate complexes was proposed basing on literature data and results of our own experiments. Generalized catalytic cycle is given in fig. 1. The mechanism was studied considering that linear Pd_3 metal core is kept through the catalytic cycle using the DFT approach implemented in the Priroda software package [3]. The model system included $Pd_3(NO)_2(\mu\text{-}CF_3CO_2)_4(PhH)_2$ complex as a catalyst, PhH as a substrate and $CF_3CO_2^-$ anion as an external base.

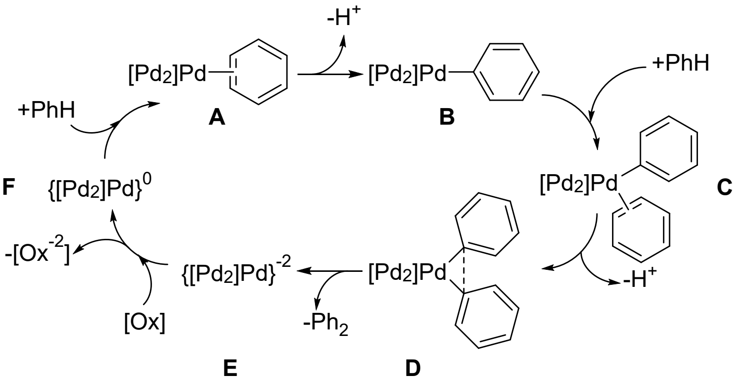

Fig. 1. Generalized catalytic cycle of C-H/C-H oxidative coupling of arenes in the presence of palladium complexes.

Fig. 2 shows the total energy profile for the formation of diphenyl in coordination sphere of [Pd_3] complex. The starting point is isolated molecule of [$Pd_3(NO)_2(CF_3CO_2)_4(PhH)_2$] (complex **A**). The energies are given against the starting points and corrected by the energies of free ions and molecules when it is necessary to keep the total composition of the system. The following key aspects of the mechanism were identified through the study:

1) Different deprotonation pathways are realized for the first and the second molecules of arene (SEAr and intramolecular concerted metalation-deprotonation (CMD), respectively).
2) The CMD of the second arene molecule is the rate-limiting stage, the energy barrier is about 40 kcal/mol, the total energy reduction in the cycle is about 50 kcal/mol.

Observation of two different deprotonation pathways for the first and second molecules of arenes gives an explanation to different trends in reactivity of the system towards homo- and heterocoupling of electron deficient arenes. If we consider that in heterocoupling reaction the first deprotonation occurs for benzene, then it is not affected by EWG in the other arene. The second deprotonation occurs as CMD and, in fact, is *facilitated* by EWG. As a result, a higher yield of the product is observed for electron deficient arenes in heterocoupling with benzene. Details of the study can also be found in publications [4,5]

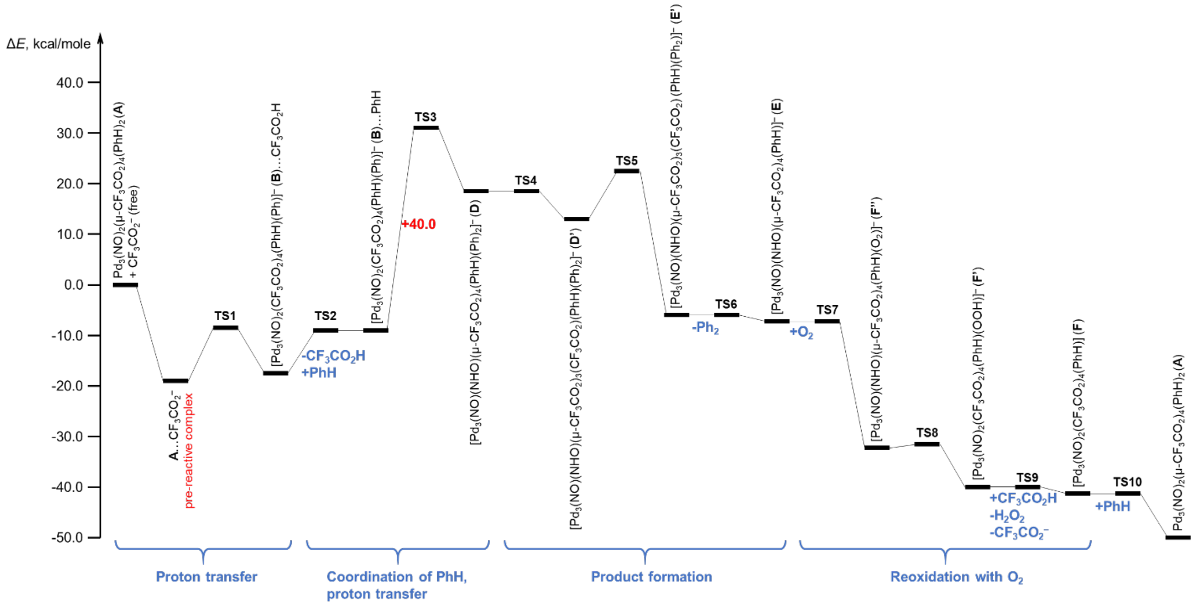

Fig. 2. Calculated energy profile for C-H/C-H coupling of benzene in the presence of $Pd_3(NO)_2(CF_3CO_2)_4(PhH)_2$

Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-73-00123.

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VP-27

Cooperative Catalysis by Iodine and Pyridine of Nitroxyl Radical-Mediated Electrooxidation of Alcohols

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We have established that electrochemical oxidation (ECO) of alcohols (ROH) in a two-phase medium $CH_2Cl_2/NaHCO_3(aq)$ with the participation of the KI/4-AcNH-TEMPO/Py catalytic system leads to the formation of the corresponding carbonyl compounds. ECO of alcohols to carbonyl compounds is known with the participation of the mediator system $I^-/I_2(I^+)$, but in the presence of catalytic amounts of nitroxyl radical (NR) – 4-AcNH-TEMPO, the efficiency of oxidation of alcohols increases significantly. The use of pyridine (Py) as a cocatalyst in the NR/KI system makes it possible to increase the speed and selectivity of ECO of alcohols.

To understand the role of all participants in the NR/KI/Py system in the electrocatalytic oxidation of ROH, spectral and CV studies were performed. CH_2Cl_2 and $NaHCO_3$ (aq) were used as solvents for spectral studies. Electronic absorption spectra make it possible to trace possible interactions between participants in the NR/KI/Py catalytic system both in H_2O (Fig. 1) and CH_2Cl_2 (Fig. 2).

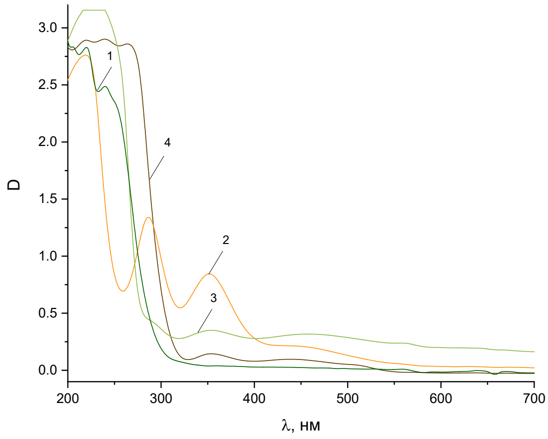

Рис.1

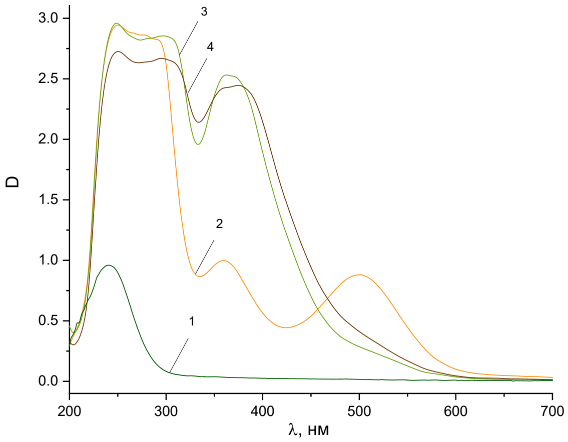

Рис.2

Fig. 1 – Electronic absorption spectra in H_2O: 1 – 0.2 mM 4-AcNH-TEMPO; 2 – 0.2 mM 4-AcNH-TEMPO+ 1 mM I_2; 3 – 1 mM Py + 1 mM I_2; 4 – 0.2 mM 4-AcNH-TEMPO + 1 mM I_2 + 1 mM Py;
Fig. 2 – Electronic absorption spectra in CH_2Cl_2:1 – 0.2 mM 4-AcNH-TEMPO; 2 – 0.2 mM 4-AcNH-TEMPO+ 1 mM I_2; 3 – 1 mM Py+ 1 mM I_2; 4 – 0.2 mM 4-AcNH-TEMPO + 1 mM I_2 + 1 mM Py.

The absorption spectrum of NR in H_2O has one intense band at 230 nm (Fig. 1, curve 1). When I_2 is added to the NR solution, a decrease in the intensity of the I_2 band at 460 nm and an increase in the intensity of the bands at 280 nm and 360 nm are observed (Fig. 1, curve 2). The band at 280 nm belongs to the oxoammonium cation (OA), and at 360 nm – to I_3^-.

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The low intensity of the absorption band related to I_2 (λ=460 nm, Fig. 1, curve 2) indicates the formation of the $OA{\cdot}I^-$ ion pair. The addition of Py to a solution of I_2 in H_2O changes the intensity of the bands at 290 nm (I^+) and 460 nm (I_2), which indicates the active interaction of Py with I_2 and I^+. This is reflected in the appearance of a high-intensity absorption band in the region of 220-280 nm (Fig. 1, curve 3). The electronic spectrum of the NR/I_2/Py system contains an intense band (region 200-320 nm) (Fig. 1, curve 4), which indicates the formation of an OA–Py complex, which interacts with ROH to form a new ROH–OA–Py complex, where a rapid transfer of hydride ion to OA and H^+ to Py occurs, with the conversion of ROH into a carbonyl compound. In CH_2Cl_2, the electronic spectrum of NR (Fig. 2) also contains one absorption band at 250 nm, but its intensity is lower compared to the NR band in H_2O (Fig. 2, curve 1 and Fig. 1, curve 1), which is explained by lower polarity CH_2Cl_2. In the electronic spectrum of the HR/I_2 system, a hyperchromic shift is observed for the absorption band in the region of 220-320 nm, probably related to the $OA{\cdot}I^-$ ion pair. The absorption band at 380 nm belongs to OA, and at 504 nm – to I_2 (Fig. 2, curve 2). Comparing the spectra of the I_2/Py and I_2/Py/HP systems shows their identity, which indicates the predominant formation of a Py complex with iodine in CH_2Cl_2 (Fig. 2, curves 3 and 4).

