



# RCS NCMT – 2012

**Russian-Chinese Seminar on New Catalytic  
Materials and Technologies**

**Российско-китайский семинар по новым  
каталитическим материалам и технологиям**

August 13-16, 2012  
Novosibirsk, Russia

SCIENTIFIC PROGRAM

ABSTRACTS

**Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia**  
**Heilongjiang University, Harbin, China**  
**Dalian Institute of Chemical Physics Chinese Academy of Sciences, Dalian, China**

## **Russian-Chinese Seminar on New Catalytic Materials and Technologies**

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## TIME-TABLE

### Russian-Chinese Seminar «New Catalytic Materials and Technologies»

August 13-16, 2012, Novosibirsk, Russia

Monday, August 13		Tuesday, August 14	
10.40	A r r i v a l	09.00	B r e a k f a s t
14.00	L u n c h	10.00	O p e n i n g (academician Valentin N. Parmon)
15.30	Excursion: Museum of history and culture of Siberia and Far East	10.30	<b>PL-1 FU Hong-gang</b> <i>Designed synthesis and application of crystalline carbon-based materials</i>
18.00	Welcome Dinner	11.10	<b>KL-1 G.V. ECHEVSKII</b> <i>Processes of hydroisomerization of the different hydrocarbonic fractions using metal-containing SAPO-31 catalyst</i>
		11.40	C o f f e e
		12.00	<b>KL-2 JING Li-qiang</b> <i>Synthesis of high active nano-structured photocatalyst materials and mechanism insight</i>
		12.30	<b>OP-1 LI Guang-ming</b> <i>Salen type lanthanum (III) complexes as lewis acid catalysts for the nitroaldol reaction in water</i>
		12.50	<b>OP-2 A.E. RUBANOV</b> <i>Single-stage hydroconversion of vegetable oil to iso-alkanes using metal-containing SAPO-31 catalyst</i>
		13.10	L u n c h
		14.10	<b>PL-2 V.I. BUKHTIYAROV</b> <i>Size effects in combustion of hydrocarbons and CO over supported metal catalysts for abatement of car exhausts</i>
		14.50	<b>OP-3 XIAO Lin-fei</b> <i>Functional ionic liquid: a highly effective catalyst for synthesis of cyclic carbonates</i>
		15.10	C o f f e e
		15.30	Excursion: Boreskov Institute of Catalysis SB RAS

You may present your report either English or Russian language.

## TIME-TABLE

### Russian-Chinese Seminar «New Catalytic Materials and Technologies»

August 13-16, 2012, Novosibirsk, Russia

Wednesday, August 15	Thursday, August 16
<b>09.00 B r e a k f a s t</b>	<b>09.00 B r e a k f a s t</b>
<b>10.00 PL-3 LIU Zhong-min</b> <i>Methanol to olefins</i>	<b>10.00 Free time</b>
<b>10.40 KL-3 YANG Qi-hua</b> <i>Asymmetric catalysis in nanoreactor</i>	<b>12.00 Picnic</b>
<b>11.10 KL-4 V.A. SADYKOV</b> <i>Catalysis in the intermediate temperature solid oxide fuel cells: design and performance of nanocomposite cathode and anode materials</i>	
<b>11.40 C o f f e e</b>	
<b>12.00 OP-4 S.R. KHAIRULIN</b> <i>The process of H<sub>2</sub>S selective catalytic oxidation for on-site purification of hydrocarbon gaseous feedstock. Technology demonstration</i>	
<b>12.20 OP-5 CHENG Mo-jie</b> <i>Research and development of SOFC at DICP</i>	
<b>12.40 OP-6 I.V. DELIY</b> <i>The comparison of CoMoS and NiMoS catalysts in HDO of aliphatic ethers and rapeseed oil</i>	
<b>13.00 L u n c h</b>	
<b>14.00 KL-5 WU Wei</b> <i>Molecular Sieves with ATO structure: Synthesis, Characterization and Catalytic Properties in n-decane hydroisomerization</i>	
<b>14.30 Round table</b>	
<b>18.00 Closing Dinner</b>	

## SIZE EFFECTS IN COMBUSTION OF HYDROCARBONS AND CO OVER SUPPORTED METAL CATALYSTS FOR ABATEMENT OF CAR EXHAUSTS

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Understanding why activity, expressed as a turnover frequency, depends upon the particle size of a catalytically active metal has been an area of considerable study in supported metal catalysis. This problem is not only of fundamental, but also of practical interest, since its elucidation allows one to regulate the properties of metal nanoparticles and to synthesize supported metal catalysts with improved performance. Particular importance of this direction of science and technology has for development of competitive catalysts which use expensive Pt-group metals as active component.

Literature and own recent data in this field allows us to conclude that systematic study of the size effects and their practical application is impossible without:

- 1) development of the methods for reproducible synthesis of the supported metal particles with variation of the mean particle size in nanometer scale (1-10 nm), but with homogeneous size distribution for each specific size;
- 2) application of the fool-proof methods for characterization of nanosized particles and determination of their size distribution;
- 3) testing the catalytic properties and comparison of the TOF values depending on the mean particle size;
- 4) investigation of electronic, structural and adsorption properties of the nanosized metal particles with the aim to understand the reasons of the size effects.

The results of investigations of the size effects in oxidation of alkanes over Pt/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> catalysts and low temperature CO oxidation over Au/Al<sub>2</sub>O<sub>3</sub> catalysts presented in this report illustrate this affirmation.

A series of supported metal catalysts with narrow particle size distributions were prepared by incipient wetness impregnation (Pt/Al<sub>2</sub>O<sub>3</sub>, Pd/Al<sub>2</sub>O<sub>3</sub> and Au/Al<sub>2</sub>O<sub>3</sub>), by deposition-precipitation and chemical vapor deposition (Au/Al<sub>2</sub>O<sub>3</sub>). The catalysts were used both for catalytic testing and for physical-chemical characterization with UV-Vis spectroscopy, XRD, XPS, SAXS, EXAFS, XANES and TEM. It has been shown that the optimal size of the metallic nanoparticles for each

specific reactions depends on the nature of the oxidized molecules, peculiarities of metal-support interaction and reaction conditions. Practical result of the study is a possibility to improve essentially the performance of the catalysts and/or to decrease (up to few times) of loading the Pt-group metals via optimization of the mean sizes of active metal nanoparticles.

### **Acknowledgement**

The author acknowledges financial support from RFBR (project # 12-03-01104) and RAS Presidium (program # 21, project # 51).

