Boreskov Institute of Catalysis SB RAS
N.D. Zelinsky Institute of Organic Chemistry RAS
A.V. Topchiev Institute of Petrochemical Synthesis RAS
Lomonosov Moscow State University
Novosibirsk State University

Russia

Moscow

May 20-23, 2018

5th International School-Conference on Catalysis for Young Scientists

Catalyst Design:

“From Molecular to Industrial Level”

ABSTRACTS

Novosibirsk - 2018

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УДК 544.47
ББК 22.54 + 35.115
С31

С31 **Catalyst Design: From Molecular to Industrial Level.** 5th International School-Conference on Catalysis for Young Scientists (May 20-23, 2018, Moscow, Russia) [Electronic resource] : Abstracts / Boreskov institute of Catalysis SB RAS; ed.: prof. V.I. Bukhtiyarov, prof. O.N. Martyanov – Novosibirsk: BIC, 2018. – 1 electronic optical disc (CD-R). ISBN 978-5-906376-21-3

В надзаг.: Boreskov Institute of Catalysis SB RAS
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The collection includes abstracts of plenary lectures, oral and poster presentations.
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- Catalysts preparation
- Characterization and in situ studies of catalysts
- Mechanism and kinetics of catalytic reactions
- Catalysis for environmental protection
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- Catalysis for energy efficient processes, photocatalysis and electrocatalysis

УДК 544.47
ББК 22.54 + 35.115

ISBN 978-5-906376-21-3

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Financial Support

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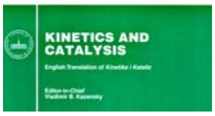
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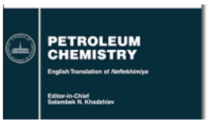
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PLENARY LECTURES

PL-1 ÷ PL-12

PL-1

Development of Novel C–H Functionalization Methodologies

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We have developed a set of new transition metal-catalyzed C-H functionalization methodologies employing a silicon-tether motif. These methods feature: (a) use of silyl group as a tether between a substrate and a reagent, thus transforming intermolecular reaction into an intramolecular reaction; (b) employment of a silicon-tethered directing group, which is traceless or easily convertable into valuable functionalities; (c) use of reactive silyl-tethered hydrosilane group; and (d) introduction of new N/Si-chelation concept that allows for a remote activation of aliphatic C-H bonds.

We have also uncovered new reactivity of hybrid Pd-radical species, generated at room temperature under visible light without exogenous photosensitizers, which lead to development of novel transformations, including new types of Heck reaction and proximal and remote C–H functionalization methods.

The scope of these transformations will be demonstrated and the mechanisms will be discussed.

PL-2

Multiple Proton-Coupled Electron Transfer for Electrochemical Generation of Fuels

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This talk will outline a simple but general theoretical analysis for multiple proton-electron transfer reactions, based on the microscopic theory of proton-coupled electron transfer reactions, recent developments in the thermodynamic theory of multi-step electron transfer reactions, and the experimental realization that many multiple proton-coupled electron transfer reactions feature decoupled proton-electron steps in their mechanism. It is shown that decoupling of proton and electron transfer leads to a strong pH dependence of the overall catalytic reaction, implying an optimal pH for high catalytic turnover, and an associated optimal catalyst at the optimal pH. When more than one catalytic intermediate is involved, scaling relationships between intermediates may dictate the optimal catalyst and limit the extent of reversibility that may be achievable for a multiple proton-electron-transfer reaction. These scaling relationships follow from a valence-bond-type binding of intermediates to the catalyst surface. The theory is discussed in relation to the experimental results for a number of redox reactions that are of importance for sustainable energy conversion, including the electrocatalytic reduction of CO_2, focusing on their pH dependence and structure sensitivity.

PL-3

Metal Particle Size Effects: an Interference of Activation and Adsorption Factors

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High metal dispersion improves utilization of noble metal. On the other hand, reactivity of the surface atoms may depend significantly on the size of metal particles, since changes in the metal particle size lead to alterations of the relative ratio between edges, corners and terrace atoms, as well as changes in the electronic structures. Therefore, turnover frequency (TOF), defined as the activity per unit of exposed surface, can become dependent on the size of metal particle (particle size effect). As a result, the overall activity of the catalyst becomes a function of two major factors: (1) metal dispersion (fraction of exposed atoms) and (2) the particle size effect, which requires careful management of metal particle size for achieving optimal performance and/or minimizing noble metal loading.

The discussion of the relationship between particle size and TOF will be based on the concept proposed by Van Santen et al. [1], which rationalizes the relationship of TOF of catalytic reactions on transition-metal particle size. The concept emphasizes the dependence of the rate-limiting activation stage and the geometry of the appropriate surface active site. In this lecture particular focus will be given on the chemisorption of the reacting molecules on metal nanoparticle surface and the impact of this factor on TOF. The lecture will concentrate on the impact of chemisorption on the reactivity of metal surface atoms neglecting metal-support interface phenomena. It will be shown that in the case of small metal particles (< 3-4 nm) adsorption and/or strong structural modification of the nanoparticle surface may dominate the activation stage and the observed TOF significantly deviate from “TOF – particle size relationship” predicted by the theory [1].

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PL-4

Design of Active Sites as the Tool for Improvement of Industrial Catalysts: Pt/Aluminum Oxides Compositions

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Supported platinum-containing catalysts are widely applied in various oxidation, hydrogenation and dehydrogenation processes and form a basis for the production of high-octane fuels and petrochemical products by reforming of gasoline fractions. In the latter case, catalyst supports are represented by aluminum oxide systems, both pristine and doped, while in some other processes – by mixed systems, for example, aluminosilicates, aluminophosphates, aluminum-magnesium hydroxides, and others.

The lecture presents an overview of the studies aimed to enhance the performance (activity, selectivity and stability) of catalytic compositions “Pt/aluminum oxides” in dehydrocyclization and dehydrogenation of individual alkanes. These studies were based on the idea of using knowledge on the active sites of such catalytic compositions to develop methods for their deliberate synthesis.

Various advanced methods (HREM, SEM, XPS, XRD, EXAFS, NMR MAS, IRS, etc.) were used to reveal regularities in the formation of ionic platinum species (the precursors of “soft” Lewis sites) anchored on the aluminum oxide support.

The location and composition of platinum complexes, which are the precursors of ion-metal sites, were elucidated by the adsorption-desorption studies of H_2PtCl_6 sorption along with the analysis of the adsorbed species – their composition, structure, and reactivity toward hydrothermal treatment, reduction by hydrogen and interaction with alkanes.

According to gradient elution, EXAFS and SR-XRD data, such complexes have the composition $[PtCl_{1,2-1,5}(OH)_{4,8-4,5}]_{2-4}$ and are located in the surface defects (cationic vacancies in octahedral positions) of γ-alumina.

The indicated catalysts demonstrate the highest activity and selectivity in aromatization and hydroisomerization of alkanes.

The listed fundamental results formed a basis for developing the production technology of advanced reforming catalysts.

In order to create highly selective and stable catalysts for dehydrogenation of alkanes (propane, decane, etc.), the formation of platinum-magnesium-aluminum oxide systems, particularly those doped with other elements, was studied in detail using modern physicochemical methods (HREM, SEM, NMR MAS, IR, etc.). The initial compounds for the synthesis of such systems were represented by mixed layered aluminum-magnesium hydroxides with the hydrotalcite-type structure, which made it possible to vary quite accurately the Mg/Al atomic ratio in the layer and isomorphously substitute Mg by other cations.

The use of layered double hydroxides (aluminum-magnesium ones) containing readily exchangeable anions in the interlayer space (for example, OH^{-}) allows anchoring of anionic platinum complexes in the interlayer space by anionic exchange. As a result, the formation of platinum sites (the reduction of interlayer anionic Pt complexes) under restricted conditions of the layered structure produces platinum particles with the flat morphology.

A partial isomorphic substitution of Mg^{2+} cations by Zn^{2+} during the catalyst synthesis initiates the interaction between platinum intercalated into layered double hydroxides and the dopant with the formation of Pt particles bound to the reduced Zn species. As a result, the platinum particles decrease in size and acquire (according to XPS $Pt3d_{5/2}$) a negative charge. This increases selectivity of the $Pt/Mg(Zn)AlO_x$ catalyst in dehydrogenation of propane up to 100%. The results obtained are important for developing the production technology of new-generation catalysts for dehydrogenation of alkanes.