CV studies (Fig. 3) showed that when Py is added to an electrolyte containing NR, an increase in the catalytic current of NR oxidation to OA, and a decrease in the re-reduction peak current (Fig. 3, curve 3). OA binds into a complex with Py and leaves the near-electrode space. The addition of ROH to an electrolyte containing OA and Py leads to a decrease in overvoltage from 0.5 V to 0.4 V and an increase in the catalytic current in the potential range of 0.55-0.75 V. There is no peak of OA re-reduction current (Fig. 3, curve 4). The CV method also showed that the generation of I_2 and/or I^+ occurs at the anode as a result of the oxidation of I^-. On the glass carbon electrode in 0.5 M $NaHCO_3$, the oxidation potential of I^- is +0.55 V (relative to Ag/Ag^+), which is 0.1 V lower than the oxidation potential of NR (+0.65 V relative to Ag /Ag^+), therefore, iodine is the terminal oxidizing agent in relation to NR.

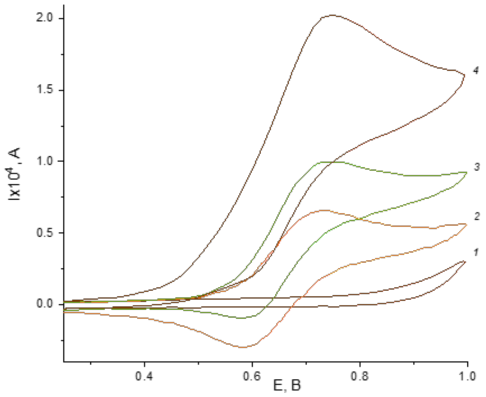

Fig. 3 – CV of the glass carbon electrode: 1 – 0.5 M $NaHCO_3$ (pH 8.6); 2 – 0.5 M $NaHCO_3$ + 4-AcNH-TEMPO (1 mmol); 3 – 0.5 M $NaHCO_3$ + 4-AcNH-TEMPO (1 mmol) + Py (1 mmol); 4 – 0.5 M $NaHCO_3$ + 4-AcNH-TEMPO (1 mmol) + Py (1 mmol) + 1-octanol (50 mmol); temperature- 25 ^{0}C; potential sweep speed – 0.01 V/s.

Thus, studies have shown the advantages of the corporate action of all participants in the KI/4-AcNH-TEMPO/Py catalytic system for effective ECO of alcohols to carbonyl compounds.

VP-28

Oxidation of Benzene to Phenol by Nitrous Oxide over Me-ZSM-5 Zeolites with Low Concentration of Active Sites. Single Site Catalysis

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The ZSM-5 zeolites with Si/Al ratio 50 and 80 (ZSM-5-50 и ZSM-5-80) modified by Ca-, Sr-, Cr-, Mn- и Sb-ions were synthesized and investigated in oxidation of benzene to phenol. It was shown that more active and selective in direct oxidation of benzene to phenol by nitrous oxide are catalysts containing about 0.1-0.2 % of Sb. These concentrations correspond to substitution of 1/12 and 1/6 ions of hydrogen by Sb-ions in the starting zeolite. As follows from the Table, yield of phenol equal to 61.4 % was obtained for reaction mixture of 5% benzene and 10% nitrous oxide at 450oC and contact time 1 sec. with selectivity to phenol 96% in the presence of (ZSM-5-50 + 1/12 Sb) sample. Such yield is about twice as much than an average value of yield reported in literature for other Me-ZSM-5 catalysts. Also (ZSM-5-50+1/6Sb) sample revealed much higher stability than other catalysts based on ZSM-5 zeolites.

Table 1. Catalytic performance of ZSM-5 zeolites with Si/Al ratio 80 and 50 in benzene oxidation to phenol versus Me-ions concentration. Contact time= 1s, T= 450°C, 5-6% benzene and 10-11% nitrous oxide in He. The samples were preliminary treated at 750°C.

Sample	benzene conversion, %	phenol selectivity, %	phenol yield, %	Yield (CO + CO2), %	Balance of carbon products, %
ZSM-5-50+1\4Sb	64,3	93	60	3,5	99
ZSM-5-50+1\6Sb	64,0	91,7	58,8	5,3	100
ZSM-5-50+1\12Sb	64,0	96	61,4	2,1	99
ZSM-5-80+1\12Sb	58,0	93	54,2	0,9	97
ZSM-5-80+1\6Sb	62,0	93	57,8	3,1	99
ZSM-5-50+1\8Ca	53,7	80,3	43,5	2,1	92
ZSM-5-50+1\8Sb+1\8Ca	67,3	87,3	58,8	5,1	99

A model of nitrous oxide decomposition over single active sites (the sites are located very distant from each other) of the catalyst is suggested. The suggested model of single site adsorption and catalysis explains the higher efficiency of nitrous oxide as oxidant than that of molecular oxygen in reaction of direct oxidation of benzene to phenol especially over Me-ZSM-5 zeolites with a low concentration (less than 0.1%) of Me-ions, as well as over ZSM-5 zeolites with a low concentration of Lewis acidic sites (LAS).

VP-29

The Role of Surface Oxygen in Increasing the Stability of a Carbon Support to an Oxidizing Environment for Pd/C and Rh/C Catalysts

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Catalysts based on platinum metals supported on carbon are widely used for various processes [1]. In contact with oxidizing environment, there is a danger of their deactivation caused by the oxidation of the carbon support. To search for ways of carbon support stabilization, the interaction of model catalysts prepared by vacuum deposition of Pd or Rh particles of 3-5 nm in size onto highly oriented pyrolytic graphite (HOPG) with a strong oxidizing agent (NO_2) was studied by XPS at room temperature and a pressure of 10^{-6}-10^{-4} mbar.

In the case of Pd and Rh were deposited on HOPG with a minimum content of surface oxygen (atomic ratio [O]/[C] ~ 0.0004-0.0006), the subsequent interaction of the resulting Pd/HOPG and Rh/HOPG samples with NO_2 led to the oxidation of the support accompanied by destruction of the upper layer of graphite and formation of oxygenated surface species [2] (Fig. 1a). The Pd and Rh particles retained their metallic state, but judging by the weakening of the 3d photoemission lines penetrated into the subsurface layer of HOPG (Fig. 1b). At the increased atomic ratio $[O]/[C] \geq 0.01$, the oxidation of carbon support with NO_2 was stopped (Fig. 2a), but Pd (or Rh) particles converted partially to PdO (or Rh_2O_3) (Fig. 2b).

NO_2 adsorbs on the surface of metal particles of M/HOPG and M/O-HOPG catalysts with dissociation leading to the formation of oxygen atoms, which penetrate into the particles or diffuse over its surface. When oxygen atoms reach the interface between the metal particle and the support, they can oxidize carbon (Fig. 1a). In the M/O-HOPG samples, oxygens that are present on the graphite surface before the metal particles are deposited, are proposed to block the centers from which the carbon support oxidation can start. The carbon support protection by surface oxygen against an oxidizing environment was demonstrated by us for real Pd/Sibunit catalysts [3].

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis. The studies were carried out using the equipment of the Center for Collective Use “National Center for the Study of Catalysts” (SPECS X-ray photoelectron spectrometer).

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VP-29

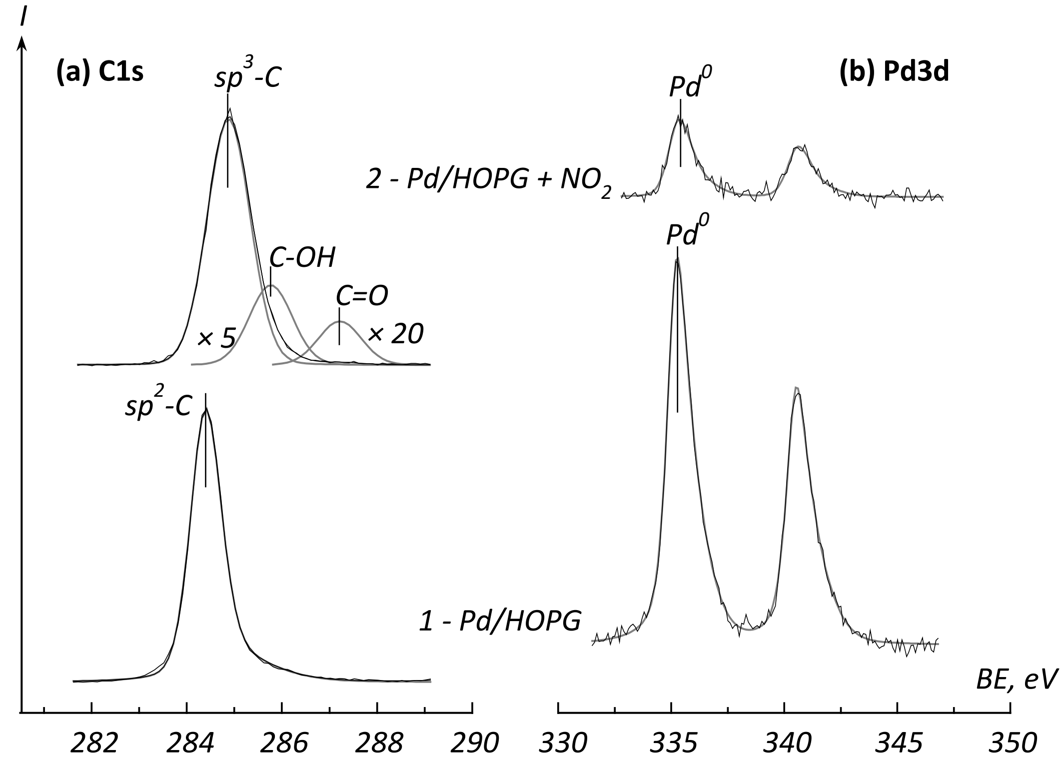

Fig. 1. XPS spectra in C1s (a) and Pd3d (b) regions of a Pd/HOPG sample before (1) and after (2) the treatment in NO_2 at room temperature and pressure of 10^{-6} mbar.