## RESEARCH AND DEVELOPMENT OF SOFC AT DICP

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Solid oxide fuel cell is one of most promising technologies for the high efficient and clean conversion of chemical energy into electricity in the centralized and distributed generations. Started from 1990, the research and development on solid oxide fuel cells (SOFC) at DICP has experienced with two periods, fundamental research in the first ten years and research on key technologies in the second ten years. These experiences including understanding of electrochemical phenomena of electrode materials, electrodes and cells, and practices of various technologies for the fabrication cells, construct a solid basis for the research and development. Now, the research and development of SOFC at DICP is getting into a period of system integration. The presentation will summarize what we have done in the past and looks into the future.

# FUNCTIONAL IONIC LIQUID: A HIGHLY EFFECTIVE CATALYST FOR SYNTHESIS OF CYCLIC CARBONATES

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Carbon dioxide is the most abundant waste produced by human activities and is one of the most important greenhouse gases. As a C1 resource, however, CO<sub>2</sub> is recognized to be naturally abundant, inexpensive, recyclable, and nontoxic source [1]. Under these circumstances, chemical fixation of CO<sub>2</sub> has become more important for both the ecological and economic advantage. The reaction of coupling carbon dioxide and epoxides to generate five-membered cyclic carbonates is one of the most promising route for the utilization of CO<sub>2</sub> as a C1 building block in organic synthesis [2]. Significantly, cyclic carbonates can be used in many application areas such as solvents, monomers, valuable raw materials and intermediates in the production of pharmaceuticals and fine chemicals [3].

In the last decades, various homogeneous and heterogeneous catalysts have been developed for the coupling of carbon dioxide and epoxides[4], such as alkali metal salts, metal oxides, transition-metal complexes, supported choline chloride/urea, N-heterocyclic carbenes, polyoxometalate, ion-exchange resins, zeolites, and ionic liquid. Although many catalytic systems have been reported, the development of more efficient catalysts for the synthesis of cyclic carbonates from the reaction of carbon dioxide and epoxides under mild conditions is still an interesting topic.

Recently, the functional ionic liquids have received attention in the synthesis of cyclic carbonates from carbon dioxide and epoxides. Our group have designed and synthesis carboxyl functional ionic liquids[5], it showed the high catalytic activity in the synthesis of cyclic carbonates. In order to achieve the separation and chemical fixation carbon dioxide, our group synthesized the amino functional ionic liquids (Fig. 1).

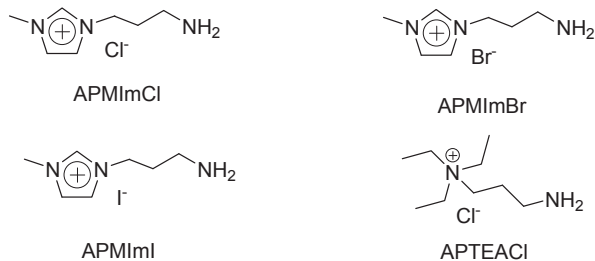


Fig. 1. Amino functional ionic liquid



The catalytic activity of amino functional ionic liquids was investigated in the reaction of carbon dioxide and propylene, and the results were shown in Table 1.

**Table 1. The reaction result of different ionic liquids on synthesis of propylene carbonate<sup>[a]</sup>**

Entry	Ionic liquid	Yield <sup>[b]</sup> (%)
1	APMImCl	43.3
2	APMImBr	88.4
3	APMImI	97.2
4	APTEACl	58.3

[a] Reaction conditions: ionic liquid 71.45 mmol, propylene epoxide 5 mL, reaction pressure 1.5 MPa, reaction temperature 120 °C, reaction time 1.5h.

[b] The selectivity of propylene carbonate was more than 98%.

From the Table 1, it can be seen that the catalytic activity was slightly affected by the structure of cation in ionic liquid, but the species of anion was the key role in this reaction. When chloride as the anion, the catalytic activity of ionic liquid was bad, the Cl<sup>-</sup> was replaced by I<sup>-</sup>, the catalytic activity of ionic liquid was excellent and the yield of propylene carbonate was achieved at 97.2% in the presence of 1-aminopropyl-3-methylimidazolium iodide (Table 1).

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## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21006021).

## DESIGNED SYNTHESIS AND APPLICATION OF CRYSTALLINE CARBON-BASED MATERIALS

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Carbon has played a vital role throughout the development of human society. The microstructures of the carbon materials have essential effect on their performance and applications. We have performed our work mainly in three aspects. First, based on the group-interaction principle, we have developed a effective method for the synthesis of various carbons and carbon based composites, in which the cheap polymer, biomass and some agricultural residues with certain organic groups were selected as carbon source. The carbon capsules, belts and plates with good crystalline were easily obtained by tuning the types and numbers of groups in resin and their complex mode with metal ions [1]. When we selected the glucose as carbon source, the carbon capsule and nanobelts was formed followed similar procedure. In addition, by introducing the ferrous gluconate in the hydrothermal carbonization of glucose, the magnetic components can also be distributed in whole carbon spheres [2], and the magnetic-graphitic carbon (hollow) microspheres [3] can be obtained. Interestingly, graphene with few-defect, high conductivity have been prepared through "in-situ" self-generating template route by tuning the types and numbers of groups in carbon source [4]. We have also prepared carbide/carbon composites through the "in-situ simultaneous" route. In detail, the carbide ( $WC$ ,  $V_7C_8$ )/carbon composites could be prepared by using resin [5], chitoson [6] and foxtail [7] as carbon source. Compared with traditional synthesis methods for carbide/Carbon, the in-situ simultaneous route has obvious virtue of simple handle, low-temperature process and smaller size of carbide (below 10 nm) than conventional methods, and was well contact with carbon components due to the unique preparation process.

The Pt (Pd) oading on carbon is state of the art catalysts for many fields. We have developed several effective methods to load the metal NPs with small size and good dispersion on our-prepared carbon support. By adopting an effective separated step chemical reduction route, the Pd particles with small size (about

2nm) and good dispersion were successfully loaded on the GO-derived graphene [8]. In addition, through the simple galvanic displacement process between Pd ion and Cu template [9], and taking the reducing ability oxygenated groups of graphene obtained by in-situ simultaneous route, the small-size and high dispersed Pd particles could also be loaded on the graphene with good conductivity [10]. These Pd/graphene composites have showed good catalytic activity and stability toward formic acid electro-oxidation. Notably, Pt-WC/crystalline carbon composites displayed higher activity and stability toward menthol electro-oxidation reaction [5-7]. By using graphene as support, the WC with small size below 5nm has been formed. Electrochemistry tests show that the contacting Pt-WC nanostructures on graphene have the superior CO tolerance, high catalytic activity and durability to methanol oxidation, with a mass activity of 1.98 and 4.52 times to those of commercial PtRu/C and Pt/C catalysts, respectively [11].