PL-5

Operando Nanocatalysis

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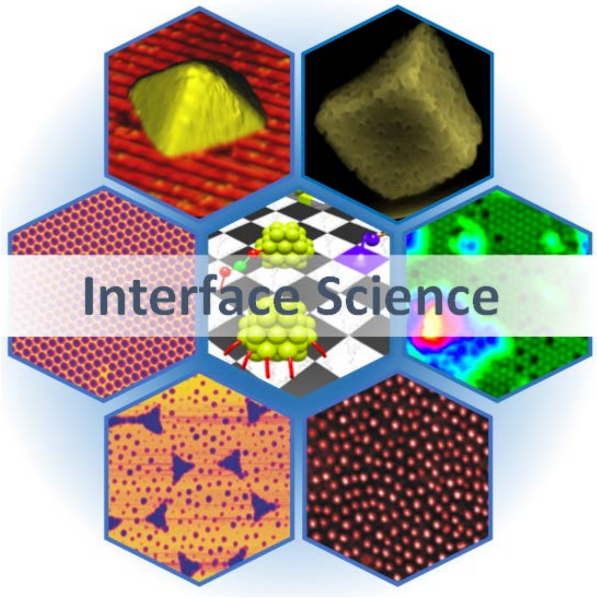
Tailoring the chemical reactivity of nanomaterials at the atomic level is one of the most important challenges in catalysis research. In order to achieve this elusive goal, we must first obtain a fundamental understanding of the structural and chemical properties of these complex systems. In addition, the dynamic nature of the nanostructured films and nanoparticle (NP) catalysts and their response to the environment must be taken into consideration, since their working state might not be the state in which the catalyst was prepared, but rather a structural and/or chemical isomer that adapted to the particular reaction conditions.

This talk provides examples of recent advances in the preparation, plasma-functionalization and characterization of nanostructured films and NP catalysts with well-defined morphology, size, and shape [1,2]. It discusses how to resolve the structure and composition of nm-sized metal catalysts via a combination of *in situ* and *operando* microscopy (AFM, STM, TEM) and spectroscopy (XAFS, XPS) methods, and how to follow its evolution under different gaseous or liquid chemical environments in the course of a catalytic reaction.

It will be highlighted that for structure-sensitive reactions, catalytic activity, selectivity and stability against sintering can be tuned through controlled synthesis. Examples of catalytic processes which will be discussed include the gas- and liquid-phase oxidation of 2-propanol [3-5] and the reduction of CO_2 in the gas phase at high pressure as well as electrochemically [1,2,6-8]. Emphasis will be given to elucidating the role of the NP size, shape, composition and chemical state of the catalysts in the activity and selectivity of the former reactions.



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PL-6

Mechanism and Kinetics on the Example of the Heterogeneous Catalytic Deacon Reaction

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Catalytic reaction mechanism and kinetics are tightly coupled. Neglecting secondary processes such as heat and mass transport, the kinetics of a catalytic reaction is routed in the reaction mechanism. Under heterogeneous catalytic reaction mechanism we understand a sequence of elementary steps that describe the catalytic cycle and regenerate the initial surface state. The elementary reaction step is defined by an individual chemical bond-breaking or forming event that link local equilibrium states of gas phase molecules, adsorbates, intermediates and surface states.

To understand the reaction mechanism, people use various approaches. A simple phenomenological approach is to collect kinetics data as a function of process conditions, such as partial pressure of reactants (and products), temperature, potentially reactor type, residence time, etc. DFT calculations are nowadays highly powerful and can predict thermodynamic and kinetic aspects of elementary reaction steps on the assumed catalyst surface. As has been demonstrated in the literature many times, fitting kinetic data does not lead to a singular potential mechanism. Also vice versa, when theory based on a proposed reaction mechanism predicts kinetics, unfortunately the good agreement with measured data cannot be taken as a proof for the particular mechanism, as an alternative mechanism may result in very similar kinetics. A potential way out of this dilemma is to utilize in situ (operando) spectroscopic techniques to better understand the actual surface (oxidation) state, adsorbate types and coverages. The combination of careful kinetic investigations, in situ spectroscopy and DFT calculations can bring us closer to the ultimate dream of heterogeneous catalytic research to understand a catalytic system from bottom up and thus be able to design improved catalysts. In my talk I will use the heterogeneous catalytic Deacon reaction as an example to guide you through questions on mechanism and kinetics in heterogeneous catalysis.

Acknowledgement. The author acknowledges the fruitful collaboration with numerous colleagues while working on the Deacon reaction. In no particular order: Ramzi Farra, Robert Schlögl, Nuria López, Javier Pérez-Ramírez, Herbert Over, Reinhard Schomäcker, László Szentmiklósi, Timm Schmidt.

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PL-7

Bio-Based Aromatics from Biomass

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The identification and subsequent commercialization of added value chemicals from biomass is high on the global research and development agenda [1]. An attractive approach involves the conversion of suitable biomass sources to products that are already on the market place and commercially available (drop-in approach). As such, this strategy exploits existing value chains, markets and infrastructure, which will speed up the pace of the development and reduce investment costs. In this presentation, research activities in our group aiming at the identification of suitable catalytic technology for particularly aromatics from biomass sources will be reported.

The focus will be on the use of two technologies, *viz*. catalytic pyrolysis [2] and catalytic hydrotreatment [3] in combination with the use of biomass residues such as lignin. Typical features of both technologies will be presented and recent results will be highlighted, with a particular focus on the yields of bio-based aromatics. Finally, a techno-economic evaluation will be provided to identify the technologies with the highest chance for future implementation.

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PL-8

Balancing Reductionist and Systems Approaches in Computational Catalysis: Questions of Accuracy and Adequacy

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Over the last decade, computational chemistry has become one of the key components of catalysis research and has deserved a place in the catalysis toolbox next to common laboratory techniques such as FTIR, NMR or XRD [1]. The progress in fundamental understanding of catalytic phenomena currently relies largely on quantum chemical computations. State-of-the-art quantum chemical methodologies and, particularly, the density functional theory (DFT) methods have matured to the level that they can be nowadays routinely used not only to rationalize, but also to direct experimental catalysis studies [2,3]. Accuracy is the corner stone of computational chemistry and it represents the key focus of this lecture (Figure 1).

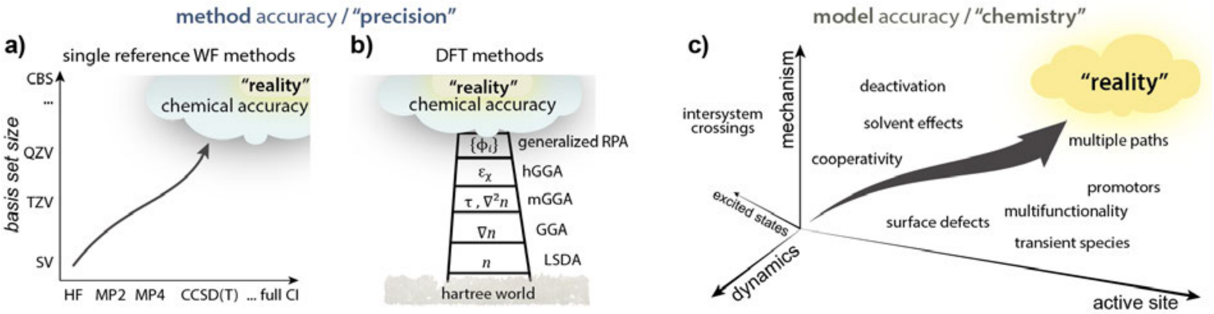

Figure 1. Method (a,b) and model (c) accuracy in computational chemistry. The accuracy of wavefunction-based methods (a) systematically increases with improving the description of the electron correlation (level of theory) and increasing flexibility of the description of the wave-function (basis set size). The hierarchy of DFT methods (b) is commonly illustrated by the "Jacob's Ladder", where the rungs represent the number and kind of local ingredients included in the particular density functional approxima-tion. The model accuracy (c) is a system-specific parameter, which often represents a highly complex multidimensional problem encompassing a wide variety of factors and phenomena. [4]

In this talk I will illustrate the problem of a balance between the model and method accuracy in computational studies on industrially-relevant catalytic systems [4]. The discussion on the issues related to modeling accuracy will be supported by representative examples from recent research of my group on catalysis by zeolites including selective catalytic oxidation of methane [5] and production of biomass-derived aromatics [6]. Along the discussion, I will touch upon possible implications of the selective agreements between reductionism-dominated theories and highly complex catalytic experiments (Figure 2).[4,7] I will emphasize the necessity of establishing a balance between the reductionist and systems approaches to studying complex multicomponent reactive systems.

model A

“catalytic system”

model B

Figure 2. Illustrative examples of the excessively reductionist approaches common for the physical (model A) and chemical (model B) communities to modeling catalytic systems. Despite being partially representative to the actual system (spectral characteristics, general shape and size of the particles, etc), none of them is sufficient for an adequate description of the main functions of the experimental objects.[4]

Acknowledgement. I thank the Government of the Russian Federation (Grant 074-U01) for my personal research professorship supported through the ITMO Fellowship and Professorship Program.