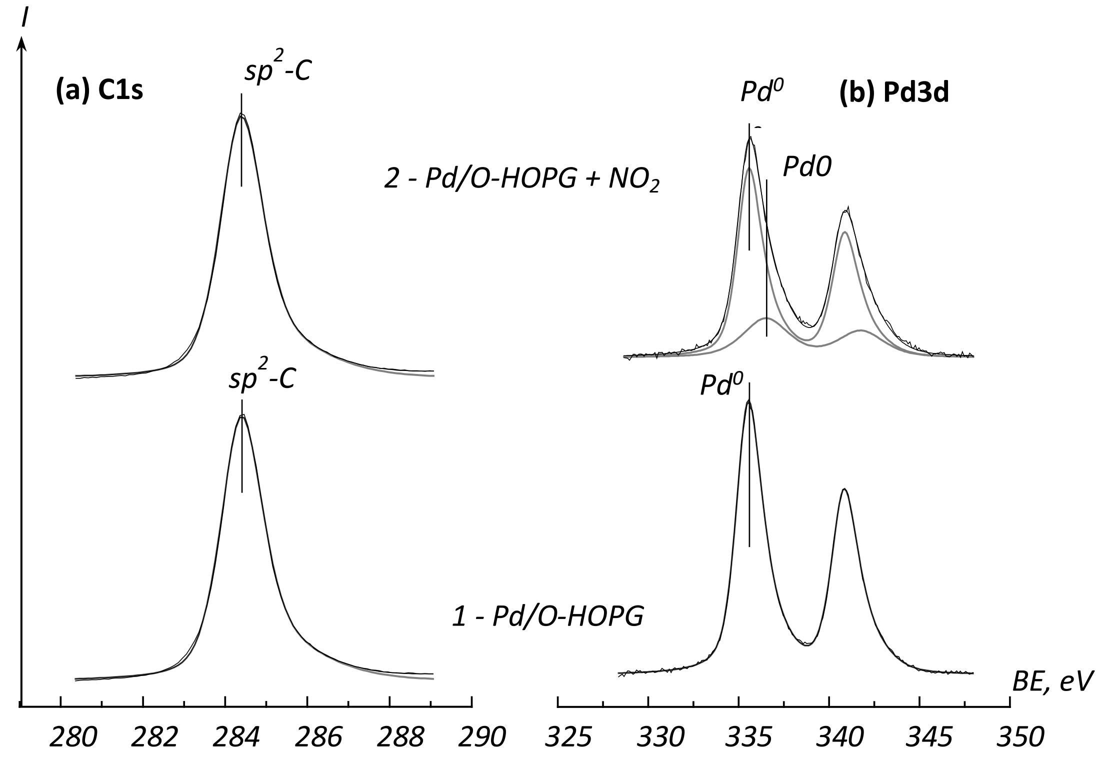

Fig. 2. XPS spectra in C1s (a) and Pd3d (b) regions of a Pd/O-HOPG sample before (1) and after (2) the treatment in NO_2 at room temperature and pressure of 5×10^{-6} mbar.

VP-30

Influence of the Dopant Nature on the Selectivity of Silver-Modified Mesoporous Silica Gel in the Hydrogenation Reaction of Hexyne-1/Hexene-1 and Heptyne-1/Heptene-1 Mixtures

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Silica gel is widely used as adsorbents and carriers for catalysts because it has a developed surface and high porosity [1]. The porous structure of silica gels can be controlled both at the synthesis stage and during subsequent processing [2]. Acetylene hydrocarbons are catalytic poisons and reduce the quality of oil, so it is important that the content of alkyne impurities is reduced to the minimum permissible value [3]. A number of studies have noted the high activity of silver in hydrogenation reactions of triple bonds [3-5].

Catalysts based on mesoporous silica gel doped with lanthanum, dysprosium, cerium, terbium and modified with silver (La - Ag/MS, Dy - Ag/MS , Ce-Ag/MS, Tb-Ag/MCS) were obtained by the template method [6]. The physicochemical characteristics of the resulting catalysts were studied by low-temperature nitrogen adsorption-desorption, scanning electron microscopy, X-ray fluorescence and X- ray diffraction analysis, inductively coupled plasma mass spectrometry, and IR spectrometry. It has been established that doping silica gel with rare earth metals followed by modification with silver leads to a decrease in its specific surface area. Determination of the quantitative content of rare earth metal by the ICP method showed that in the synthesized samples the concentration of terbium was 1.3%, dysprosium - 1.8%, lanthanum - 1.4%, cerium - 1.8%; the concentration of the modifier - silver in all samples was 8%. SEM studies showed that the synthesized catalysts are particles close to spherical in shape, the average particle size is in the range of 150-350 nm .

The study of the kinetics of hydrogenation of mixtures of hexyne-1/hexene-1 and heptyne-1/heptene-1 was carried out using an original installation that allows the hydrogenation process and analysis of the reaction mixture to be carried out online. The selectivity in the hydrogenation reaction of samples La-Ag/MS, Dy-Ag/MS, Ce-Ag/MS, Tb-Ag/MS was studied in the temperature range 130-160 °C.

Analysis of the products of the hydrogenation reaction of the hexine-1/hexene-1 mixture 20 minutes from the start of the reaction on an Agilent 7890 GC gas chromatograph with a mass selective detector showed that hexane, 1-hexene, cis-2-hexene, trans-2-hexene are formed , cis-3-hexene and trans-3-hexene.

Figure 1 shows the value of heptene-1 selectivity and heptene-1 conversion on Tb-Ag/MS. From Fig. 1 it is clear that with increasing temperature, the conversion of heptin-1 and selectivity for hexene-1 increase on the Tb-Ag /MS catalyst. Similar data were obtained on other samples.

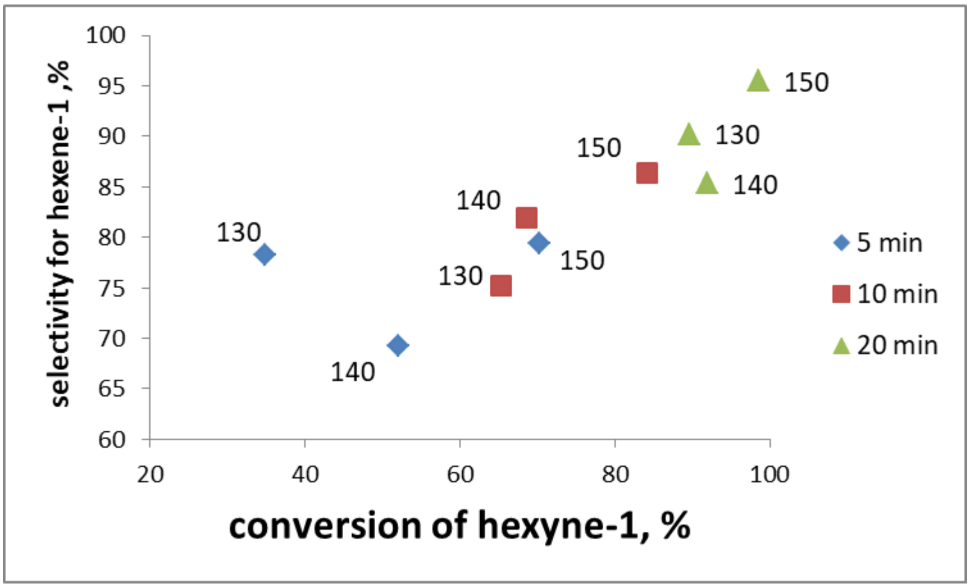

Fig. 1. Value of selectivity for heptene-1 and conversion of heptyne-1 at different temperatures Tb-Ag /MS (3 atm, 5, 10, and 20 minutes from the start of the reaction).

Research have shown that catalysts containing terbium and dysprosium are the most effective and selective in the hydrogenation reactions of a mixture of acylene and olefin hydrocarbons. Available literature data confirm that when a rare earth metal is introduced into the structure of a support, the greatest efficiency and selectivity in hydrogenation reactions is observed in metals that have a larger number of electrons at the f-sublevel [7,8].

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VP-31

Multi-Level Information Method for Developing Kinetic Models of Low-Temperature Steam Reforming of Light Alkanes

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Gas flaring at gas and oil fields, and refineries is an actual problem today. The issue of flaring mainly concerns associated petroleum gas (APG), which is a mixture of saturated hydrocarbons produced at oil fields. At the moment, one of the most promising ways of efficient utilization of APG is to use it directly at the field to generate electricity and heat at small-scale power plants for matching the field's own needs and supplying the nearest settlements [1]. The use of the initial APG as a fuel is problematic, because it has high content of C_{2+}-hydrocarbons, variable composition and low methane index. To solve this problem, it is proposed to use low-temperature steam reforming (LTSR) of C_{2+}-hydrocarbons that make up APG, with the predominant formation methane-hydrogen mixtures [2].

In the present work the properties of highly dispersed Rh catalysts deposited on various supports were studied in the LTSR of model APG mixtures containing C_2H_6-C_4H_{10} in the excess of methane. 1 wt. % Rh/$Ce_{0.75}Zr_{0.25}O_2$ catalyst was prepared by sorption-hydrolytic deposition [3]. The properties of the obtained catalyst were investigated in the LTSR of model APG mixtures at temperatures of 200-400 °C and WHSV = 2500-5000 $ml \cdot g_{cat}^{-1} \cdot h^{-1}$. The catalyst was stable and provided complete conversion of C_{2+}-hydrocarbons into CH_4, CO_2 and H_2 at T = 320-350 °C. In addition, the conversion of propane and heavier alkanes over Rh catalysts in the low temperature range (200-300 °C) increases the concentration of ethane in the reaction mixture. Ethane is formed by a parallel reaction of propane hydrogenolysis. Ethane has a higher heating value than methane and can compensate the negative effect of the dilution by carbon dioxide and hydrogen on the characteristics of the fuel mixture. This unique property of Rh catalysts makes it possible to obtain gaseous mixtures containing a certain amount of ethane in steam reforming reactions, which in turn is useful for varying the thermal properties (net calorific value, Wobbe index, methane number) of the resulting fuel mixtures.

Using a dynamic information-computing analytical system (DICAS) for solving inverse problems of chemical kinetics, based on experimental data, a macrokinetic scheme of this process is proposed and kinetic parameters are obtained. DICAS includes a database of full-scale and computational experiments. The database allows one to process the probable mechanisms of chemical transformation schemes, both single-stage and multi-stage. The mathematical model for calculating all substances involved in the reaction is a system of ordinary nonlinear differential equations, which were solved numerically using the 5th order Kutta-Merson method with automatic selection of the integration step [4]. The inverse problem of chemical kinetics - minimizing the difference between calculated and experimental data for different temperatures over contact time - was solved by the parabolic descent method [5].

Experimental data were obtained for selected one- and two-stage schemes of chemical transformations, which made it possible to carry out computer modeling in stages, from simple to complex. First, the activation energy for the reaction of ethane and propane hydrogenolysis was determined as 41.327 and 63.411 kcal/mol. Further, the kinetic parameters for a three-stage reaction were determined.

The adequacy of the results obtained satisfies the 4th level. The database also contains experimental data for multi-stage chemical reaction schemes for different times of contact of the reaction mixture with the catalyst. After developing a complete picture of the kinetic model of the reactions under consideration, optimization problems will be solved for various parameters of the experimental setup.