Final aspect of our work has been focused on the designed synthesis and application of plate-structure carbon materials. Expanded graphite (EG) can be produced from graphite by simple chemical treatment. EG could not only keep the excellent conductivity and layer-shape structure of graphite but also overcome some defects of natural graphite. This special expansion structure is more helpful for the occurrence of quenching cracks, which result in the complete exfoliation of graphite layers and the formation of graphenes through a hydrazine hydrate or concentrated ammonia assisted quenching method [12]. As a nanoparticles or polymer was used as inserting agent under special conditions, the polymer/Graphene and mesoporous carbon/graphene and oxide/graphene [13] can be obtained followed this idea. The doping of the plate-like carbon and their composite with other functional materials has showed good performance for photocatalytic and storage-energy fields.

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### **Acknowledgements**

We gratefully acknowledge the support of the Key Program Projects of the National Natural Science Foundation of China (no 21031001), the National Natural Science Foundation of China (no 20971040, 91122018, 21101061), the Cultivation Fund of the Key Scientific and Technical Innovation Project, Ministry of Education of China (no 708029)

# CATALYSIS IN THE INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS: DESIGN AND PERFORMANCE OF NANOCOMPOSITE CATHODE AND ANODE MATERIALS

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Solid oxide fuel cells (SOFC) are the most efficient, promising and environment friendly power generators especially for such applications as distributed energy supply, mobile and emergency power sources. As fuel, they can use not only hydrogen but syngas as well as hydrocarbons and biofuels in the internal reforming mode. Priority task in their design is decreasing the working temperatures to 600-800 °C which allows to improve performance stability by suppressing undesirable solid state reactions and decrease cost by using inexpensive construction materials. Approaches used to deal with this task include design of new solid electrolytes with enhanced ionic conductivity, decreasing thickness of electrolyte, development of new cathode and anode materials compatible with solid electrolytes and possessing high catalytic activity and oxygen mobility in the intermediate temperature (IT) range. In this presentation, results of research aimed at design of efficient nanocomposite cathode and anode materials [1-6] are reviewed.

For cathode materials -complex oxides with perovskite  $\text{Ln}_{1-x}\text{Sr}_x\text{MeO}_3$  or Ruddlesden-Popper (R-P)  $\text{Ln}_2\text{MeO}_4$  (Ln =La, Pr; Me= Mn, Co, Ni, Fe, Cu etc) structure and their nanocomposites with solid electrolytes (Zr-Y-O, Ce-Gd-O, doped La silicate with apatite structure) kinetics and mechanism of  $\text{O}_2$  activation and oxide ions diffusion in solids were studied by oxygen isotope heteroexchange, impedance spectroscopy and conductivity/weight relaxation after step-wise changing  $p\text{O}_2$ . Dependence of the specific rate and mechanism of heteroexchange on the type of transition metal cation, Me-O bond strength and real/defect structure of the surface and bulk of oxide was elucidated. The highest rate of oxide-ions diffusion was found for oxides with R-P structure due to a low barrier for oxygen interstitials migration via ca cooperative mechanism. Redistribution of transition metal cations between perovskite and electrolyte domains generates new highly active sites of  $\text{O}_2$  dissociation. Perovskite-electrolytes interface provides a channel for fast oxygen migration with diffusion coefficients exceeding by up to 6 orders of magnitudes those within electrolyte domains.

Nanocomposite anode materials comprised of NiO-YSZ co-promoted by fluorite-like Ln-Ce-Zr-O, (Ln = Pr, La, Sm) or perovskite-like La-Pr-Mn-Cr-O oxides

with a high oxygen mobility and Pt, Pd, Ru were designed and studied in reactions of methane and biofuels (ethanol, acetone) steam/autothermal reforming. Their composition and synthesis procedures were optimized and main kinetic parameters of catalytic processes were estimated including those for structured catalysts on heat-conducting substrates made of deformation strengthened Ni-Al foam alloy. Optimized systems provide a high efficiency of fuels transformation into syngas and coking stability in the IT range (600-700 °C) at a low steam/carbon ratio (1-2) at short contact times. Optimized nanocomposite cathode and anode materials ensure a high and stable power density of thin film SOFC in the IT range (up to 800 mW/cm<sup>2</sup> at 700 °C) using both wet H<sub>2</sub> or CH<sub>4</sub> + H<sub>2</sub>O feeds in the internal reforming mode (S/C =2). Kinetic analysis revealed that under anode polarization, nanocomposite anode materials provide not only efficient CH<sub>4</sub> steam reforming but also oxidation of a part of CH<sub>4</sub> via direct electrochemical route..

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## Acknowledgements

Support of this research by International projects (NATO SFP 980878, SOFC 600, MATSILC, Russian-German Project N-Cath of CLIENT Program) and Russian projects (Integration Projects of SB RAS 95, 57 and 8; Project of Presidium RAS 50, Federal Program "Scientific and Educational Cadres of Russia") is gratefully acknowledged.

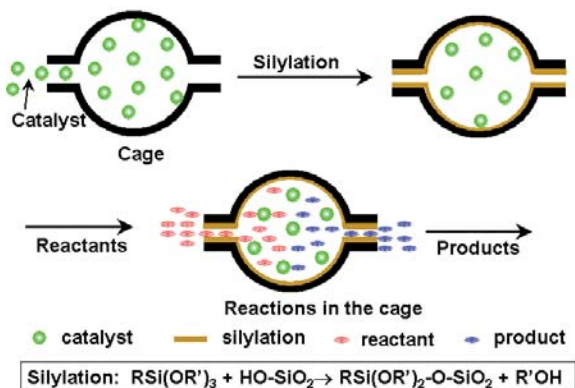
## ASYMMETRIC CATALYSIS IN NANOREACTOR

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Heterogeneous chiral catalysts, mostly solid catalysts possess inherent features of practical advantages for industrial processes, such as simple separation and reuse of chiral catalysts, easy purification of products, and convenient operation processes. Therefore heterogeneous asymmetric catalysis is becoming a fascinating area for both the academic research and the commercial applications. However, the activity and enantioselectivity of most chiral solids is not high which impedes the practical applications of heterogeneous asymmetric catalysis.

Recently, the novel chiral porous materials, the chiral periodic mesoporous organosilicas, were synthesized by our group and these materials show application potentials in heterogeneous asymmetric catalysis [1]. Moreover, our group developed an efficient method for the preparation of nanoreactors for asymmetric catalysis by encapsulating transition metal complexes in the nanocage of mesoporous silicas (Scheme 1) [2-5]. For example, chiral [Co(Salen)] complexes have been confined in the nanocage of SBA-16 by reducing the pore entrance size through a silylation method, resulting in a solid catalyst for the hydrolytic kinetic resolution (HKR) of epoxides. It was found that the activity of the solid catalysts increased with the number of [Co(Salen)] molecules per nanocage increasing, and the solid catalyst with more than two chiral [Co(Salen)] molecules in one nanocage of SBA-16 exhibits much higher activity and enantioselectivity than the homogeneous [Co(Salen)] catalyst in the HKR of epoxides at low substrate/catalyst ratio. The significantly improved activity of the solid catalyst is due to a high local concentration of [Co(Salen)] in nanospace because of the enhanced cooperative activation effect of [Co(Salen)] molecules. This work provides a new opportunity for the design of efficient solid catalysts for the asymmetric reactions as well as many other reactions, which involve cooperative activation by separate catalytic centers or second-order kinetic dependence on the local concentration of catalysts.