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PL-9

Oxygen Activation and Pathways in High Temperature Catalytic Oxidation

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During the last decades the processes of direct transformation of light alkanes into value-added products, such as oxidative coupling of methane (OCM), oxidative dehydrogenation (OD) of C_{2+} and oxidative cracking (OCr) of C_{3+} alkanes have been extensively studied, which, as a rule, proceed at high temperatures (>1000 K). The research activity has been focused on the development of efficient catalysts and mechanistic aspects, such as the elucidation of the nature of surface active sites, alkane molecule activation and pathways of their transformation to final products, contribution of free-radical chemistry, reaction kinetics, etc. Unlike catalysts for partial oxidation of non-saturated hydrocarbons and functionalized organic compounds and for total oxidation, typical catalysts for such processes do not contain precious and transition metals. This required some re-consideration of the existing notions about the activation of the oxidant – primarily, molecular oxygen – including the key factors that govern its interaction with surface active sites and involvement into the catalytic cycle. The following aspects of oxygen activation and pathways will be analyzed in this presentation:

- general features of oxygen activation in gas phase oxidation and in heterogeneous catalysis;
- comparison of 'classical' kinetics of catalytic oxidation with kinetics of high-temperature oxidation reactions;
- redox catalysis over non-redox oxides (Li/MgO, rare-earth oxides);
- thermochemistry of surface active sites and mechanism of their re-oxidation.

An focus will be on the complex relationships between the structural features, nature of chemical processes involved into the redox cycles (oxygen removal and consumption) and reaction kinetics for particular OCM, OD and OCr catalysts.

PL-10

From Catalytic Reaction Mechanism to Catalyst Design: A Valuable but Complex Pathway

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In the wide field of heterogeneous catalysis and at variance with homogeneous or molecular catalysis, the proper mechanism of most reactions is intimately linked to the structure of the catalyst. By structure, we may consider both the surface structure, interfacing the reaction medium and the catalyst itself, but also the bulk structure of the catalyst, including the active phase(s) and the support of the active phase. All these key structural parameters are mainly determined from the overall catalyst design, from synthesis to activation and possibly regeneration steps. These phenomenological sequences illustrate the complex links between catalyst design and reaction mechanism, all these ones contributing to the targeted catalyst performances for a given reaction. Indeed the reaction mechanism which controls the elemental surface steps also combines with heat and mass transfer processes, being themselves closely related to the type of reactor considered for the considered reaction. The combination of all these processes control the observed performance of tested systems.

Such a long sequence of elemental events can be tackled via a number of widely distinct strategies.

A first strategy deals with a combinatorial search of new catalyst formulas by using mechanistic and characterisation knowledge in a high throughput (HT) statistical approach. As an example, in order to develop new acid and bi-functional catalysts for refinery applications, a HT method was developed for the characterization of Brønsted acidity of bifunctional catalysts library by means of isomerization of 3,3-dimethylbutene testing [1] (Figure 1). It was shown to allow quantifying very accurately the acid strength leading to catalyst ranking and selection in conditions similar to practical applications. The pros and cons of the use of model reactions for HT quantitative characterization will be discussed.

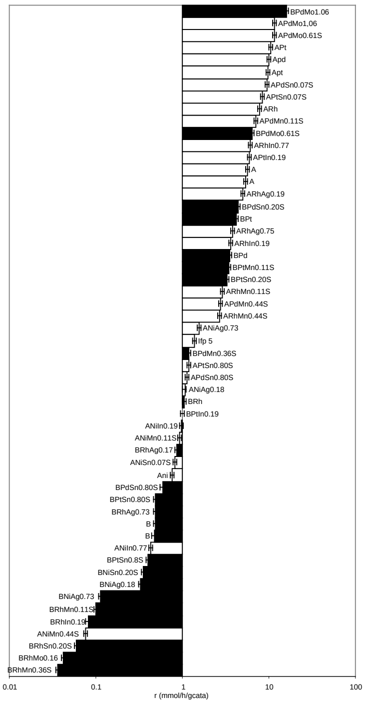

Figure 1: Example of classification histogram of a catalysts library tested for isomerization of 3,3-dimethylbutene. Black bars: αθ-alumina; white bars: δ-alumina [1]

A second major strategy consists in analysing the mechanistic and kinetic behaviour of various catalysts under realistic conditions (e.g., using operando spectroscopies combined with transient kinetic investigation) and to derive from these observations adapted changes in catalyst formulation and/or structure to improve their efficiency, selectivity and resistance to deactivation. A case study deals with deactivation processes during bio-syngas methanation and Fischer-Tropsch catalysts (Figure 2).

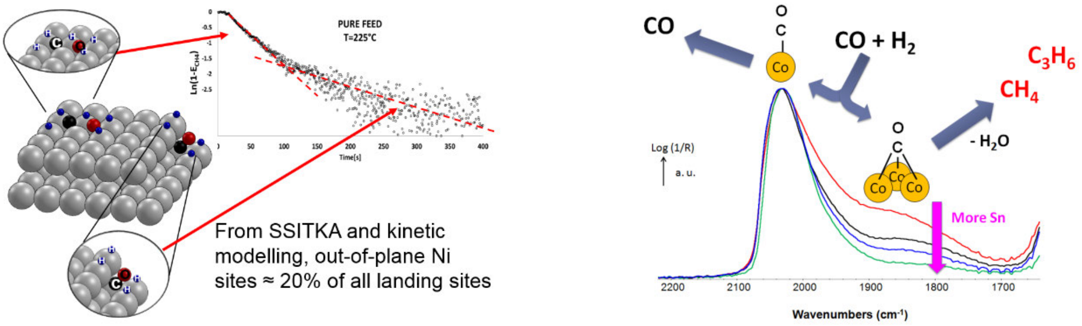

Figure 2: Links between SSITKA/DRIFT operando analysis and metal (Ni and Co) particles structure for a better understanding of the poisoning and ageing of methanation and FT catalysts [2, 3].

Finally a third strategy is based on nanoscale engineering combining nano structures and size controlled metal particles for improved selectivities and resistance to ageing. An example of these new materials is given in Figure 3 where a yolk/core–shell material allows to protect nanoparticles against poisoning or sintering by a thin zeolite shell where chemical reactions can proceed as in nanoreactors.

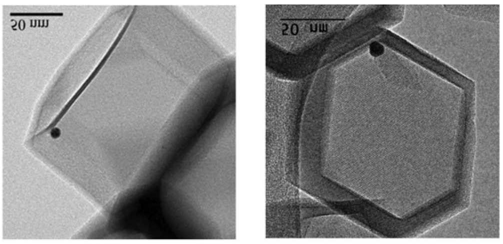

Figure 3: Representative images or Au@silicalite-1 (left) and Pt@silicalite-1 (right) hollow zeolites [3].

These various strategies can be applied to most industrially relevant cases such as light alkanes and alcohols reforming, syngas chemistry, catalytic cracking of biomass derived pyrolytic oils and oxidative coupling of methane.

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PL-11

Molecular Recognition and Supramolecular Catalysis: from Homogeneous Systems to Nanostructured Hybrid Materials