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VP-32

Computer Analysis of the Kinetics of the Catalytic Synthesis of Methyl Tert-Butyl Ether

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A kinetic model for the catalytic synthesis of methyl tert-butyl ether (MTBE) has been developed. An experiment was carried out on the intermolecular dehydration of tert-butyl and methyl alcohols under the action of a HY zeolite catalyst and a catalyst system based on $CuBr_2$ supported on HY zeolite [1]. Using experimental data and the development of a multi-stage scheme of chemical transformations (Fig. 1), a kinetic model was built based on the law of acting surfaces, which takes into account the processes of adsorption and desorption on the surface of the catalyst, taking into account the change in the number of moles of the reaction mixture N [2], where X_i – these are the components of the reaction, x_i are the concentrations of the components and θ_i are the proportions of the surface occupied by the i-th component:

N	Stage	Kinetic equations
1	$HY\ (\boldsymbol{\theta_1}) + (CH_3)_3COH\ (\boldsymbol{X_1}) \rightarrow (CH_3)_3COH_2Y\ (\boldsymbol{\theta_2})$	$\omega_1 = \frac{k_1 x_1 \theta_1}{N^2}$
2	$(CH_3)_3COH_2Y\ (\boldsymbol{\theta_2}) \rightarrow (CH_3)_2C{=}CH_2\ (\boldsymbol{X_2}) + H_2O\ (\boldsymbol{X_3}) + HY\ (\boldsymbol{\theta_1})$	$\omega_2 = \frac{k_2 \theta_2}{N}$
3	$(CH_3)_2C{=}CH_2\ (\boldsymbol{X_2}) + HY\ (\boldsymbol{\theta_1}) \rightarrow (CH_3)_3CY\ (\boldsymbol{\theta_3})$	$\omega_3 = \frac{k_3 x_2 \theta_1}{N^2}$
4	$(CH_3)_3CY\ (\boldsymbol{\theta_3}) + MeOH\ (\boldsymbol{X_4}) \rightarrow (CH_3)_3COMe\ (\boldsymbol{X_5}) + HY\ (\boldsymbol{\theta_1})$	$\omega_4 = \frac{k_4 x_4 \theta_3}{N^2}$

Fig. 1. Stages of chemical transformations and kinetic equations of MTBE

The mathematical description of the direct problem of non-stationary chemical kinetics is a system of ordinary nonlinear differential equations [3] with initial data x_1 = 0.2 mol.dol.; x_4 = 0.8 mol.dol.; θ_1 = 1; $x_i = 0$ at $i = 2,3,5$; $\theta_i = 0$ at $i = 2,3$ with temperatures for the HY catalyst: T = 140°C, 150°C, 160°C, for the CuBr2/HY catalyst: T = 100°C, 140°C, 160°C.

In the MatLab development environment, the inverse problem was solved using a genetic global optimization algorithm [4] in the form of an optimization problem for the functional deviation of the concentrations of experimental data components from the calculated values. The condition for exiting the algorithm was a minimal change in the value of the functional:

$$EE(k_j) = \sum_{i=1}^{I} \sum_{p=1}^{P} \frac{\left| x_{i,p}^{\exp} - x_{i,p}^{calc} \right|}{x_{i,p}^{\exp}} \rightarrow \min,$$

where n is the number of nodes; P – number of experiments for each component; $x_{i,p}^{\exp}$ and $x_{i,p}^{calc}$ – experimental and calculated values of component concentrations.

Figures 2 and 3 show the kinetic dependences of tert-butanol consumption (experimental and calculated) and MTBE formation using the HY and CuBr2/HY catalyst, respectively. The value of the functional is within 10%, which indicates a satisfactory description of the experiment.

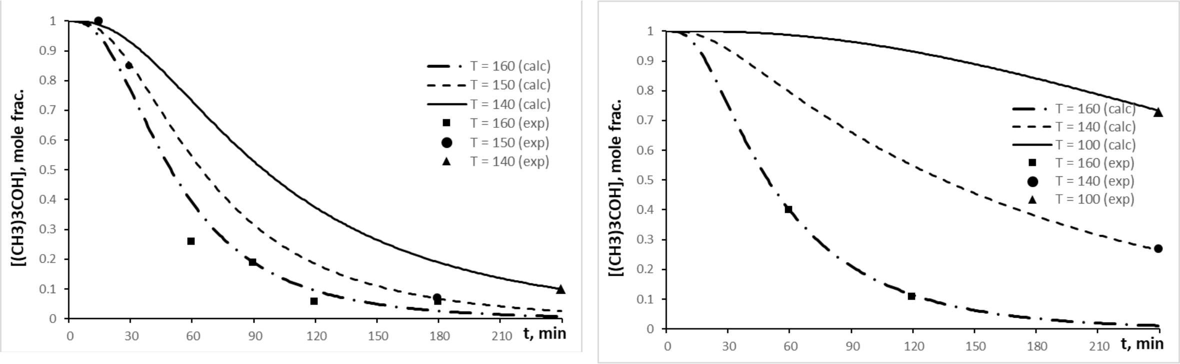

Fig. 2. Change in tert-butanol concentration in the presence of HY and CuBr2/HY

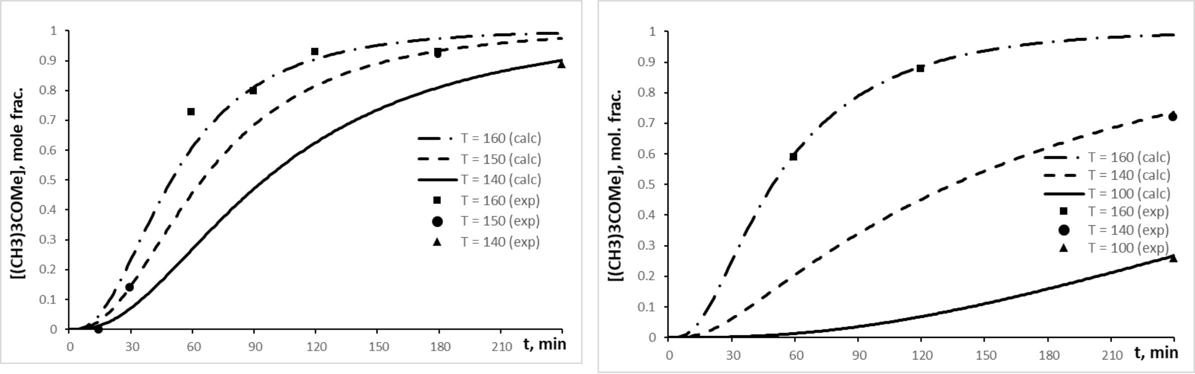

Fig. 3. Change in MTBE concentration in the presence of HY and CuBr2/HY

This work describes the scheme of chemical transformations, including adsorption and desorption reactions, developed a kinetic model, and determined the model parameters using a genetic algorithm for global optimization when solving the inverse problem. Graphs of the correspondence of the concentrations of key components of the experimental data to the calculated ones are presented.

Acknowledgement: The work of Gubaydullin I.M. was funded by the Institute of Petrochemistry and Catalysis of the Russian Academy of Sciences (theme No. FMRS-2022-0078).

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VP-33

Investigation of 1-Methyl Decalin Stereoisomers Transformations in Hydrogenation-Dehydrogenation Reactions Applied to Liquid Organic Hydrogen Carriers

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LOHC – liquid organic hydrogen carrier – one of the promising ways of hydrogen storage. LOHC are usually a pair of hydrocarbons arene-naphthene, which can be reversibly hydrogenated and dehydrogenated with accumulation, store and evolution of hydrogen. Arene that is the product of naphthene dehydrogenation reaction can be reused such as hydrogen carrier after «charging» (hydrogenation) [1].

In the present work, we evaluated the possibility of using the pair of conjugated substrates 1-methyldecalin (1-MD) - 1-methylnaphthalene (1-MN) as LOHC. Melting temperature of both substrates are about -22°C that allows their operation in cold seasons [2]. However, the presence of a substituent in the molecule of 1-MD causes the appearance of two isomers differing in the direction of the methyl substituent (*syn*- and *anti*-) in addition to each of the *cis*- and *trans*-isomers. It is known that for unsubstituted decalin which has two spatial isomers, the dehydrogenation conversion of the *cis*-isomer at 320°C is 30% higher than that of the *trans*-isomer [3].

The behavior of 1-MD spatial isomers in the dehydrogenation reaction was studied on the example of mixtures with different ratio of *cis/trans*-isomers, which was carried out in a plug-flow reactor with a stationary catalyst bed (1%Pt (wt.) deposited on an oxidized carbon carrier - Sibunite). The reaction was carried out at 320°C, atmospheric pressure, in the range of liquid hourly space velocity from 0.5 to 3.5 h^{-1}. Mixtures of isomers were obtained by hydrogenation of 1-MN (98%) in a batch reactor (autoclave) in different reaction conditions. The reaction was carried out on 3%Pt/AC catalyst (Sigma Aldrich) in the temperature range 240-280°C, at hydrogen pressure 60-80 atm and catalyst:substrate ratio from 1:10 to 1:15 (vol.). Conversion and selectivity of reactions were determined by gas chromatographic analysis of liquid products. Formal values of equilibrium constants of dehydrogenation reaction elementary acts were calculated with the complex reaction kinetics mathematical modeling computer program KINET 0.8 using the obtained experimental data.

The data obtained in the hydrogenation reactions showed that, at equal pressure, mixtures with a high content of *cis*-1-MD are formed when the reaction temperature is decreased. At the same time, a change in the partial pressure of hydrogen has a smaller effect on the value of the ∑trans/∑cis ratio in the final product than a change in temperature. The comparison also showed that the hydrogenation rate of 1-MN is two times slower than that of unsubstituted naphthalene.

On the example of the dehydrogenation reaction it was shown, as in the case of decalin, the spatial isomers of 1-MD behave differently: the *cis-syn*-isomer is the most active, and the isomers with *trans*-ring junction are the least active, and they practically do not react under the chosen conditions. At the same time a mutual transition of *cis*-isomers into *trans*-isomers is also observed during the reaction. It affects negatively on the conversion of the substrate and, consequently, on the amount and rate of released hydrogen.

In general, the ways of formation and transformation of spatial isomers of 1-MD obtained on the example of hydrogenation reactions of 1-MN and dehydrogenation of 1-MD indicate that the presence of a methyl substituent in one of the rings of the condensed bicyclic system in position 1 leads to additional spatial difficulties for both types of reactions, as compared to similar ones realized for naphthalene and decalin. Apparently, this is caused by additional steric hindrances in the adsorption of the substrate on the active centers of the catalyst associated with the influence of the methyl substituent direction in the ring both at their *cis*- and *trans*-ring junction.