**Scheme 1.** General process for encapsulating molecular catalysts into the nanocages of mesoporous silicas and the chemical reactions in the nanoreactor catalyzed by the encapsulated molecular catalysts.

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## Acknowledgements

This work was financially supported by the National Basic Research Program of China (2009CB623503), and the National Natural Science Foundation of China (20921092).



## THE COMPARISON OF CoMoS AND NiMoS CATALYSTS IN HDO OF ALIPHATIC ETHERS AND RAPESEED OIL

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HDO is considered as important commercial rout for producing of distillate range bio-fuels from triglyceride-based feed-stocks such as vegetable oils, animal fats etc. The promising strategies to produce hydrocarbons with the required technical and environmental fuel standards could be the hydrodeoxygenation (HDO) of triglycerides alone [1] or the co-hydrotreatment of triglycerides with petroleum fractions [2]. In both cases the typical HDT catalysts, like CoMoS/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMoS/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, can be used. The HDO selectivity (through the H<sub>2</sub>O or CO/CO<sub>2</sub> removal) is a crucial factor for the process design and operation.

The aim of the present work is a comparison of selectivity of aliphatic methyl ethers (methyl heptanoate and methyl palmitate) transformation as the model compound on the sulfided CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and the validation of the obtained results in the hydroconversion process of the rapeseed oil/SRGO blend.

The HDO of methyl heptanoate and methyl palmitate were performed in a batch reactor at 300°C and hydrogen pressure 35 bars over CoMoS/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMoS/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (0,14-0,25 mm particle size). The catalytic properties in HDO of the rapeseed oil/SRGO blend was evaluated in trickle-bed down-flow reactor at 340-360°C and 4.0-7.0 MPa of hydrogen using the full-size granule of catalysts (the trilobes with the l=3-5mm, d ~1,2 mm). The hydrogen flow rate was 150-250 mL/min, and the organic phase was introduced at a rate of 15 mL·h<sup>-1</sup>, corresponding to a space velocity of 1.5 h<sup>-1</sup> (WHSV). The reaction products were identified by GC/MS technique (Agilent Technologies 7000 GC/MS Triple QQQ GC System 7890A) using HP-5MS quartz capillary column (30m×0.25mm) and quantified by gas chromatography system (Agilent 6890N) equipped with HP-1MS column (60m×0.32mm×0.25µm) and atomic emission detector (GC-AED). The total oxygen content in the reaction mixture was determined using CHNSO elemental analyzer Vario EL Cube ("Elementar", Germany). For monitoring of H<sub>2</sub>O content produced in the reaction mixture the coulometric Karl Fischer titration (coulometer DL39 KF, Mettler Toledo GmbH) was used.

Methyl heptanoate has been usually used as model compound to investigation of fatty acid methyl esters HDO over conventional sulfided catalysts [3], whereas the major components of vegetable oils possess the more lengthy carbon chain. We observed that the initial HDO rate of methyl heptanoate was about two times higher than the initial HDO rate for methyl palmitate, but the HDO product distribution is similar. It was stated that methyl palmitate completely transformed into C<sub>15</sub> and C<sub>16</sub> hydrocarbons through the formation of oxygen- and sulfur-containing intermediate compounds, the tentative reaction scheme of methyl palmitate transformation was considered. The main product of HDO of methyl palmitate obtained over CoMoS/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was hexadecane whereas pentadecane is preferably formed over NiMoS/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, pointing out to the different reaction routes of methyl palmitate conversion (hydrodeoxygenation versus decarboxylation). It was shown also that the activity of the CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts in methyl palmitate HDO in the presence of different solvents decreases in order: n-Tetradecane > HTDF  $\approx$  m-Xylene. Decrease the catalytic activity of the catalysts in methyl palmitate HDO in the presence of m-xylene or HTDF, containing appreciable quantities of aromatic compounds, testify the inhibition of some reaction stage by the aromatic components. The solvent possess the complicate effect on the reaction products distribution, as the ring alkylation products of benzene had been found in the reaction mixture during methyl palmitate HDO over CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts in the presence of m-xylene.

The same dependence was obtained in the case of rapeseed oil hydroprocessing: CoMoS/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts promote the direct HDO route, when NiMoS/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts essentially enable to the decarbonylation/decarboxylation transformation. The effects of reaction temperature, hydrogen pressure and the ratio of H<sub>2</sub> to feed on the routs of rapeseed oil HDO were investigated. It was obtained that the increase of the reaction temperature from 340 to 360°C results in the decrease of the HDO route selectivity, whereas with H<sub>2</sub> pressure growth from 40 to 70 bar a higher HDO selectivity was obtained. The promotion of the catalysts with P and Mg leads to the increase of the stability and HDO selectivity of CoMoS/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

The HDO results of the methyl ethers and rapeseed oil are in good agreement. CoMoP/MgO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst displays a better selectivity of hydrodeoxygenation versus decarboxylation route.

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**Acknowledgements:** The research work was supported by RFBR Grant No. 11-03-00611.

## SINGLE-STAGE HYDROCONVERSION OF VEGETABLE OIL TO ISO-ALKANES USING METAL-CONTAINING SAPO-31 CATALYST

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In the past 10 years, the importance of biofuels has increased, and this tendency is expected to continue. Usually, the production of diesel fuel from vegetable oil (triglycerides of carbonic acids) is performed in two stages. On the first stage, the process over conventional hydrotreating catalysts gives a deoxygenated hydrocarbon product, mostly a mixture of *n*-alkanes C<sub>15</sub>-C<sub>18</sub>. A substantial drawback of such fuel is its bad low-temperature properties. To improve them, the hydroisomerization of the *n*-alkanes-rich product is necessary.

We have demonstrated that Pd or Pt-containing SAPO-31 could be a perspective catalyst for the one-stage hydroconversion of vegetable oil into the diesel range hydrocarbon mixture with improved low-temperature properties [1, 2]. The content of *n*-alkanes in the reaction product can be lowered up to 10% that corresponds to the *n*-alkanes content in the arctic diesel fuel. Due to the unique properties of SAPO-31 structure, the isomerization is limited to the formation of mono- and di-branched alkanes that have high cetane number and good cold-flow properties.