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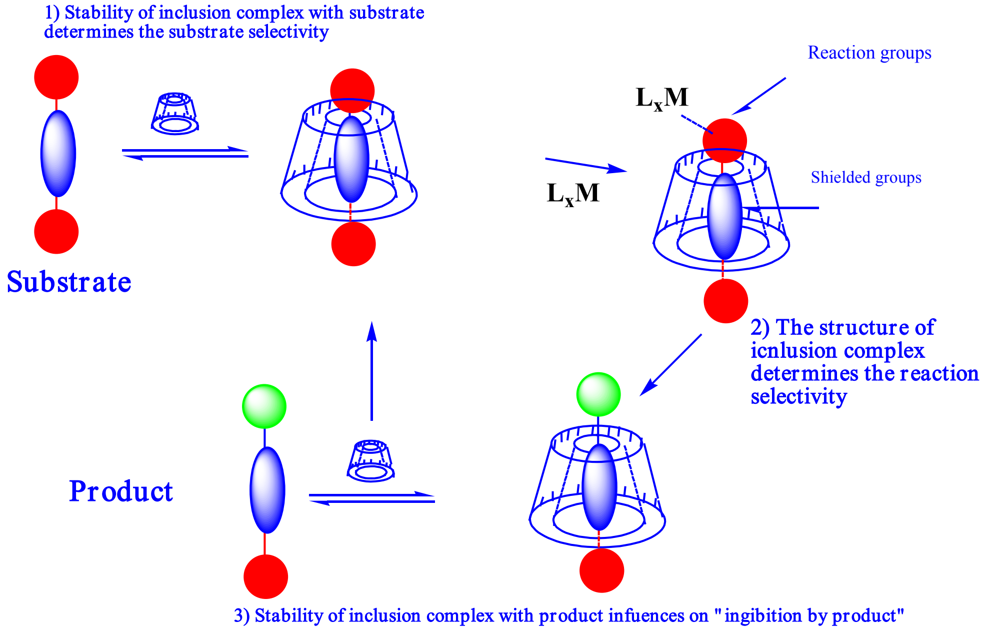
Catalysis is a key component in contemporary industrial and synthetic chemistry and the variation of catalysts selectivity is an ever challenging area of research. Promising approach in designing selective metal based catalytic systems is the synthesis of the new composites that sense and respond to some change in reaction conditions, structure of substrate in a controlled and reproducible manner and embed **"smart"** features in catalysis. Emerging concepts in catalysis point to a critical role of supramolecular organization in the control by such materials of *nonproductive* competing pathways and therefore substrate and reaction selectivity. Supramolecular systems can be considered as new tools of modern catalytic chemistry and should be design to achieve catalysis by placing converging binding sites in such a way that reactant molecules are brought together in close proximity and by stabilization of the intermediate or transition state owing to broad arsenal of noncovalent interactions (electrostatic, hydrogen bonding, π- π stacking and van der Waals interactions, hydrophobic and solvatophobic effects).

Approaches for design of supramolecular catalysts described here includes:

Development of metal complexes with macrocyclic ligands for oxidation catalysis (Wacker oxidation, phenol oxidation), hydroformylation, hydrogenation. The supramolecular ligands to be used are derived from cyclodextrins and calixarenes and have been shown to provide a scaffold for homogeneous transition metal catalysts that afford high selectivity and reactivity.



PL-11

Catalyst synthesis using molecular imprinting technique. This method has been developed as a new methodology for synthesizing a tailor-made receptor for the target substrate by molecular imprinting.

Heterogeneous catalysts based on cross-linking dendritic megamers. Varying the size, flexibility and polarity of the cross-linking agent molecule allows to control spacing between dendrimer molecules and selectivity of binding organic ligands and nanoparticles by such materials.

Ordered porous polymers. The catalyst based on metal nanoparticles or anchored complexes and phenol-aldehyde resins or polyaromatic frameworks demonstrate a molecular recognition ability and favorable catalytic properties.

Presented methods make it possible to develop new supramolecular and "nanovessel" catalysts with a wider range of binding site sizes with the goal of moving from binding studies to the development of well-defined materials with specifically tailored "active sites".

"The lecture based on conferences MMC (Macromolecule- Metal Complexes)"

PL-12

Understanding the Selectivity of the Methanol to Hydrocarbons Process at the Molecular Level

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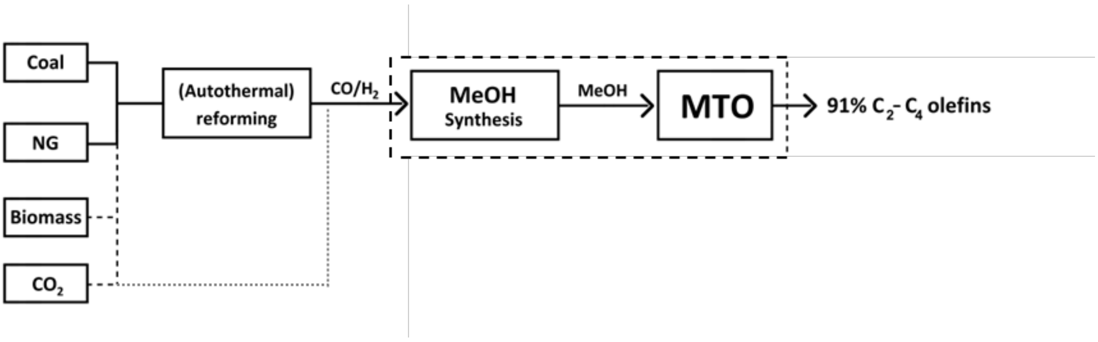
Methanol to Hydrocarbons (MTH), and in particular Methanol to Olefins (MTO), is currently the fastest growing industrial process for converting coal and natural gas to value-added hydrocarbons (C_{2+} alkenes, alkanes and aromatic products) via the following general process scheme [1]:



Recently, process intensification efforts were made, in which a catalyst for syngas (CO and H_2) conversion to methanol was combined with an MTO catalyst to directly yield hydrocarbons from syngas (dotted square in process scheme) [2-4]. Even more recently, CO was replaced by CO_2, to directly use CO_2 as carbon source in the process (grey dotted lines in process scheme) [5].

Product selectivity is key to the successful implementation of individual as well as combined processes. For MTH, which is an autocatalytic reaction catalysed by Brønsted-acidic microporous zeolites and zeotypes, product selectivity depends on a subtle combination of thermodynamic restrictions, diffusivities, the strength and chemical environment of the acid site, as well as steric constraints and the confinement effects offered by Van der Waals interactions between each transition state complex and the surrounding lattice [6-10].

In this lecture, I will introduce the audience to the state-of-the-art approaches and insight gained about the complex and fascinating chemistry of the MTH process, and discuss how thermodynamic and kinetic insight may be used to tune process selectivity.

Acknowledgement. The Norwegian Research Council is acknowledged for long-term support of this work through project grants 174893 and 239193.

PL-12

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ORAL PRESENTATIONS

Specified Oral Presentations

OPS-1 ÷ OPS-4

Section 1. Catalysts preparation

OP-I-1 ÷ OP-I-12

Section 2. Characterization and in situ studies of catalysts

OP-II-1 ÷ OP-II-7

Section 3. Mechanism and kinetics of catalytic reactions

OP-III-1 ÷ OP-III-7

Section 4. Catalysis for environmental protection

OP-IV-1 ÷ OP-IV-5

Section 5. Catalysis for fine organic synthesis, natural gas and oil processing, petroleum chemistry

OP-V-1 ÷ OP-V-15

Section 6. Catalysis for energy efficient processes, photocatalysis and electrocatalysis

OP-VI-1 ÷ OP-VI-2

OPS-1

Thermocatalytic Conversion of CO_2 into Renewable Synthetic Fuels: Catalysis and Reactor Design

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Converting CO_2 into synthetic fuels and platform chemicals is an attractive approach to decrease CO_2 emissions and to reduce our dependence on fossil fuels. Thermocatalytic hydrogenation provides advantages of fast reaction rates and high conversion efficiencies (as compared to electro-catalytic and photo-catalytic routes), thus allowing for compact, high-throughput operation [1]. To make the process sustainable, H_2 required for CO_2 hydrogenation should have zero or negligible carbon footprint, which is achievable if H_2 is produced via water electrolysis using renewable or surplus electricity.

Among possible reaction pathways is the Reverse Water Gas Shift reaction ($CO_2 + H_2 = CO + H_2O$) that has the advantage of low H_2 consumption. The generated CO can be mixed with H_2 to produce syngas, which is a valuable feedstock for chemical industry, i.e., methanol synthesis and Fischer-Tropsch. Another option is to convert CO_2 into synthetic methane, so-called renewable natural gas (RNG) via the Sabatier reaction ($CO_2 + 4H_2 = CH_4 + 2H_2O$). There are multiple sources of concentrated CO_2-containing streams including biogas and landfill gas (up to 50 mol% CO_2). However, a number of technological issues remain to be resolved, mostly related to the catalyst activity, selectivity and stability, and reactor design.

This talk outlines recent advances achieved in my group with respect to the thermocatalytic conversion of CO_2 into synthetic methane and syngas. High-performance catalytic formulations are being developed based on the ultra-low metal loadings and emerging catalytic materials (transition metal carbides). Novel reactor configurations are being designed using modelling tools, focusing on thermal management and performance optimization [2, 3]. The results of the catalytic performance evaluation (conversion, selectivity, and stability) and catalyst characterization (including temperature programmed reactions) of several transition metal carbides and Ru-promoted catalysts will be presented. The simulation results of the actively-cooled packed bed membrane Sabatier reactor with the distributed H_2 feed will be also presented. Altogether, our recent developments provide a new avenue for CO_2 utilization into useful fuels.