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VP-34

Acentric Factors in Kinetic Modeling of the Oxidation Process of Alkyl-Fermented Aromatic Hydrocarbons

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Despite of extensive knowledge base on the mechanism of the oxidation process alkylaromatic hydrocarbons, it is still impossible to identify adequate kinetic model that allows taking into account the structural features of oxidizable substances such as ethylbenzene (EB), para-xylene (PX), 1,2,4-trimethylbenzene (TMB) and isopropylbenzene (IPB). Finding structural parameters that depend on the properties of compounds and their further implementation in the kinetic model will make it possible to develop a unified concept linking the reactivity and structure of alkylarenes.

In this work we considered the static factor of complexity of intermolecular interaction (Ψ-factor), this factor quantitatively describes deviations of reactions of substance under study from simple intermolecular influence. This factor was previously considered only for nonpolar molecules [1]. However, it has been shown that it can also be used for oxygen-containing substances that have a dipole moment, dividing them into classes [2]. The obtained dependences made it possible to calculate the rate constants of reactions in which oxygen-containing oxidation products participate.

A comparison of the elementary stages of oxidation mechanism using the example of specific alkylarenes EB [3] and PX [4] revealed the presence of key stages of hydrocarbon oxidation, determined by the participation of peroxides, alcohols, ketones and acids. The rate constants values differ for stages ROO· + RH → ROOH + R· (a), ROO$^{\bullet}$ + ROH → RO$^{\bullet}$ + ROOH (б), 2ROO· → molecular products (c), ROO$^{\bullet}$ + RO → R`COOH + RO$^{\bullet}$ (г), ROOH + RCOOH ↔ ROH + RCOOOH (e and Co[III] + RCOOOH ↔ [Co[III]…RCOOOH] (f for EB and PX, while the other values of the constants are close to each other. Consequently, it is sufficient to determine the numerical values for the substances under study only for the indicated stages from the entire set of reactions rate constants describing the transformation of hydrocarbons during their oxidation. The remaining constants should be equated to the values of the constants for EB/PX.

It is advisable to calculate the rate constants of an elementary act based on the resulting hydroperoxide, since it participates in almost all key stages of the transformation of molecular products. However, in reactions (a), (b) and (d) it is not the hydroperoxide itself that participates, but its radical, so the calculation was carried out for the hydrocarbon, alcohol and intermediate carbonyl, respectively.

For reactions (e) and (f), the constants were calculated using the final product acid and for reaction (c) on the hydroperoxide itself.

Table 1 includes the results of calculations of constants based on the ψ-factor and experimental data.

Table 1

Numerical values of the reaction rate constants for the oxidation process of IPB and TMB

Oxidizable substance/ reactions	(a)	(b)	(c)	(d)	(f)	(g)
Substance for which the calculation is carried out	hydrocarbon	alcohol	hydroperoxide	acetophenone	benzoic acid	benzoic acid
Oxidation IPB						
Calculation by Ψ-factor	2850	$2,9\cdot10^{6}$	$7\cdot10^{4}$	500*	1,5*	1,5*
Final calculation	250	$1,5\cdot10^{3}$	$2\cdot10^{4}$	500	1,5	1,5
Oxidation TMB						
Calculation by Ψ-factor	2850	$8,1\cdot10^{5}$	$0,3\cdot10^{5}$	$1\cdot10^{5}$	42	42
Final calculation	700	$10\cdot10^{5}$	$0,3\cdot10^{5}$	$5\cdot10^{5}$	42	42

** - these constants were not calculated, but equated to the reaction constants according to EB, due to the identical intermediate product formed*

According to table 1, significant discrepancies are visible between constants calculated from ψ-factor and those determined as a result of kinetic modeling based on experimental data for IPB and, to a lesser extend, for TMB, which may be caused by the presence of steric hindrances in the case of a branched substituent during the oxidation of IPB and the presence of ortho-effect of the location of methyl substituents for TMB.

Thus, the proposed acentricity factor can be used to indirectly determine the rate constants of elementary stages only for hydrocarbons having alkyl substituents of normal structure such as TMB, mesitylene, etc.

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VP-35

Investigation of a Fibrous Catalyst in the Liquid Phase Oxidation of Anthraquine and Azo Dyes

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Synthetic dyes are often used in the dyeing of fabrics, and they are present in the wastewater of many enterprises. Pre-treatment of wastewater at the plant never reduces the dye content below 0.5-5 mg/l, leaving the water highly colored and toxic. Aftertreatment and discoloration is a complex and expensive task. One of the possible ways to solve this problem is the oxidation of dyes on heterogeneous catalysts with hydrogen peroxide. Homogeneous catalysts are not applicable in this case due to their unavoidable loss with treated wastewater. And also, their activity is low and requires large doses of peroxide for discoloration. Insoluble catalysts containing complex transition metal compounds on their surface are promising. The following complexes were studied: Ni^{2+}, Fe^{3+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Cr^{3+}, and Ag^{+}. Such materials have a number of advantages. Complexes concentrates on the surface, having a high local concentration and is not released into the solution. There is a wide range of complex compounds, active metals and methods of applying them to substrates. The materials have a sorption capacity for the dye, so that the substrate is also concentrated in the zone of action of the catalytic complex. This ensures high rates of discoloration and decomposition of dyes. Catalysts of this type are universal and can be used for the oxidation of many other organic and inorganic impurities, aldehydes, phenols, sulfides, mercaptans, and surfactants [1].

For the catalytic substrate, a knitted material made of strong polypropylene (PP) monofilament and a complex polyacrylonitrile (PAN) yarn connected to it in a single whole was chosen. With its bulk elastic shape, low hydraulic resistance, and large surface area available for reagents, this material works well as a carrier of the catalytic layer [2].

A complex of polyethylenepolyamine (PEPA) with a transition metal ion was used in this study. It is quite strong and has a catalytic activity. PEPA is an affordable reagent and can be crosslinked with epoxy resins, becoming strong, insoluble in any known solvents, resistant to oxidizing agents, concentrated acids and alkalis. The catalytic complex was synthesized in an aqueous solution with the addition of PEPA and a transition metal salt (for example, nickel nitrate). Further, the knitted material was soaked in this solution and dried, forming a thin film on the PAN fiber. To fix the catalytic film, the material was impregnated with an acetone solution of ED-20 epoxy resin based on the mass ratio of PEPA : ED-20 equal to 1:10. The metal content on the fibrous material was 0.05 mmol/g. To accelerate polymerization, after air drying, the material was heated for 0.5 hours at 110 ^{o}C.

The catalytic activity of the material was measured under dynamic conditions with continuous supply of the initial dye solution to a temperature-controlled reactor containing a catalyst sample. At the same time, the reaction volume was maintained constant. Mixing was carried out by a jet of air. The dye concentration at the reactor inlet and outlet was measured photocolorimetrically. The reaction rate was measured as the difference between the inlet and outlet concentrations related to the average residence time of a portion of liquid in the reactor. The oxidation rate of the following dyes was studied: Alizarin, Dispersed blue K, Acid blue 45, Acid orange, Acid scarlet in the concentration range of 0-30 mg/l, with the content of hydrogen peroxide in a solution of 0-100 mg/l with a pH change in the range of 1-7, the temperature range of 10-70 °C., the amount of catalyst changed axis in the range of 20-200 g/l.

Results.

For pH 1-4, the rate of discoloration was almost independent of the acidity of the medium, and with an increase in pH above 4, it dropped sharply. The concentration of dye, hydrogen peroxide, and catalyst dose affects the oxidation rate linearly. The effect of temperature corresponds to the formal activation energy in the range of 7.2 – 7.5 kJ/mol. For example, for a Ni^{2+} containing catalyst, in the case of decomposition of the Acid Blue 45 dye, the decomposition rate can be calculated by the equation: $k \cdot \exp(-Ea/RT) \cdot C1 \cdot C2 \cdot M$, mg/(l·min), where $k = 3.18 \cdot 10^{-3}$ $l^2/(\min \cdot mg \cdot g)$, Ea = 7380 J/mol, R = 8.314 J/(mol·K), T, K-absolute temperature, C1, C2, mg/l - concentrations of dye and peroxide, M, g/l – amount of catalyst.

The results of the study show the potential of such catalysts for removing dyes from wastewater.

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VP-36

Hydrate –Anion Complex of Protone $[H(H_2O)_n]^+A^-$ as the Basis of the Complex Acidity Function H_o^w of Aqueous Solutions of Strong Mineral Acids

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Aqueous solutions of mineral acids provide changes in the acidity of the medium (h_o=1) in a wide range of the function $H_o = 0 \div -12.0$ and are used as a medium for various catalytic reactions [1-3]. The functions of protic acidity pH and H_o of catalytically active two-component systems "water - strong acid" are experimentally determined and described using real values in the form of transcendental equations $-pH = \log(C_{H+}\cdot f_{H+}) = \log(a_{H+})$ and $(-H_o) = \log[(C_{H+})\cdot(f_{H+}\cdot f_B/f_{BH+})]$, having no solution. We propose a method for describing protic acidity, based on the concepts of mathematics of complex numbers and ultimately obtaining a calculated complex function that gives an approximate solution to transcendental equations. Such equations are based on the natural logarithm of complex functions of protic acidity from complex numbers, which allows for a correct description and deeper understanding of the catalytic mechanisms of the processes. Basic postulates of our approach: 1- water, as an equal participant in chemical transformations along with the proton; 2- acid properties of the medium are determined not only by the number of protons per unit volume, but also by the degree of their hydration: the acidic properties of the medium are stronger for the less hydrated proton [4,5]. As an alternative to the existing empirical H_o scale, we have adopted [6] the concept of an electrically neutral proton hydrate-anion complex $[H(H_2O)_n]^+A^-$ of variable composition (HACP) as a basic active particle. This complex reflects the inhibitory effect of the hydration shell on the activity of protons and is involved in the mechanism of proton transfer from the medium to the substrate, ensuring the catalytic process. In an excess of water, it is proposed [6] to consider the empirical function H_o as a function for aqueous solutions of mineral acids from two conjugate variable parameters: *protic acidity* ($\log C_{H+}$) and *excess acidity X* [7]: $-H_0 = \log C_{H+} + X$. The value of C_{H+} and the parameter X can be expressed in terms of proton and water the relative concentrations in the form of the final equation: $-H_o^w = \log C^*_{H^+} + \log(C^*_w)^B$. The independent contribution $B\cdot\lg C^*_w = \log(C^*_w)^B$ reflects the influence of water concentration in HACP, and parameter B characterizes the nature of the anion, its physical properties, i.e. the ability of an anion to compete with a proton for the formation of a hydration shell, thereby reducing the hydration of the proton and increasing the acidity of the medium. The calculated function H_o^w is comparable to the H_o scale, but does not use concepts of activity coefficients and does not require a labor-intensive experiment to determine H_o. The calculated values H_o^w reproduce the H_o values in the concentration range from pure water, pH range to 68 wt.% H_2SO_4, 40% HCl, 70% $HClO_4$. HACP is a hydrate-separated ion pair of a proton and an anion, existing under conditions of a constant volume of solution equal to 1 liter. Under these conditions, a change in the concentration of the acid HA, and therefore the H^+ and A^- ions in such a complex, is associated with a coordinated change in "antiphase" in the concentration of water. In this case, the sum of the volumes of hydrated ions should be equivalent to the volume of water excluded from 1 liter of solution by adding HA.