Unfortunately, the hydrogenation and isomerization activity of the Me/SAPO-31 catalysts declines with time on stream. To find out the reasons of deactivation, the physico-chemical properties of fresh and spent catalysts were compared. A decrease in Pt and Pd dispersion measured by hydrogen chemisorption was observed in spent Me/SAPO-31 catalysts. Comparing the IR-spectra of pyridine adsorbed on Pt/SAPO-31 samples before and after the reaction, we have found a detectable decrease in the Brönsted acid sites concentration for spent samples. However, it looks doubtful that the acid sites blocking is a primary reason of activity drop in the oil transformation, because the partially deactivated catalyst demonstrates rather good activity in the hydroisomerization of *n*-undecane. Moreover, the *n*-undecane treatment of the spent catalyst restores its activity. Therefore, we have proposed that the weakening of metal function is a primary reason for deactivation of Me/SAPO-31 catalyst during the hydroconversion of vegetable oil. The decrease of noble metal hydrogenation activity results in incomplete conversion of intermediate oxygen-containing products that are likely to block acidic sites of SAPO-31.

From this point of view, a study of influence of noble metal concentration and conditions of oxidation treatment on Me/SAPO-31 physico-chemical properties and their catalyst behavior is of a great importance. To examine the influence of oxidation treatment conditions a series of 1wt% Pt/SAPO-31 samples was prepared by wet impregnation of the microporous material with a solution of  $\text{H}_2\text{PtCl}_6$  and further calcination in air at different temperatures. The varying of calcination temperature in the range of 300-450°C had no notable influence on Pt dispersion and catalytic properties of Pt/SAPO-31 samples. The decrease in the Pt dispersion was observed when the oxidation temperature exceeded 500°C that accompanied by lowering of catalyst stability. The oxidation temperatures less than 300°C results in the increasing of Pt dispersion but gives the samples with a low isomerization activity. This fact shows that the catalytic properties of Pt/SAPO-31 samples are determined not only the particle size but also the oxidation state of platinum.

To examine the influence of noble metal concentration a series of Pt/SAPO-31 samples with Pt loading from 0.5 to 2 wt.% was prepared. It was showed that the increase in the Pt content leads to improvement of isomerization activity and catalyst stability. However, it is accompanied by the decrease in selectivity toward  $\text{C}_{15}$ - $\text{C}_{18}$  hydrocarbons because of formation of cracking products corresponding to the hydrocarbons of gasoline fraction.

The obtained results give evidence that poor stability of Me/SAPO-31 catalyst in the hydroconversion of vegetable oil should be considered as a main drawback of the process. Optimization of noble metal content as well as conditions of the samples pre-treatment and catalytic experiment is the task for future research.

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## Acknowledgements

The support of government contract № 16.516.11.6049 “Development of technology for production of the third generation biofuels by catalytic processing of microalgae lipid” within the framework of federal target program “Research and development on priority directions of scientific-technological complex of Russia in 2007-2012” is gratefully acknowledged.

# SALEN TYPE LANTHANUM (III) COMPLEXES AS LEWIS ACID CATALYSTS FOR THE NITROALDOL REACTION IN WATER

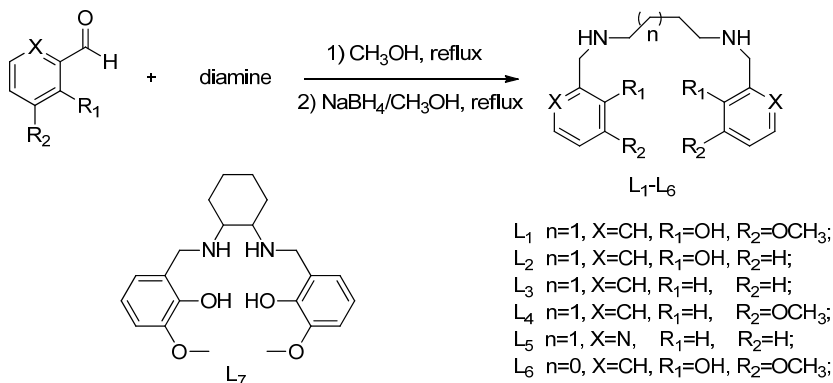
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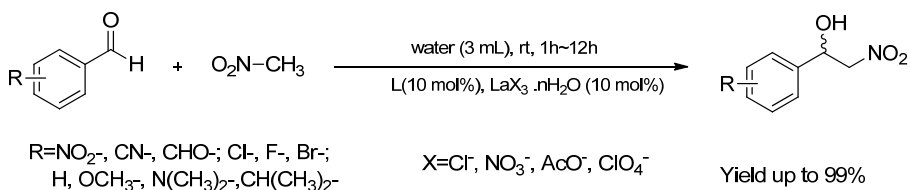
Catalytic asymmetric reactions that can be performed in or on water are of current interest, because water is cheap, safe, and unique reactivity and selectivity are often observed when water is used as a solvent. [1] However, its use in organic reaction processes is rather limited because many organic materials do not dissolve in water, and therefore in most cases reactions proceed sluggishly. In addition, many reactive intermediates and catalysts are decomposed by water. This is the case for Lewis acid catalyzed reactions, which are of great current interest because of the unique reactivities and selectivities they can achieve and for the mild conditions used.

Nitroaldol (or Henry) reaction is an important carbon–carbon bond formation reaction widely used in organic synthesis. [2] Henry reactions are usually performed in organic solvents and only a few studies have involved water as the reaction medium. [3] Herein, we describe a series of diamine lanthanide complexes which can efficiently catalyze Nitroaldol reaction in water.

The target diamine ligands L<sub>1</sub>-L<sub>7</sub> could be synthesized in two steps in good overall yield (Scheme 1). Diamine lanthanide complexes proved to be a very efficient catalyst system that can promote the reaction of a wide range of aromatic aldehydes to give the expected nitroalcohol products in high yields (up to 99 %) (Figure 1). This catalyst system is very general, requires no additives for activation, and is also simple in operation because no special precautions are taken to exclude moisture or air from the reaction flask.