Acknowledgement. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

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OPS-2

Dehydration of Light Alcohols over Heteropoly Acid Catalysts in the Gas Phase

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Dehydration of methanol and ethanol has attracted much interest in the context of sustainable development to produce hydrocarbons as well as dimethyl (DME) and diethyl (DEE) ethers (eq. 1 and 2) from non-petroleum feedstock. These ethers, especially DME, play important role in the energy sector as clean fuel alternatives [1]. The dehydration reaction is usually carried out in the gas phase in the presence of solid acid catalysts such as metal oxides and zeolites [1].

$$2\ CH_3OH \longrightarrow (CH_3)_2O + H_2O \qquad (1)$$

$$2\ CH_3CH_2OH \longrightarrow (CH_3CH_2)_2O + H_2O \qquad (2)$$

We have studied the dehydration of methanol to DME and ethanol to DEE in the gas phase over a wide range of bulk and supported Brønsted acid catalysts based on tungsten Keggin heteropoly acids (HPA) and compared with the reaction over HZSM-5 zeolites (Si/Al = 10-120). The HPA catalysts included bulk $H_3PW_{12}O_{40}$ (HPW) and $H_4SiW_{12}O_{40}$ (HSiW), HPW and HSiW supported on SiO_2, TiO_2, Nb_2O_5 and ZrO_2 at sub-monolayer HPA loading, as well as bulk acidic Cs salts of HPW.

Details on catalyst preparation, characterization (BET, ^1H and ^{31}P MAS NMR, XRD, FTIR and NH_3 adsorption microcalorimetry) and activity testing are given elsewhere [2,3]. The dehydration of alcohols was studied in a continuous flow fixed-bed reactor in the temperature range of 90-300°C at 1-17 kPa alcohol partial pressure.

DME and DEE are the thermodynamically favored products at lower temperatures, whereas increasing the temperature leads to formation of hydrocarbons at the expense of ethers. Fig. 1 shows the effect of temperature on alcohol conversion and product selectivity over 15%HSiW/SiO_2. The conversion of methanol reaches equilibrium value of 89% at 150°C, with a slight decline at higher temperatures probably due to catalyst coking. DME is the only product up to 200°C, with C_1-C_3 hydrocarbons also forming at higher temperatures. Similarly, ethanol conversion reaches 100% at 180°C with high DEE selectivity at 90-120°C, and ethene becoming the main product at higher temperatures (Fig. 1). The catalyst showed very good performance stability; no catalyst deactivation was observed at 120-150°C for at least 20 h time on stream. The HPA catalysts exhibited higher activity than HZSM-5, which can be explained by stronger acidity of HPA. With HPA, equilibrium conversions are reached at temperatures about 50°C lower than with HZSM-5.

The formation of DME and DEE may be represented by two different pathways termed the associative pathway and the dissociative pathway [4]. Both pathways are thought to involve alcohol adsorption on Brønsted acid sites. Under the conditions studied, the dehydration of alcohols was zero order in alcohol, i.e., catalyst active sites were fully saturated with alcohol.

OPS-2

To gain mechanistic insights, we determined catalyst turnover frequencies (TOF) and measured catalyst acid strength by ammonia adsorption microcalorimetry in terms of the initial adsorption enthalpy (ΔH_{NH3}). Good correlations between the catalyst activity (TOF) and the catalyst acid strength were established for methanol and ethanol dehydration (Fig. 2 shows the results for methanol), which demonstrate that Brønsted acid sites of HPA indeed play important role in these reactions. Both bulk and supported HPAs obey these plots, which indicates surface type catalysis in both cases. The results for methanol dehydration over HZSM-5 obey the activity-acid strength correlation as well (Fig. 2). This indicates that both HPA and zeolite catalysts operate via a similar mechanism, and the turnover rate of alcohol dehydration for both catalysts is primarily determined by the strength of catalyst acid sites regardless of the catalyst pore geometry.

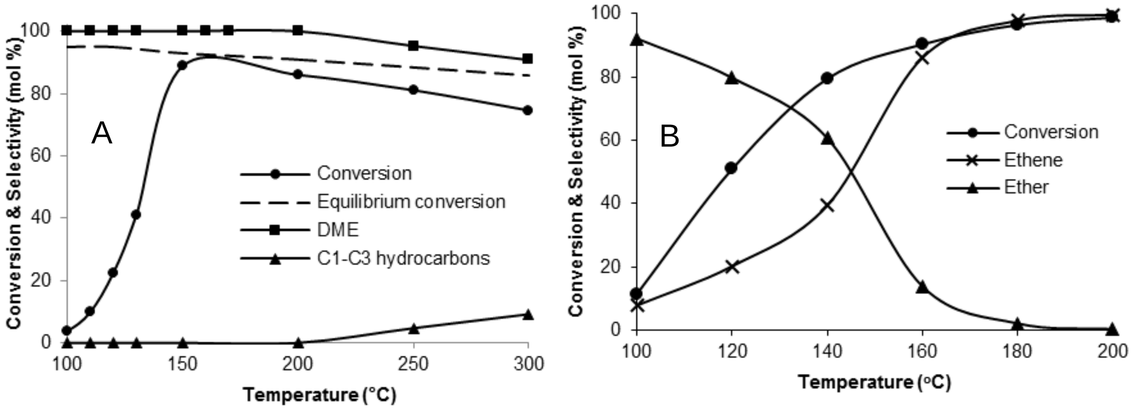

Fig. 1. Effect of temperature on alcohol dehydration over 15%HSiW/SiO$_2$ (0.2 g catalyst, N$_2$ carrier gas, 20 mL min^{-1} flow rate): (A) methanol (3.83 kPa partial pressure); (B) ethanol (1.48 kPa partial pressure).

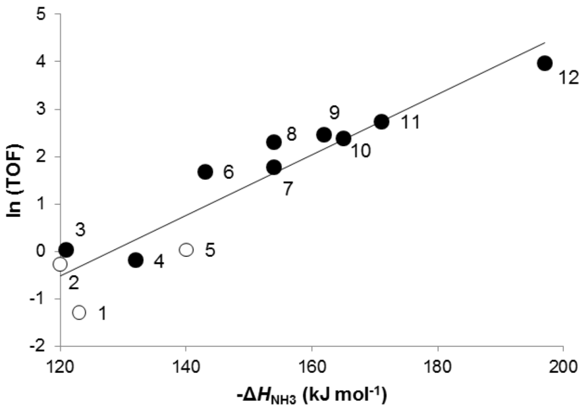

Fig. 2. Plot of ln (TOF) for methanol dehydration (TOF in h^{-1}) over tungsten HPA catalysts (closed circles) and HZSM-5 (open circles) versus initial heat of NH$_3$ adsorption (120°C, 0.20 g catalyst amount, 3.83 kPa methanol partial pressure, N$_2$ carrier gas, 20 mL min^{-1} flow rate; (1) HZSM-5 (Si/Al = 10), (2) HZSM-5 (Si/Al = 120), (3) 15%HPW/ZrO$_2$, (4) 15%HPW/Nb$_2$O$_5$, (5) HZSM-5 (Si/Al = 30), (6) 15%HPW/TiO$_2$, (7) 15%HPW/SiO$_2$, (8) 15%HSiW/SiO$_2$, (9) Cs$_{2.25}$H$_{0.75}$PW, (10) Cs$_{2.5}$H$_{0.5}$PW, (11) bulk HSiW, (12) bulk HPW).

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OPS-3

Tuning of the Nanostructured Metal-Oxide Phase Boundary for Selectivity Control of Methanol Reactions

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Copper-based catalysts are important catalysts in methanol chemistry with use in methanol synthesis from syngas, CO_2 hydrogenation to produce recyclable methanol or methanol steam reforming (MSR). Tunable and reproducible steering of the product selectivity is a prerequisite for technical applications. For MSR the important parameters include high CO_2 selectivity, low CO content and maximum H_2 yield. As for the use of ZrO_2 in the methanol steam reforming reaction, addition of ZrO_2 to Cu/ZnO catalysts allows suppressing the poor sintering stability of the latter. Synergistic Cu-ZrO_2 interactions have similarly been reported for pure Cu/ZrO_2 catalysts, exhibiting direct Cu-O-Zr bonds at the phase boundary. These interactions are considered to play a key role in steering the methanol reforming selectivity to maximum CO_2 yield. A nanocrystalline Cu/tetragonal ZrO_2 catalyst was already reported to be particularly promising in terms of activity, selectivity and stability especially with respect to a technically used Cu/ZnO/Al_2O_3 methanol synthesis catalyst. Efforts to explain the high selectivity have been considerable and are mainly centered at around two important beneficial parameters: the redox chemistry of Cu at the interface and structural properties within the metallic Cu phase (such as defects or disordered phases).