Two types of proton-anion interaction (isolated through water molecules and directly through an electric field) allow acidity to be mathematically described by a quadratic function

(w) of the complex function z, which is the volume of excluded water in the form: $w = z^2$. Here $z = (V_w) = \{V_{H+,} + V_{A-}\}$ plays the role of a complex number: the volume of excluded water corresponds to the sum of the volumes of hydrated protons and anions. The acidity scale of aqueous solutions of sulfuric acid is proposed to be divided into two areas. In a dilute medium (< ≈ 68 wt.% H_2SO_4), the acidity of the medium is characterized by the participation of HACP and is described by the function H_o^w (7 ÷ -5,5), and in more concentrated solutions it is ensured due to the solvate complex with the participation of H_2SO_4 molecules and is described by the function H_o^s = -5,5 ((wt. 68% H_2SO_4) ÷ ≈ -11 (wt. 99,5% H_2SO_4). The concepts of HACP and the proposed scale H_o^w determine the catalytic activity of the proton and significantly clarify the interpretation of the principles associated with the interpretation of the mechanisms of acid-catalyzed reactions.

The proton, together with its hydration shell in the HACP, participates in the formation of transition states of processes in the form of a chain of water molecules, a proton and an anion, which is closed to the reaction center, in which coordinated proton transfer occurs in cyclic transition states of catalytic processes.

In accordance with the stated principles, the process of sulfonation of arenes/hydrolysis of arenesulfonates in dilute aqueous solutions of strong acids is irreversible and should proceed by a one-stage mechanism [8].

At the reaction center of the arenesulfonate anion $ArSO_3^-$, during its protodesulfurization, an electrically neutral intermediate $ArSO_3^-[H(H_2O)_n]^+$ is formed, structurally similar to the proton hydration complex, which then passes through a cyclic transition state and regeneration of the catalyst in the form of the complex $[H(H_2O)_{n-1}]^+HSO_4^-$.

In concentrated solutions of sulfuric acid (i.e., in excess of acid), the protohydrolytic replacement of a sulfonic group by a proton becomes a reversible process of resulfuration.

Due to excess sulfuric acid, a hydrate-solvate complex of the proton is formed, also through a one-step mechanism of reversible sulfonation of arenes/hydrolysis of sulfonic acids: $ArSO_3H[(H_3O)^+HSO_4^-] \leftrightarrow [CPS]^{\neq} \leftrightarrow ArH\cdot(H_2SO_4)_2$.

The proposed interpretation of the one-step mechanism of electrophilic substitution in the aromatic series through the formation of an intermediate contradicts the multi-step mechanism of electrophilic substitution generally accepted in the literature.

It allows the formation of a σ-complex - an unstable electrophilic particle (+E) and the complete transfer of its positive charge to the aromatic nucleus, leading to a violation of the stability of the conjugated π-system [6, 8, 9].

Acknowledgement: This work was funded by the Ministry of Science and Higher Education of the Russian Federation (Project No. FZZW–2024–0004).

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VP-37

Alternative Liquid and Solid-Phase Methods for the Synthesis of 3,6-di-tert-Butylcatechol on Ortho-Orienting Titanium Metal Complexes

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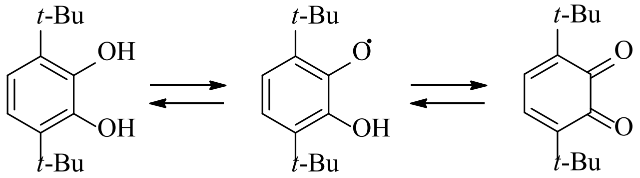
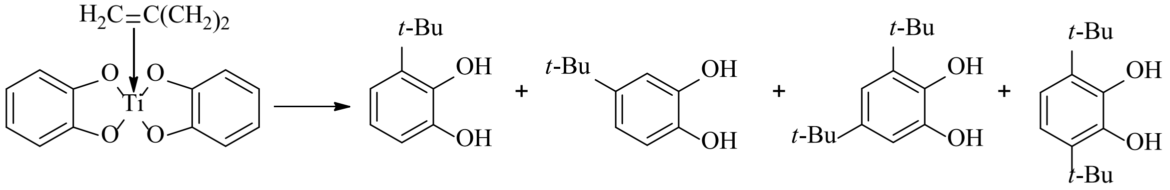
Redox triad 3,6-di-tert-butylcatechol – 3,6-di-tert-butyl-o-semiquinone – 3,6-di-tert-butyl-o-quinone



3,6-Cat **3,5-SQ** **3,6-Q**

is used in studies of the mechanisms of organochemical reactions to detect active short-lived particles (radicals, biradicals, radical ions, carbenes, etc.) that form more stable derivatives with triad components available for spectral observations. This is due to the symmetric shielding of OH-groups, which radically distinguishes the 3,6-triad from derivatives of the isomeric 3,5-di-tert-butylcatechol (3,5-Cat).

For the first time, ortho-selective tert-butylation of catechol with the formation of 3,6-Cat was carried out at the Institute of Chemical Physics of the USSR Academy of Sciences in the laboratory of the synthesis of polymer stabilizers (later the laboratory of antioxidant chemistry of the Institute of Biochemical Physics of the Russian Academy of Sciences) by V.V. Ershov, I.S. Belostotskaya et al. [2]. The selectivity of the process was provided by a specially synthesized catalyst - titanium bis-catechate, which forms with isobutylene a coordination-catalytic complex, ortho-orienting the entry of tert-butyl groups into catechol rings. The process was carried out in a shaking autoclave at high temperature and pressure, in o-xylene solution with an excess of isobutylene. Duration of the process was 6-8 hours. The alkylate was separated into individual components by high-vacuum fractionation. Isomeric mono-3- and 4-tert-butyl (3- and 4-Cat), 3,5- and 3,6-di-tert-butyl (3,5- and 3,6-Cat) catechols were identified by NMR. When analyzing by TLC on Silufol UV-254, an interesting feature was discovered - the coloring of the spots of compounds on air:



3-Cat black **4-Cat** lilac **3,5-Cat** crimson red **3,6-Cat** brown

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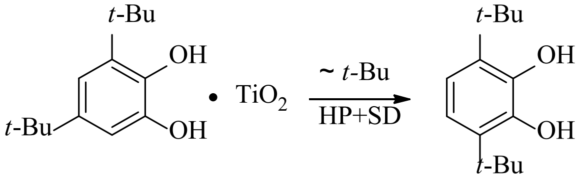
The yield of 3,6-Cat is 60-65%, which indicates the high selectivity of the catalytic process. Among the disadvantages of the process are the impossibility of catalyst regeneration and the formation of a ballast product in form of a bottom residue after fractionation.

These negative factors were completely eliminated in the synthesis of 3,6-Cat by solid-phase isomerization of 3,5-Cat on TiO_2 under the action of high pressure and shear deformation (HP+SD) on Bridgman rotary anvils (pressure 10 MPa, relative angle of anvils rotation 100°, duration 10 min). The process was carried out with the use of commercially available compounds. The titanium metal complex 3,5-Cat with TiO_2 was formed *in situ*. The yield of the target 3,6-Cat was quantitative, the formation of by-products and the presence of the initial 3,5- Cat weren't registered.



3,5-Cat **3,6-Cat**

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VP-38

Hybrid Materials Based on Covalent Triazine Frameworks for the Process of Electrocatalytic Synthesis of Ammonia

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Energy-efficient and environmentally friendly processes are essential in various industries. A striking example of such a process is the electrocatalytic synthesis of ammonia. We proposed to use graphite as an electrode with hybrid materials deposited on it, including a substrate of covalent triazine frameworks (CTF) coated with cobalt nanoparticles.

Microwave synthesis of CTF based on cyanuric chloride and biphenyl as a linker was carried out in n-octane in the presence of aluminum chloride. The reaction time was 1 hour at 140^0 C and a pressure of 1 atm. After removing the solvent and subsequent treatment of the black precipitate with 0.5 M hydrochloric acid for 24 hours, a yellow precipitate was obtained, which was repeatedly washed with ethanol and dried. An elemental analysis was performed and an X-ray diffraction pattern of the yellow powder was obtained.

Subsequently, the yellow powder was dispersed in acetone by ultrasound and applied to a graphite electrode, while cobalt nanoparticles were placed on the CTF by electrochemical deposition for 5 minutes (Fig. 1).

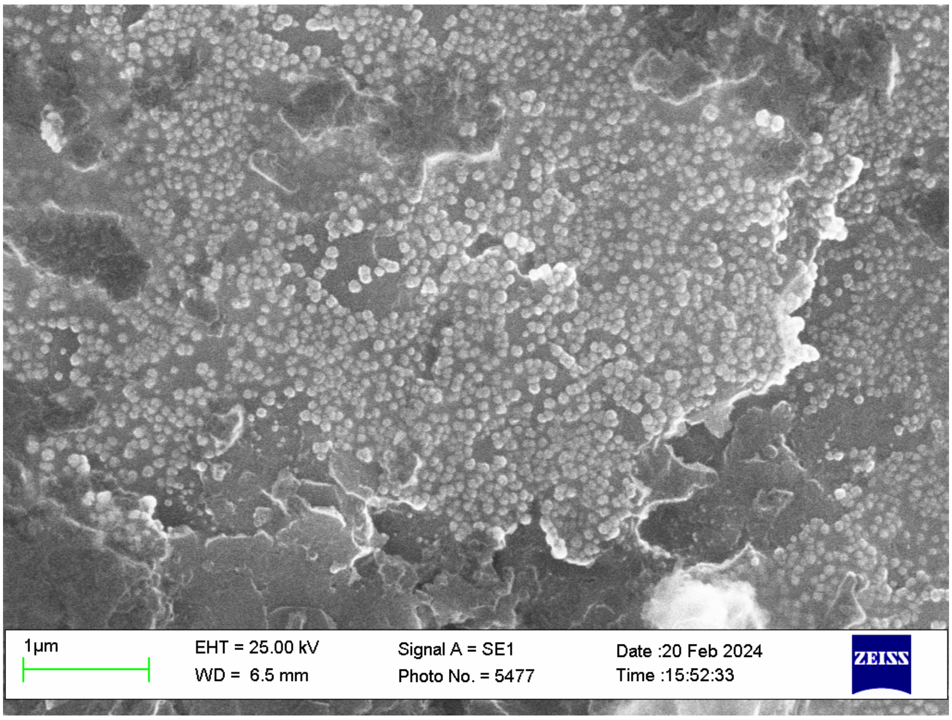

Fig. 1. SEM image of a fragment of a hybrid material based on CTF containing cobalt nanoparticles

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An electrocatalytic reaction for the reduction of nitrates to ammonia was proposed as a test reaction [1]. As experiments have shown, a CTF substrate significantly increases the durability of a nanocatalyst, while the selectivity of the process (which is expressed in Faraday efficiency, or current efficiency) remains virtually unchanged (over 40%) both for samples containing CTF and for nanocatalysts with cobalt nanoparticles applied directly to the graphite substrate.