**Scheme 1** Synthesis of the ligands L<sub>1</sub>-L<sub>7</sub>



**Figure 1** Diamine-Lanthanum(III) complexes catalyze the Nitroaldol reactions in water

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## SAPO-31 MOLECULAR SIEVES: SYNTHESIS, CHARACTERIZATION, AND CATALYTIC PERFORMANCE IN N-DECANE HYDROISOMERIZATION

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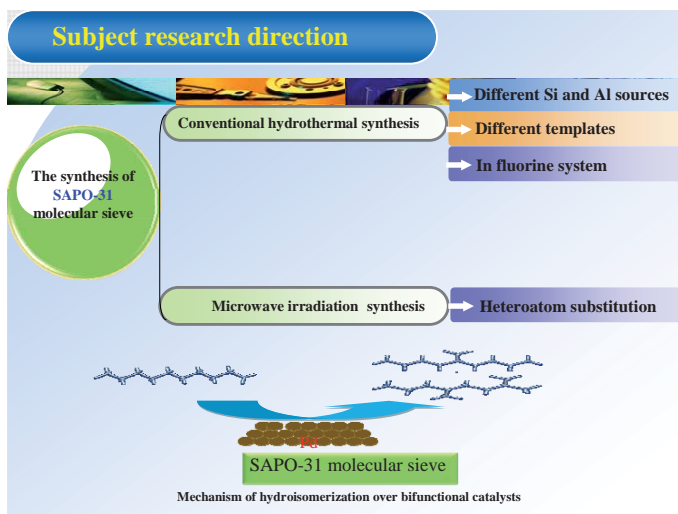
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SAPO-*n* molecular sieves with unidimensional pore system of average size can be used as suitable acid support of the bifunctional catalysts for the hydroisomerization of *n*-alkanes to increase the octane number of gasoline and to improve the low temperature performance of diesel fuels and base oils [1-2]. The unique parameters of crystal structure of these microporous materials are responsible for high isomerization selectivity and, hence, for high yield of the target products. On the other hand, the activity of bifunctional catalysts in the conversion of *n*-alkanes is mostly determined by concentration of strong acid sites accessible to the reactant molecules. For microporous aluminophosphates the formation of these centers takes place as a result of isomorphous substitution of atoms of aluminophosphate framework by atoms of modifying elements (M). At the same time this substitution results in a change of lattice parameters, size and morphology of obtained crystals as well as their textural properties which, in turn, may also affect the catalytic properties of the resulting systems. Therefore, the link between the method of preparation of aluminophosphate molecular sieves and their physico-chemical and catalytic properties is of a great importance.

This paper presents the results of a systematic study of the effect of preparation procedure of molecular sieves with ATO structural type on their physico-chemical properties, as well as on catalytic properties of Pd-containing systems in the *n*-decane hydroisomerization. The main guidelines of the research were as follows (see Figure): the influence of aluminum source [3], nature and amount of a modifying element (M = Si, Mg, Co) [3], as well as kind of template [4]; the effect of a presence of fluoride ions in the reaction medium; the influence of heating method of the reaction mixture [5]. All prepared samples were characterized by a complex of physico-chemical methods: XRD, SEM, XRF, XPS, N<sub>2</sub> adsorption, NH<sub>3</sub>-TPD, Py-IRS, <sup>29</sup>Si NMR, H<sub>2</sub> chemisorption. For each research direction we have identified



key parameters that are more responsible for the activity of catalysts in the *n*-decane conversion and their isomerization selectivity.



As an example, for the first time the properties of SAPO-31 samples with different Si content prepared by conventional hydrothermal synthesis has been compared with those obtained by microwave irradiation method. According to the  $^{29}\text{Si}$  NMR data, the two heating methods of SAPO-31 synthesis resulted in different Si distribution in the molecular sieve framework. Microwave irradiation method ensured more uniform Si distribution and formation of silica islands with relatively small dimensions. It was found that the bifunctional catalysts Pd/SAPO-31 synthesized by microwave irradiation possessed comparable activity in *n*-decane conversion but improved isomerization selectivity at  $T_{\text{reac}} \geq 350^\circ\text{C}$  due to smaller grain size and appropriate acidity of MW-SAPO-31 samples.

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## Acknowledgements

This work is supported by the National Natural Science Foundation of China (No. 21076065).

# THE PROCESS OF H<sub>2</sub>S SELECTIVE CATALYTIC OXIDATION FOR ON-SITE PURIFICATION OF HYDROCARBON GASEOUS FEEDSTOCK. TECHNOLOGY DEMONSTRATION

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Direct oxidation of hydrogen sulfide:



is the most promising reaction for purification of natural and oil-associated gases for their further use. The application of this reaction provides the following advantages:

- High selectivity for the formation of elemental sulfur (not lower than 98%)
- A continuous process with simultaneous purification of gases and production of commercial sulfur
- Mild process conditions (the process temperature is 220-280°C) provided by highly active catalysts.

An important advantage of the proposed engineering decision is the possibility to construct compact units for on-site gas purification

In the Boreskov Institute of Catalysis, new processes based on direct catalytic oxidation of hydrogen sulfide were developed [1-2]. The technology is schematically depicted in Fig. 1.

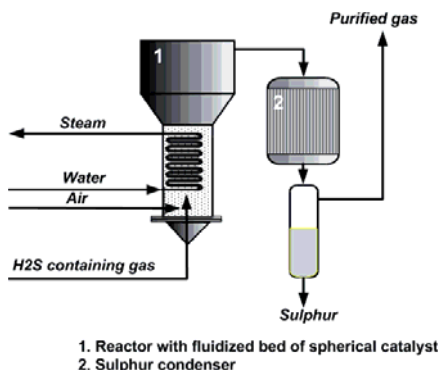


Fig. 1: The technology of direct selective oxidation of hydrogen sulfide.

The technology was successfully tested in pilot scale on the largest sour gas fields, refineries and gas processing plants in Russia [3-4]. In 2011 full scale

industrial installation was set into continuous operation at the Bavy deposit (OJSC “Tatneft” – company-operator) [5].

The general view of the industrial installation is presented in Fig. 2.

The Installation comprises the following main units: reactor with a fluidized bed of catalyst (Fig. 3, shell-in-tube sulfur condenser (Fig. 4), trap for removal of fine particles of elemental sulfur (Fig. 5), system of process computer control (Fig. 6)



Fig. 2: Industrial installation for direct selective oxidation of H<sub>2</sub>S



Fig. 3: Catalytic reactor



Fig. 4: Sulfur condenser



Fig. 5: Sulfur trap



Fig. 6: Process computational control

The efficiency of hydrogen sulfide removal was proven to exceed 99%.

Since 10.05.2011 to 01.08.2012:

- 1600000 m<sup>3</sup> of purified commercial gas was produced;
- 150 tons of hydrogen sulfide were recovered as elemental sulfur;
- emission of 300 tons of sulfur dioxide and sulfuric acid to the atmosphere was prevented;
- pollution damage for the amount of \$ 0.4 million was averted.

Characteristics of the produced sulfur surpass those specified by Russian National Standard #127.1-93 (commercial grade sulfur 9990).