We have recently reported not only on the structural and chemical steering effects of Cu-ZrO_2 catalysts prepared by different synthesis routines to identify the complex structural prerequisites for CO-, CO_2,- and formaldehyde-selective methanol steam reforming, but also exemplified the surprisingly high activity and extremely high selectivity of a bimetallic Cu/$Cu_{51}Zr_{14}$ pre-catalyst, *operando* decomposed via contact to the MSR reaction mixture.[1-5] In this case, CO_2-selective reaction channels were controlled by the resulting Cu-ZrO_2 interface, suppressing full dehydrogenation of methanol to CO and subsequently promoting the total oxidation of intermediate oxygenates to CO_2 by water. The most crucial outcome was the self-activating and self-stabilizing state with co-existence of dispersed Cu and partially hydroxylated tetragonal ZrO_2, responsible for efficient water activation and, consequently, high CO_2 selectivity.[1-3] In general, concise control of the preparation conditions allowed us to switch the Cu-ZrO_2 systems between purely CO-, CO_2,- and formaldehyde-selective methanol steam reforming. Dominant steering parameters were identified to be the structural defectivity and the associated reactive reversible hydroxylation.[4,5]

OPS-3

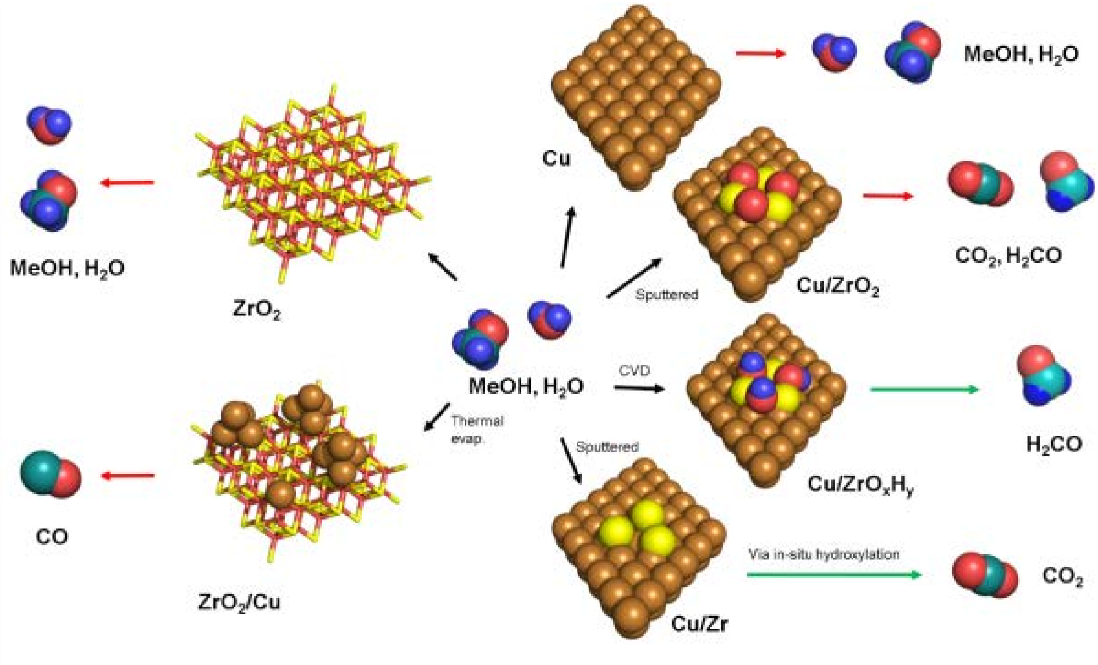

Figure 1: Reaction schemes of methanol steam reforming on selected Cu/ZrO$_2$ model and real catalysts.

Acknowledgement. This work was supported by the Austrian Science Foundation, grant F45-N16.

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OPS-4

Advanced High-Throughput Technologies for Catalysts Design

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Catalysis under all of its forms (heterogeneous, homogeneous or biocatalysis) is of upmost interest in crucial domains such as Environment, Food, Health, Energy, which are at the inner core of the current societal demands. The development of new catalysts with improved performances is therefore a highly strategic issue [1].

Innovation in catalysis is based, on the one hand, on forefront fundamental research to develop new catalytic concepts and, on the other hand, on an experimental phase devoted to the synthesis, characterization of the catalytic formulations and on the measurement of their properties/performances. The experimental part of the development of a new catalyst is time- and money-consuming, as traditional “trial and error” methods for synthesizing and testing catalysts are still needed. *A priori* theoretical prediction of optimal catalyst composition, structure and conditions of preparation for a given reaction is actually not yet possible. Therefore, there is a strong need for rapid preparation, characterization and screening of catalytic systems.

The main objective of the REALCAT project (French acronym standing for ‘Advanced High-Throughput Technologies Platform for Biorefineries Catalysts Design’), that will be presented in detail in this communication, is to set up a highly integrated platform devoted to the acceleration of innovation in all the fields of industrial catalysis with an emphasis on the field of biorefinery catalytic processes.

In this extremely competitive field, REALCAT consists in a versatile High-Throughput Technologies (HTT) platform devoted to innovation in heterogeneous, homogeneous or biocatalysts AND their combinations under the ultra-efficient very novel concept of hybrid catalysis.

The REALCAT platform is a complete, unique, and top-level HTT workflow including (i) robots for the automated synthesis of catalysts and novel biocatalysts, (ii) rapid characterization tools and (iii) a series of versatile parallel continuous and batch reactors - for gas phase, liquid phase or three phases reactions - combined with ultra-fast analytical tools at the top of the state-of-the-art for the analysis of the products in the reactors effluents [2].

Moreover, within the frame of the REALCAT project, methodological developments are also carried out in partnership with private companies in order to develop innovative HTT tools for catalysis not yet available on the market.

Three laboratories, all located in Lille University (North of France) have gathered their forces to design such a challenging project: UCCS, specialized in homogeneous and heterogeneous catalysis; Institute Charles Viollette, specialized in biocatalysis; and CRIStAL, specialized in data treatment, bio-informatics, modelling and analysis of biologic systems.

This unique integrated combination of skills is of outstanding importance for the optimization of the different operations of the platform. This makes REALCAT a major actor of high-level R&D catalysis programs on hot topics such as energy, environment, food and health applications.

In this communication examples of the great acceleration of the discoveries in the field of catalysis using high-throughput equipments and methodology will be presented.

Acknowledgement. The REALCAT platform is benefiting from a state subsidy administrated by the French National Research Agency (ANR) within the frame of the 'Future Investments' program (PIA), with the contractual reference 'ANR-11-EQPX-0037'. The European Union, through the ERDF funding administered by the Hauts-de-France Region, has co-financed the platform. Centrale Lille, the CNRS, and Lille 1 University as well as the Centrale Initiatives Foundation, are thanked for their financial contributions to the acquisition and implementation of the equipment of the REALCAT platform.

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OP-I-1

Heterogeneous Base Metal Catalyst for Hydrosilylation of Ketones

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Heterogeneous base metals catalysts are becoming increasingly popular as an alternative for homogeneous precious metal catalysts due to the economical and environmental benefits. Noble metals often possess enhanced activity and selectivity over base metals but the scarce abundance of precious metals make them undesired for industrial application. However, clever design of heterogeneous base metal catalysts may give the desired catalytic properties. This can be achieved in various ways; by mimicking homogeneous catalysts in "*single site catalysis*"[1,2] or by the formation bimetallic alloys with their "*synergetic effects*"[3,4].

Common for heterogeneous catalysts is the use of high surface area support materials like zeolites, carbon, or metaloxides to stabilize the active metal nanoparticles from sintering. These materials often show excellent thermal and chemical stability, however, the chemical stability also makes them difficult to modify and functionalize. Recently, metal-organic frameworks (MOFs) have attracted much attention in the field of catalysis due to their porous structure, high surface area, and high metal content. MOFs also possess chemical freedom for easy functionalization and modification, which can be utilized in designing materials with targeted properties[5]. However, MOFs lack the chemical and thermal stability seen for support materials like zeolites, carbon and, metaloxides. Nevertheless, if MOFs are carbonized, which facilitate the formation of metal nanoparticles supported on a carbon matrix, a material with high thermal and chemical stability will be obtained.