Electrochemical methods using hybrid materials based on CTF on a graphite electrode are an effective tool for studying the mechanisms of heterogeneous catalysis. Electrochemical methods make it possible to control the chemical composition and morphology of cobalt nanoparticles when producing a hybrid material.

Acknowledgement: This work was supported by the Program of Development of Lomonosov Moscow State University. Microwave synthesis of CTF was performed on a NOVA 2S device (China).

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VP-39

Bis-Imidazolium Salts as Catalysts for Nucleophilic Reactions: Computational Approach

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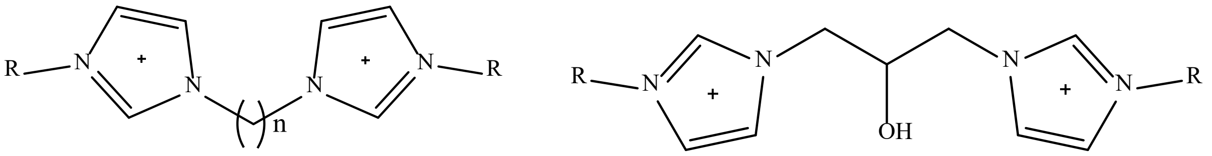
Bis-imidazolium salts (BIS) demonstrate pronounced catalytic activity in a number of nucleophilic reactions being included in ionic liquids, micellar pseudophases, and other microorganized media. The origin of acceleration is not always clear; quantum chemical study can enhance understanding and facilitate the development of new catalytic systems.

Structural details of BIS dications with short aliphatic $–(CH_2)_n$- (n = 1,2,3,4) and 2-hydroxypropylenic spacers (Fig.1) were studied in a framework of density functional theory (on a ωB97X/def2SVP + CPCM level) taking into account their conformational diversity. Results (interatomic distances and bond angles) were compared with typical values for organic compounds [1], and with known experimental data from crystal structures (see, for instance, [2]). In general, computations reproduce geometry of BIS dications adequately, and low-lying conformations plausibly represent conformational space of BIS in solution.



1 **2**

Fig.1. Structures of BIS dications with aliphatic (1) and 2-hydroxypropylenic (2) spacers.

In order to further validate the method in use, NMR spectra of simplest dications were computed for different media, and compared with experimental. Theoretical spectra reasonably represent all specific features of experimental ones. In particular, good accordance was found between computed 1H spectra for dications 2 in water and experimental chemical shifts for real dihalides in D_2O (1,3-bis(3`-nonylimidazol-1`-yl)-2-hydroxypropane dichloride, 1,3-bis(3`-octylimidazol-1`-yl)-2-hydroxypropane dichloride [3], and 1,3-bis(3`-decylimidazol-1`-yl)-2-hydroxypropane dibromide [4]). It makes possible to conclude that these dihalides dissociate in diluted water solutions into free ions; in nonpolar media, counter anions coordinate predominantly to hydroxyl and spacer hydrogens.

Distribution of electrostatic surface potential (ESP) coincide with this attribution: maximum of positive potential locates near hydroxyl hydrogen atom in a case of type II dications, and in close proximity to C^2H imidazolium atoms in a case of type 2 dications (Fig.2, $R=CH_3$).

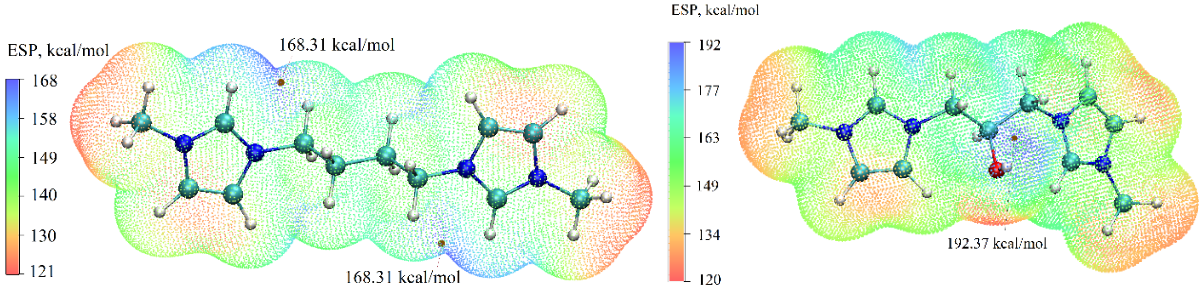


Fig.2. Dications 1 and 2 ESP (for isosurface 0.001 a.u.). ESP maxima marked in ochre and digitalized.

High positive potential of OH-group paves the way for preferential anion absorption into micellar pseudophase and their concentration in Stern layer. Base catalyzed hydrolysis of esters proceeds much faster in a presence of BIS with hydroxyl in the spacer (type 2 dications) compared with unsubstituted BIS of type 1 dications [5,6]. It appears probable that dication ESP distribution map may serve as reactivity index for micellar systems constructed on a base of bis-imidazolium salts.

Computations were made with ORCA 5.0.1 [7] and Multiwfn v.3.8 [8], results visualized in VMD [9].

Acknowledgement: This work was supported by the Ministry of Science and Higher Education of the Russian Federation, grant FRES-2023-0001.

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VP-40

Hydrodeoxygenation of Guaiacol over Halloysite Nanotubes Decorated with Ru Nanoparticles: Effect of Alumina Acid Etching on Catalytic Behavior and Reaction Pathways

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In the last decade, there has been a growing interest in liquid fuels production and petrochemicals from bio-oils produced by pyrolysis of lignocellulosic biomass. A promising technology for processing of bio-oil is catalytic hydrodeoxygenation (HDO), where bio-oil components undergo decarboxylation, decarbonylation and hydrogenation thereby increasing hydrocarbon content [1].

Halloysite nanotubes (HNTs) is a promising support for hydrodeoxygenation (HDO) catalysts due to a wide abundance, low cost and tunable properties. Herein, we have studied the effect of acid dealumination kinetic process for natural HNTs on their structural, acidic and textural properties to select the more appropriate candidate as the support for Ru-containing HDO catalysts. Acid etching of halloysite by sulfuric acid was found to enlarge lumen diameter (24.3 nm), enhance specific surface area (154 m^2/g) and acidity (0.343 mmol/g) [2].

Catalytic behaviour of the supported on pristine HNT and acid-etched HNT (HNT-t (3)) catalysts decorated with ruthenium was evaluated in HDO of model feed (10wt.% guaiacol in water) under H_2 pressure of 3 MPa in the temperature range of 120-180 °C for 3 h with a molar guaiacol/Ru ratio of 200. Fig. 1 summarizes the results of guaiacol HDO depending on reaction conditions, i.e. temperature and time.

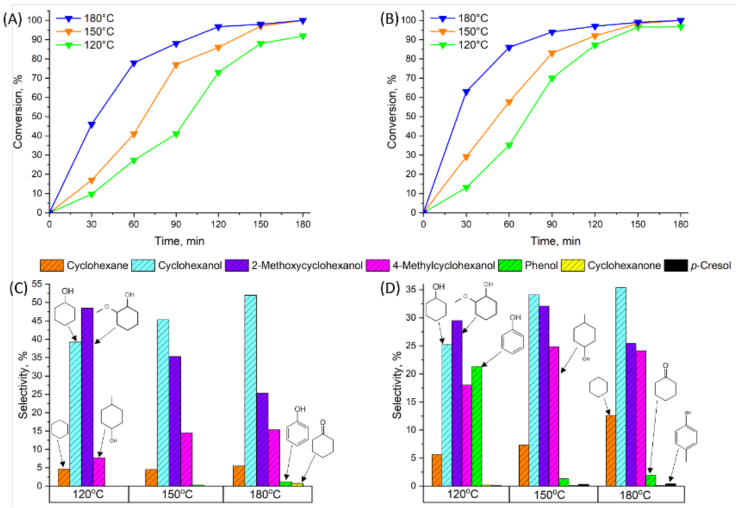

Fig. 1. Conversion (A, B) and selectivity (C, D) of guaiacol HDO as a function of time (A, B) and temperature (C, D) over Ru/HNT (A, C) and Ru/HNT-t (3) (B, D) catalysts.

Comparing the results of catalytic tests, we have concluded that the catalysts based on etched halloysite enhanced greater activity (TOF – 211 h-1) in the HDO of guaiacol compared their analogue supported on pristine HNTs. Moreover, the Ru-catalyst based on etched HNTs contributed to an increase selectivity to hydrogenolysis with effective oxygen removal. Based on the above discussed product distribution depending on temperature and time, the possible pathways for HDO of guaiacol over halloysite-based catalyst was proposed. At the initial step guaiacol transforms via two parallel pathways: (I) hydrogenation reaction route, where guaiacol converted to 2-methoxycyclohexanol; (II) direct deoxygenation, involving the cleavage of CH_3O-, i.e. demethoxylation to phenol.

Based on the results of catalysts-assisted tests, a mechanism for the HDO of guaiacol over bifunctional HNTs-supported Ru catalysts was proposed (Fig. 2).