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## METHANOL TO OLEFINS

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The Methanol-to-Olefins (MTO) process has been regarded as the most successful non-petrochemical route for the production of light olefins from abundant resources of natural gas or coal.<sup>1</sup> By the effort of the researchers of DICP since 1980s, the industrial test of DMTO process with methanol feeding of 50t/d has been successfully finished in 2008. Based on this work, in August, 2010, the world's first commercial application of the MTO process licenced by DICP with a production capacity of 600 000 tons of light olefins per annum, was proved to be completely successful in Baotou, China.<sup>2</sup>

Over the past few decades, methanol-to-olefin (MTO) conversion over acidic zeolites or zeotype molecular sieves has attracted much attention from academy and industry. The mechanism governing the conversion of methanol molecules into olefins within zeolite cages or channels has drawn considerable interest because of the concern for C–C bond formation from C1 reactants.<sup>3-4</sup> Direct formation of a C–C bond by C1 species derived from methanol has been proved to be energetically unfavorable.<sup>5</sup> Alternatively, the “hydrocarbon pool” (HCP) mechanism, an indirect pathway, avoids high energy barriers and has been consequently generally accepted due to evidence from experimental observations and theoretical calculations.<sup>6-7</sup> The HCP mechanism indicated the organics species confined in the zeolite and zeo-type catalysts govern the methanol conversion. In our recent study, for the first time the observation of the confined multimethylbenzene carbenium cations as the active intermediate was realized under real reaction condition and the important role of this reaction intermediate for olefin formation in methanol conversion was elucidated.<sup>8</sup> This consolidates the previously proposed hydrocarbon pool mechanism of MTO reaction. Part of this work has been published recently. With the employment of C13 labeling technique, the detailed the reaction route of methanol conversion was studied and a complete reaction network of methanol conversion was established in combination the reaction route of

methanol conversion following hydrocarbon pool mechanism and the reaction route of olefins methylation with methanol in the reaction with different zeolite and SAPO catalysts used.

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## ПРОЦЕССЫ ГИДРОИЗОМЕРИЗАЦИИ РАЗЛИЧНЫХ УГЛЕВОДОРОДНЫХ ФРАКЦИЙ НА КАТАЛИЗАТОРАХ НА ОСНОВЕ SAPO-31

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В передовых странах постоянно происходит усовершенствование старых и создание новых технологических процессов с целью получения высококачественных топлив и масел. В области получения дизельных топлив и базовых масел все большее развитие находят процессы гидропереработки исходного сырья.

Существенным достижением в технологии получения низкозастывающих дизельных топлив и высокоиндексных базовых масел стала разработка некоторыми западными фирмами процесса, в основе которого лежит использование селективного катализатора гидроизомеризации *n*-парафинов. Существенное снижение температуры застывания получаемой дизельной фракции не сопровождается заметным изменением значения цетанового числа, поскольку малоразветвленные изомерные парафины имеют более низкие температуры застывания, но близкие к *n*-парафинам значения цетановых чисел. В случае переработки на подобных катализаторах высокопарафинистых масляных фракций или гача (смесь *n*-парафинов с температурами выкипания от 350 до 500 °С) возможно получение низкозастывающих базовых масел со значением индекса вязкости 110-130 и более.

Основным компонентом этого катализатора является кристаллический микропористый силикоалюмофосфат со структурой SAPO-11, уникальность которого обусловлена наличием кислотных центров умеренной силы по сравнению с цеолитами. Дополнительно высокую селективность в отношении реакций изомеризации придает система каналов с размером 3.9 x 6.3 Å, в которых происходит их изомеризация с преимущественным образованием моно-метилпроизводных продуктов.

Силикоалюмофосфаты со структурой SAPO-31 представляют собой еще одну разновидность среднепористого кристаллического материала с размером каналов примерно 5,4 Å. В Институте катализа СО РАН были разработаны основные принципы синтеза и выявлены основные закономерности получения каталитических систем на основе материалов со структурой SAPO-31, обладающих широким интервалом физико-химических

свойств. На основе этого материала были разработаны высокоэффективные катализаторы гидроизомеризации различных углеводородных фракций.

Процесс гидроизомеризации дизельных фракций проводится в неподвижном слое катализатора при температурах 320-360 °С.

**Таблица. Превращение гидрообессеренной (S <10ppm) дизельной фракции с температурой застывания -14 °С на катализаторе Pt-SAPO-31. (P = 2,5 МПа, скорость подачи исходного сырья – 1,2 ч<sup>-1</sup>, H<sub>2</sub> : сырье = 2000 (об.))**

	Исходное сырье	Температура реакции, °С					
		300	310	320	330	340	350
Выход целевой фракции, %	100	98,3	97,6	96,8	96,2	95,1	93,6
Содержание н-парафинов, %	22,5	12,7	9,6	8,7	7,3	5,8	4,4
Температура помутнения, °С	-5	-29	-44	-49	-54	-58	-62
Температура застывания, °С	-14	-35	-48	-53	-57	-61	-65
Расчетное цетановое число	54,0	53,2	52,6	51,7	51,1	50,6	50,1

Испытания катализатора проводились на пилотной установке в течение 1500 часов в стационарных условиях при температуре реакции 340 °С и давлении 3,5-4 МПа, активность катализатора в течение всего пробега оставалась высокой. Температура помутнения полученного дизельного топлива составляет минус 37 – 40 °С, а температура застывания - минус 44-50°С при среднем выходе целевой дизельной фракции 98-99 %.

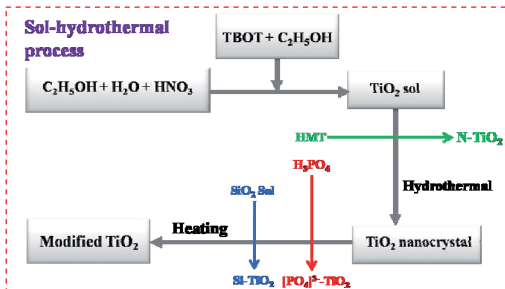
Катализатор Pt-SAPO-31 был также испытан в превращении гидроочищенного газа (смесь парафинов нормального строения, фракция 360-500 °С, температура плавления +56 °С, содержание серы менее 10 ppm). При проведении реакции при 340 °С выход масляной фракции с температурой кипения выше 350 °С составляет более 80%, а содержание н-парафинов в ней уменьшается до величины менее 5%, что приводит к снижению температуры застывания этой фракции до значений ниже минус 8 °С.