Here we present our work on replacing the use of noble metal homogeneous catalysis for heterogeneous base metal catalysis by designing and synthesizing new materials. These materials are subsequently tested in reactions traditionally catalyzed by homogeneous precious metal catalysts. A novel CoNi alloy material has been synthesized by utilizing a MOF (ZIF-67), as a consumable template. Figure 1 shows the ZIF-67 crystals to the left by a SEM image whereas the TEM picture to the right shows the CoNi alloy nanoparticles supported on porous N-doped carbon[6]. The CoNi catalyst was active in the hydrosilylation of ketones under neutral conditions. The hydrosilylation reaction for the synthesized catalyst was investigated by a time study, a leaching test, a recycle experiment, and a scope of different silanes and ketones with moderate to excellent results. A general example of a hydrosilylation of a ketone is shown in Figure 2

OP-I-1

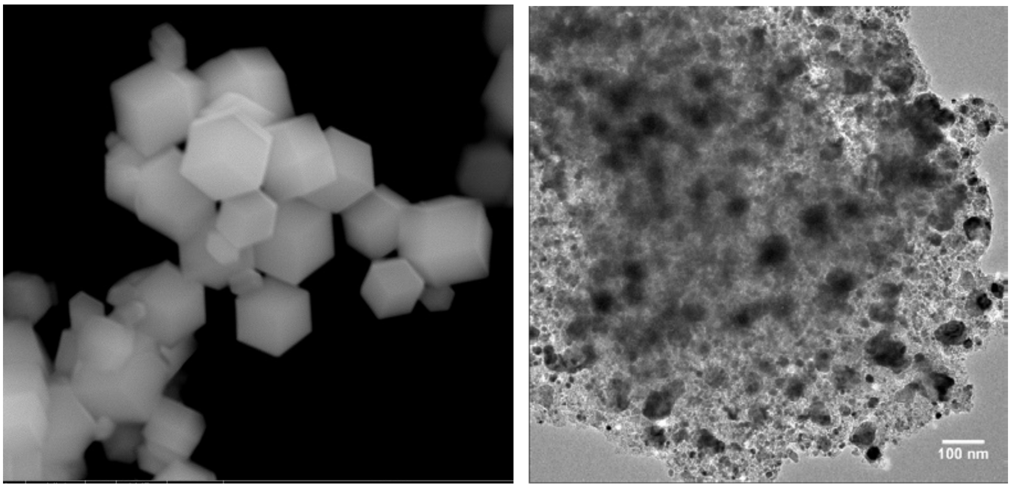

Fig. 1.: (Left) SEM image of ZIF-67 crystals and (right) TEM image of carbonized ZIF-67 crystals impregnated with $Ni(NO_3)_2$

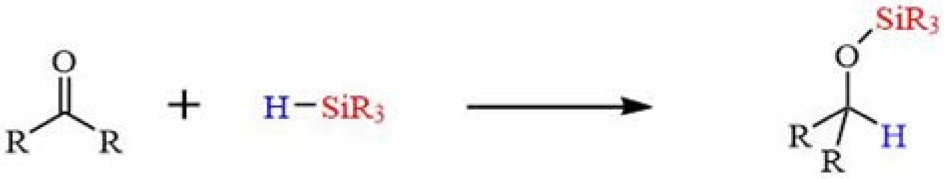

Fig. 2.: General example of a hydrosilylation of a ketone

Acknowledgments

The authors gratefully acknowledge the support of the Danish Council for Independent Research, Grant Nos. 6111-00327 and the support from Villum Fonden research grant (13158)

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OP-I-2

Development of Novel Catalysts Synthesized by Hydrothermal Method

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Last years, the development and application of nanosized catalysts have attracted an increasing attention. Supported metal nanoparticles have unique physics-chemical properties connected with a specific morphology, metal dispersity, and electronic structure of the active sites. The decrease in the size of the metal particles leads to the increase in the specific surface area, the increase in catalytic activity, as well as to the significant decrease in the concentration of the active phase compared with the industrial catalyst systems [1].

There are several methods for the synthesis of catalysts, including impregnation, precipitation, coprecipitation, ultrasonic synthesis, sol-gel method and microemulsion method using stabilizing agents [2]. The main problem with these methods is the control over the particle size and distribution of the active phase on the support. For example, the traditional methods such as impregnation and precipitation are characterized by a high degree of particles aggregation and "clogging" the pores of the support due to the high surface tension of the used solvents [3]. The sol-gel method does not find a wide application in organic and polymer substrates as precursors of the active phase. Surfactants used in microemulsion method can lead to the undesired agglomeration of the particles, especially at high temperatures [4]. Therefore, the search for new methods for the synthesis of catalytically active systems is a promising direction of modern catalysis.

Hydrothermal synthesis is a promising alternative for the deposition of metal nanoparticles on the surface of the porous supports. This method allows forming nanoparticles of metals and their compounds in the pores of the support. Superheated water near the critical point (T_c = 374 °C, P_c = 22.1 MPa) is characterized by a low dielectric constant and a low pH, a high dissociation constant, which leads to the increase in the concentration of H_3O^+ and OH^- ions. The latter interacts with metal salts, precipitating the metal in the pores of the support in the form of hydroxides with the following dehydrogenation [5].

Dehydrated alumina (Reachim, Russia) and silica (Reachim, Russia) was used as the catalyst support. Nitrates of cobalt and iron (Reachim, Russia) were used as metal precursors. The catalyst synthesis was performed in PARR-4307 high-pressure stainless steel reactor (Parr Instrument, USA). The synthesis conditions were established as the following: temperature 200 °C, total pressure 6.0 MPa. The process was carried out in water medium at the nitrogen atmosphere for 15 minutes. After the end of the synthesis, the resulted materials were filtered and washed by water till the absence of Cl^- and NO_3^- ions. The samples were further dried in the air, calcined at 450 °C for 10 hours and reduced in hydrogen flow at 300 °C. The catalyst structure was studied by the low-temperature nitrogen physisorption, X-ray photoelectron spectroscopy, ammonium and hydrogen chemisorption and IR-spectroscopy of the diffusion reflection of CO molecules. The catalytic activity of the synthesized materials was studied in Fischer-Tropsch synthesis.

The study of catalyst structure and composition showed that the use of silica as a catalyst support allows the formation of Co- and Fe-containing particles consisted of metals and their oxides (Table 1). When using alumina as a support, the Co and Fe aluminates formation was observed. Moreover, the silica-based catalysts have a higher specific surface area in comparison with those based on alumina.

Table 1 Catalysts characterization

Catalyst	Specific surface area, m^2/g	Metal surface concentration, at. %	Metal compound
Co/SiO_2	131	11.8	Co, Co_3O_4
Co/Al_2O_3	97	20.4	Co, CoO, $Co[Al_2O_4]$
Fe/SiO_2	117	9.5	Fe, FeO
Fe/Al_2O_3	93	15.7	FeO, $Fe(AlO_2)_2$

Acknowledgement. The authors thank the Russian Foundation for Basic Researches (grant 17-08-00609), the Russian Science Foundation (grant 17-79-10089).

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OP-I-3

Effect of the Synthesis Medium on Morphology and Texture of SAPO-11 Crystals

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SAPO-11 is a silicoaluminophosphate molecular sieve, the important class of zeolite-like materials. It has been used in a selective skeletal isomerization process of paraffins and olefins. The study of the regularities of the formation of zeolite and zeolite-like crystals with certain size, morphology and texture makes it easy to control these parameters to obtain materials with predetermined properties for potential application in the field of catalysis and adsorption. A lot of synthesis of SAPO with new morphologies based on the using of the hard templating method [1], addition of expensive quaternary ammonium surfactants [2] or organosilane surfactants [3] and synthesis in excess of organic template [4]. We have been used more affordable strategy and studied the influence of different medium of synthesis on morphology and texture of zeolite-like material – silicoaluminophosphate SAPO-11.

Series of experiments were carried out in the following media: water, mix of water and ethanol, ethanol. Precursor suspensions were undergone ultrasonic (US) pre-treatment before hydrothermal synthesis (HTS), and HTS was performed in a two-stage crystallization which assumes a separation of nucleation and crystal growth stages. The nucleation proceeded within 3 hours (in the presence of ethanol 5 h) at 200°C. After this stage the rate of crystal growth was reduced by lowering the temperature to 120°C. Samples synthesized in water, mixture of water and ethanol, ethanol media were labelled as W-SAPO-n, M-SAPO-n and Et-SAPO-n, respectively, where n is time of the crystal growth in hours.

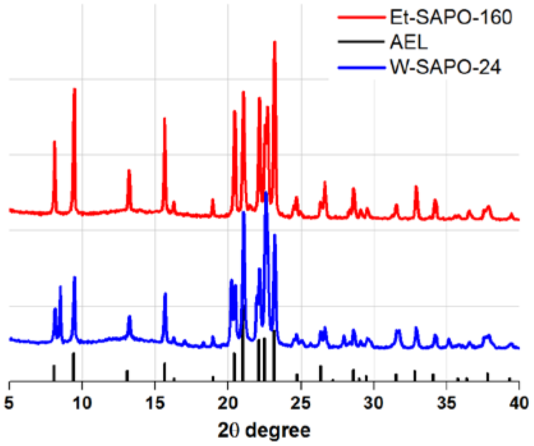

Figure 1 XRD patterns of the as-synthesized samples, which were obtained in water (blue line) and ethanol (red line) medium

According to the XRD patterns crystals of Et-SAPO-160 and W-SAPO-24 samples have the AEL topology (Figure 1). The morphology of the obtained particles is presented in Figure 2. It can be seen that ethanol significantly influences on the SAPO-11 morphology: sample, synthesized in aqueous medium has a pseudo-spherical morphology (Figure 2a), M-SAPO-144 sample represents the combination of different morphologies (Figure 2b), and, surprisingly, crystals from ethanol medium have a screw-like morphology (Figure 2c).