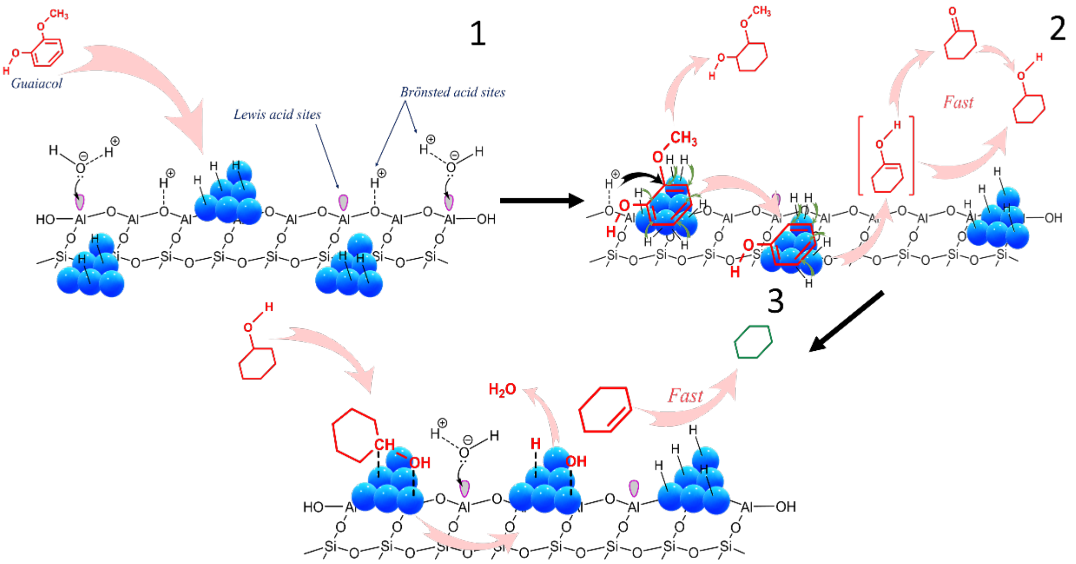

Fig. 2. Proposed reaction mechanism for HDO of guaiacol over a halloysite-supported Ru-catalysts

At the first stage phenol formed after demethoxylation of guaiacol and transforms to cyclohexanol on metal sites. Since cyclohexane was detected in the reaction products, we assumed that the cyclohexanol formed at the metal sites through the adsorption of the OH group. It was found that the actual deoxygenation step probably occurred via dehydration of cyclohexanol to form cyclohexene, which could subsequently be hydrogenated to cyclohexane as a final product.

Acknowledgement: This work was supported by the Russian Science Foundation, grant 19-79-10016.

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VP-41

Effect of Fluorinated Alcohols on the Reactivity and Selectivity of the Oxoiron(V) Intermediates in Aliphatic C-H bonds Oxidation

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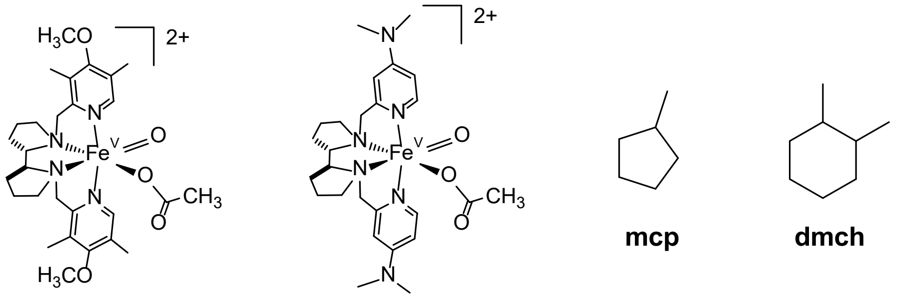
Using fluorinated alcohols as reaction solvents is known to improve the reactivity and, in some cases, selectivity of hydroxylation of aliphatic C–H bonds in catalyst systems (*L*)$Fe^{II,III}/H_2O_2$/AA (*L* is tetradentate *N*-donor ligand, AA is acetic acid). However, direct experimental data on the effect of fluorinated solvents on the reactivity of the key, formally (*L*)Fe^{V}=O intermediates have been lacking. Herein, we report such direct data, on the effect of trifluoroethanol (TFE) and hexafluoroisopropanol (HFIP) on the reactivity of the oxoiron(V) intermediates $[(PDP^{Me2OMe})Fe^{V}{=}O(OCOCH_3)](OTf)_2$ (**1a**) and $[(PDP^{NMe2})Fe^{V}{=}O(OCOCH_3)](OTf)_2$ (**2a**) toward methylcyclopentane (**mcp**) and 1,2-dimethylcyclohexane (**dmch**) (Fig. 1). Additives of fluorinated alcohols increase the second-order rate constants at –70 °C for the reaction of **1a** with **mcp** and **dmch**, and this increase is more pronounced for HFIP additives than for TFE. In agreement with these data, the conversion of **mcp** and **dmch** in the system **1**/H_2O_2/AA increases in the order CH_3CN < TFE < HFIP, while the selectivity for tertiary (3°) C–H sites decreases accordingly. The second-order rate constant for the reaction of **2a** with **mcp** at –40 °C also increases upon addition of TFE or HFIP to the reaction solution, and the catalytic oxidation of **mcp** by the system **2**/H_2O_2/AA shows higher conversion in TFE and HFIP than in CH_3CN. Contrastingly, the second-order rate constant for the reaction of **2a** with **dmch** is insensitive to the additives of HFIP. This is in line with identical conversions of **dmch** upon catalytic oxidation by the system **2**/H_2O_2/AA in various solvents (CH_3CN, TFE and HFIP). Mechanism of positive effect of fluorinated alcohols on the reactivity of the oxoiron(V) intermediates is being investigated.



1a **2a** **mcp** **dmch**

*Fig. 1. Proposed structures of the intermediates **1a** and **2a**, and those of substrates **mcp** and **dmch** used in this study*

Acknowledgement: This work was supported by the Russian Science Foundation, grant 22-13-00225.

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Scientific edition
Mechanisms of Catalytic Reactions (MCR-XII)
XII International Conference, June 17-21, 2024, Vladimir, Russia
Abstracts Editors:
Prof. V.I. Bukhtiyarov, Prof. O.N. Martyanov, Prof. E.A. Kozlova, Prof. V.V. Kaichev,
Prof. Y.V. Zubavichus, Dr. A.A. Gabrienko, Dr. I.E. Soshnikov

Научное издание
XII Международная конференция "Механизмы каталитических реакций" (МКР-XII),
17-21 июня 2024 года, Владимир, Россия
Сборник тезисов докладов
Под общей редакцией: акад. В.И. Бухтиярова, д.х.н. О.Н. Мартьянова,
д.х.н. Е.А. Козловой, д.х.н. В.В. Каичева, д.ф.-м.н. Я.В. Зубавичуса,
к.х.н. А.А. Габриенко, к.х.н. И.Е. Сошникова

Составители: С.С. Логунова, М.С. Суворова
Компьютерная обработка: Ю.В. Климова, Т.О. Барсуков
Обложка: Е.К. Казакова

Издатель:
Федеральное государственное бюджетное учреждение науки
«Федеральный исследовательский центр «Институт катализа им. Г.К. Борескова
Сибирского отделения Российской академии наук»
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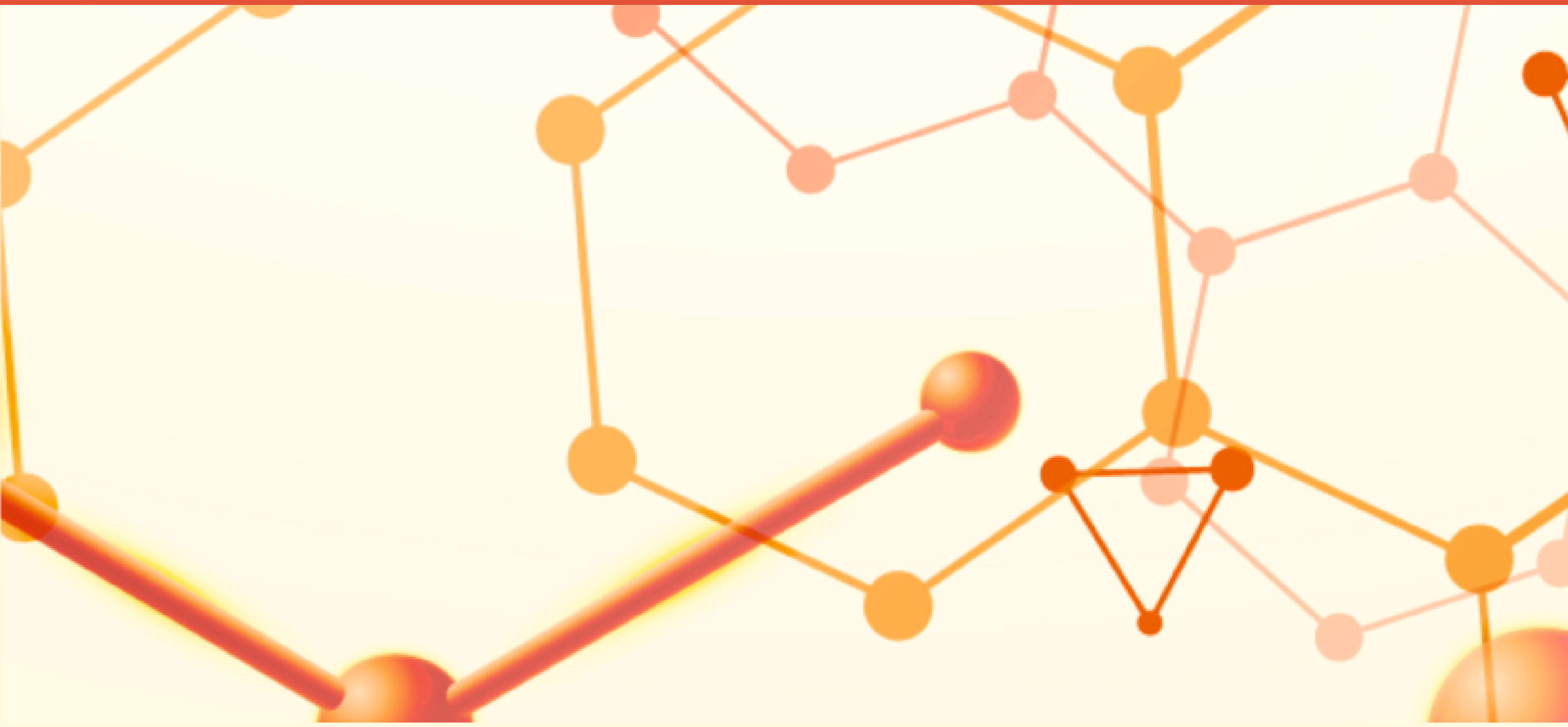
http://catalysis.ru   E-mail: bic@catalysis.ru   тел.: +7 383 330-67-71

Электронная версия:
Издательский отдел Института катализа СО РАН
E-mail: pub@catalysis.ru   тел.: +7 383 326-97-15
Объём: 16,8 КБ. Подписано к размещению: 14.06.2024
Адрес размещения:
http://catalysis.ru/resources/institute/Publishing/Report/2024/Abstracts-MCR-XII_2024.pdf
Системные требования: i486; Adobe® Reader® (чтение формата PDF) ISBN
978-5-906376-56-5



2024