# SYNTHESIS OF HIGH ACTIVE NANO-STRUCTURED PHOTOCATALYST MATERIALS AND MECHANISM INSIGHT

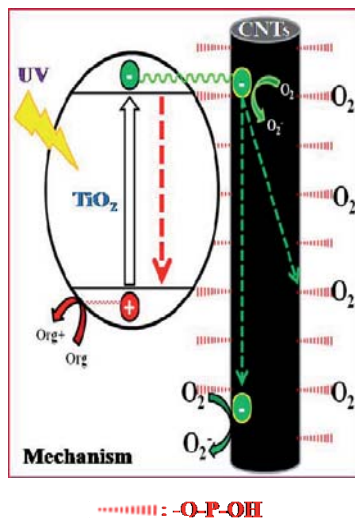
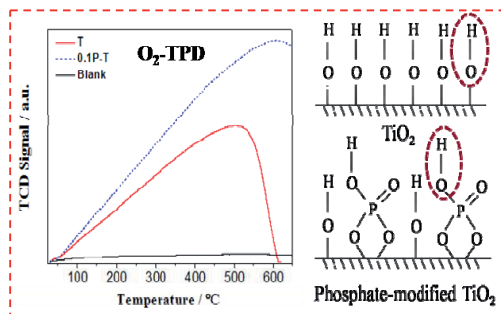
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**Abstract:** Covering the scientific questions of nanosized  $\text{TiO}_2$  photocatalysis, mainly involved with the disagreement between large surface area and too much defect, and the low ability to absorb  $\text{O}_2$  so as to be unfavorable to capture photogenerated

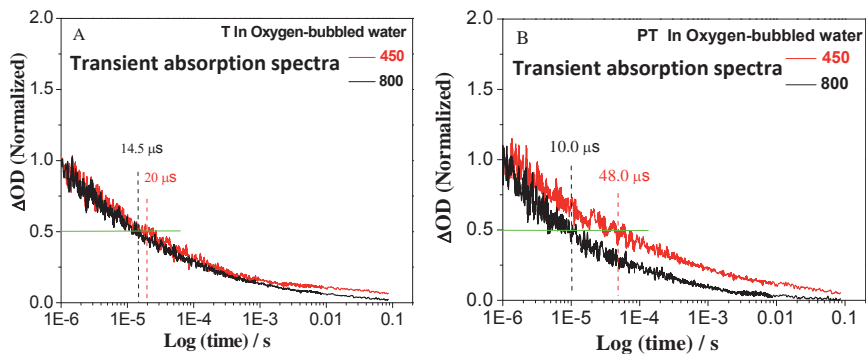


electrons, we have successfully obtained the high active  $\text{TiO}_2$ -based photocatalysts by increasing the thermal stability of nanocrystalline anatase  $\text{TiO}_2$  through introducing functional molecules as inhibitors at the subsequent thermal treatment so as to keep large surface area and to improve the crystallinity simultaneously, and by modifying with phosphate to increase the adsorption of  $\text{O}_2$ , especially for the nano-structured composite of MWCNTs and  $\text{TiO}_2$ . Meanwhile, the mechanism insights are made mainly based on the atmosphere-controlled surface photovoltage spectra, transient





absorption spectra, O<sub>2</sub> temperature-programmed desorption curve and photoelectrochemical measurements. Similarly, high active Fe<sub>2</sub>O<sub>3</sub>-based nano-photocatalysts are also synthesized.



**Keywords:** High-thermal stability; Phosphate surface modification; O<sub>2</sub> adsorption; Photogenerated charge separation; High photocatalytic activity

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## Acknowledgements

This work was financially supported by the National Nature Science Foundation of China (21071048), the Chang Jiang Scholar Candidates Programme for Provincial Universities in Heilongjiang(2012CJHB003), the Science Foundation of Harbin City of China (2011RFXXG001), and the Programme for Innovative Research Team in Heilongjiang University (Hdtd2010-02), for which we are very grateful.

**Российско-Китайский семинар  
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Обложка: Н.Ф. Потеряева

Подписано в печать 10.08.2012

Формат 60x84/16

Печ.л. 2

Заказ № 74

Тираж 50

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Отпечатано на полиграфическом участке издательского отдела  
Института катализа им. Г.К. Борескова СО РАН  
630090, Новосибирск, пр. Академика Лаврентьева, 5



## TIME-TABLE

### Russian-Chinese Seminar «New catalytic materials and technologies»

August 13-16, 2012, Novosibirsk, Russia

Monday, August 13	Tuesday, August 14	Wednesday, August 15	Thursday, August 16
10.40 <b>A r r i v a l</b>	09.00 <b>B r e a k f a s t</b>	09.00 <b>B r e a k f a s t</b>	09.00 <b>B r e a k f a s t</b>
14.00 <b>L u n c h</b>	10.00 <b>Opening</b> (academician Valentin N. Parmon)	10.00 <b>PL-3 LIU Zhong-min</b> <i>Methanol to olefins</i>	10.00 <b>Free time</b>
15.30 <b>Excursion:</b> <b>Museum of history and culture of Siberia and Far East</b>	10.30 <b>PL-1 FU Hong-gangh</b> <i>Designed synthesis and application of crystalline carbon-based materials</i>	10.40 <b>KL-3 YANG Qi-hua</b> <i>Asymmetric catalysis in nanoreactor</i>	12.00 <b>Picnic</b>
18.00 <b>Welcome Dinner</b>	11.10 <b>KL-1 G.V. ECHEVSKII</b> <i>Processes of hydroisomerization of the different hydrocarbonic fractions using metal-containing SAPO-31 catalyst</i>	11.10 <b>KL-4 V.A. SADYKOV</b> <i>Catalysis in the intermediate temperature solid oxide fuel cells: design and performance of nanocomposite cathode and anode materials</i>	
	11.40 <b>C o f f e e</b>	11.40 <b>C o f f e e</b>	
	12.00 <b>KL-2 JING Li-qiang</b> <i>Synthesis of high active nano-structured photocatalyst materials and mechanism insight</i>	12.00 <b>OP-4 S.R. KHAIRULIN</b> <i>The process of H<sub>2</sub>S selective catalytic oxidation for on-site purification of hydrocarbon gaseous feedstock. Technology demonstration</i>	
	12.30 <b>OP-1 LI Guang-ming</b> <i>Salen type lanthanum (III) complexes as lewis acid catalysts for the nitroaldol reaction in water</i>	12.20 <b>OP-5 CHENG Mo-jie</b> <i>Research and development of SOFC at DICP</i>	
	12.50 <b>OP-2 A.E. RUBANOV</b> <i>Single-stage hydroconversion of vegetable oil to iso-alkanes using metal-containing SAPO-31 catalyst</i>	12.40 <b>OP-6 I.V. DELIY</b> <i>The comparison of CoMoS and NiMoS catalysts in HDO of aliphatic ethers and rapeseed oil</i>	
	13.10 <b>L u n c h</b>	13.00 <b>L u n c h</b>	
	14.10 <b>PL-2 V.I. BUKHTIYAROV</b> <i>Size effects in combustion of hydrocarbons and CO over supported metal catalysts for abatement of car exhausts</i>	14.00 <b>KL-5 WU Wei</b> <i>Molecular Sieves with ATO structure: Synthesis, Characterization and Catalytic Properties in n-decane hydroisomerization</i>	
	14.50 <b>OP-3 XIAO Lin-fei</b> <i>Functional ionic liquid: a highly effective catalyst for synthesis of cyclic carbonates</i>	14.30 <b>Round table</b>	
	15.10 <b>C o f f e e</b>		
15.30 <b>Excursion:</b> <b>Boreskov Institute of Catalysis SB RAS</b>	18.00 <b>Closing Dinner</b>		

You may present your report either English or Russian language.