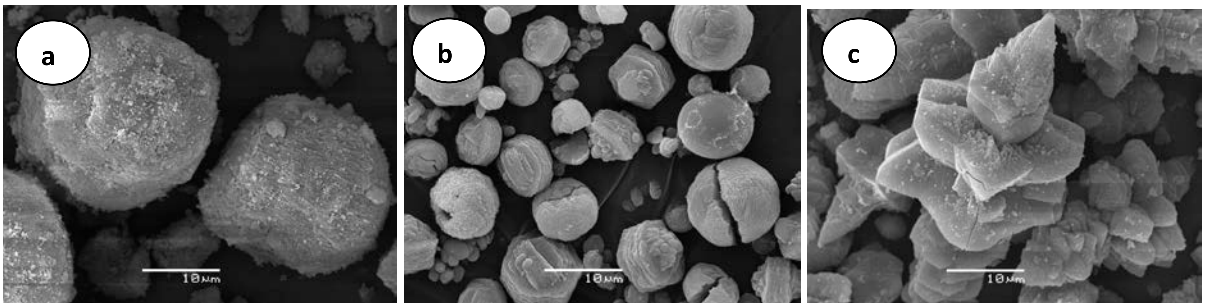

Figure 2 SEM images of a samples, synthesized in different media:
a) water (without US pre-treatment), b) mix of solvents, c) ethanol

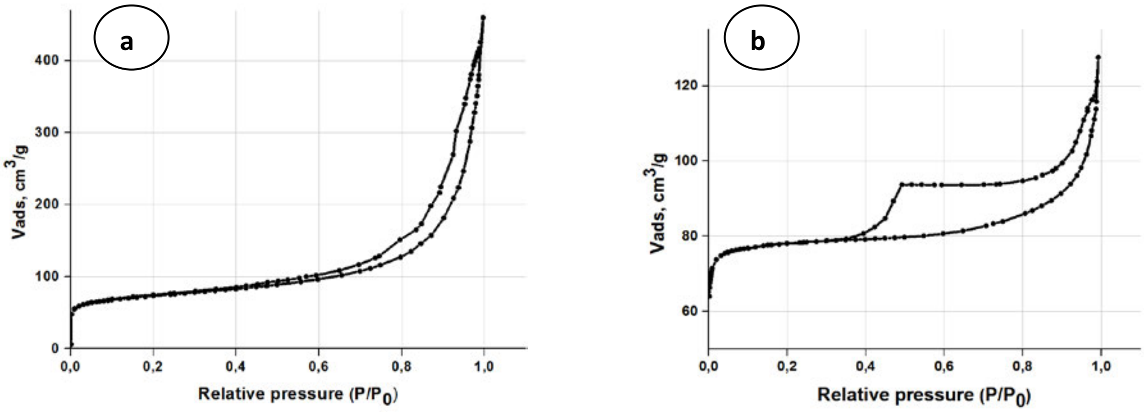

Figure 3 N_2 adsorption-desorption isotherms of the SAPO-11 crystals, synthesized by two-stage method a)during 24 hours in aqueous medium without US pre-treatment, and b) Et-SAPO-160

Screw-like crystals of SAPO-11 have a completely different texture compared with crystals, synthesized by the typical procedure (Figure 3). Hysteresis loops of N_2 adsorption-desorption isotherms indicate the presence of aggregates of microporous crystals or micro-mesoporous crystals in conventional material (Figure 3a) and open pores and partially blocked ink-bottle pores in screw-like crystals (Figure 3b).

Acknowledgement. This work was conducted within the framework of State contract with Ministry of Education and Science of the Russian Federation No.14.604.21.0159, the presentation is supported by PJSC Gazprom Neft project.

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OP-I-4

Peptization Parameters as an Instrument for Controlling Properties of Fischer–Tropsch Catalysts

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The analysis of pore structure formation revealed the important role of boehmite peptization stage during preparation of impregnated catalyst. Boehmite peptization proceeds in the presence of mineral or organic acids and results in chemical destruction of large aggregates of initial particles and hence in the increase of plasticity of precursor paste and of mechanical strength of the resulting material [1]. It is known that the intensity of boehmite secondary structure disaggregation depends on nature, amount and strength of a peptizing agent [1, 2]. Acid treatment conditions exert heavy influence over pore structure of resulting support. Boehmite peptization in the presence of organic acids have a number of advantages as compared to mineral acids. For example, organic acids are more environmentally friendly, since they can be easily get rid off during thermal treatment releasing harmless products [3]. Decomposition of inorganic acids leads to release of nitrogen, chlorine or sulfur compounds, which require complex purification systems. This is especially important for scaling up the production of catalysts. Moreover, the field of peptization by organic acids is less investigated.

Fischer–Tropsch synthesis (FTS) is a heterogeneous catalytic process of formation of liquid hydrocarbons and waxes mixture from CO and H_2. FTS catalysts consist of active metal (Co, Fe) and support (Al_2O_3, SiO_2, TiO_2, zeolites). The use of zeolite as a support in such catalyst generates additional catalytic activity in secondary transformations of hydrocarbons formed on cobalt active sites. Such transformations, which take place on the zeolite acid sites, can be cracking, isomerization, alkylation or redistribution of hydrogen [4].

The main FTS reactions are strongly exothermic, - therefore, it is necessary to ensure effective heat removal, since overheating in the catalyst bed can lead to enlargement of cobalt crystallites and decrease of catalyst selectivity. The introduction of metallic aluminum as a heat-conductive additive allows improving the catalyst thermal conductivity and catalytic properties.

The purpose of this work is to investigate the influence of the peptizing agent on the structure and properties of composite zeolite-containing cobalt FTS catalysts. Aqueous solutions of nitric, citric and oxalic acids were used as peptizing agents (Table 1).

Table 1. Peptizing agents

Sample	Peptizing agent
CatNitr	8 % solution of nitric acid
CatOxal	12 % solution of oxalic acid
CatCitr	7 % solution of citric acid

The preparation of catalysts begins with preparation of the support. It consists of the following stages: preparation of peptizing agent, mixing binder components (zeolite:boehmite=3:2), mixing the peptizing agent solution and binder, pretreatment of thermal conductive additive (binder:aluminium=1:1) and, finally, its introduction into peptized binder. After granulation by extrusion of resulting paste it was dried, calcined and cut to 2.5 × 2-3 mm size. 20 wt % cobalt is then introduced by impregnation of a composite support with $Co(NO_3)_2{\cdot}6H_2O$ solution with intermediate calcination.

Table 2 shows some properties of the prepared catalysts and their main FTS characteristics. The CatOxal catalyst is characterized by the largest volume of macropores; however, CO conversion and productivity were the lowest. The CatNitr catalyst is characterized by the lowest pore volume, however, its crush strength and productivity were the best observed. The use of nitric acid was found undesirable due to high oxidizing ability, which may lead to the loss of aluminum additive or to equipment corrosion.

Table 2. Properties of prepared catalysts and main characteristics of FTS

Sample	V macro pore , cm^3/g	S (BET), m^2/g	Crush strength, kg/pellet	K_{CO},%	S_{C5+},%	S_{CH4},%	P, $kgC_{5+}/(m^3{\cdot}h)$
CatNitr	0.322	147.9	14.7	72	53	26	405
CatOxal	0.468	143	3.8	49	50	26	254
CatCitr	0.419	143.5	2.2	55	49	30	286

Therefore, to optimize the concentration of the aqueous solution of the peptizing agent, a catalyst containing citric acid was chosen, since it was characterized by a higher CO conversion and productivity compared with CatOxal. The increase of citric acid concentration in the range from 4 to 9% lead to the decrease in macropores volume from 0.49 to 0.41 cm^3/g. Also, a decrease in the specific surface area from 144 to 128 m^2/g was observed. Moreover, the increase in the peptizing agent concentration led to increase in CO conversion from 52 to 63%, productivity rose up to 330 $kgC_{5+}/(m^3{\cdot}h)$ and crush strength increased in 2.8 times.

The conclusion is that citric acid is the best peptizing agent for preparation of Co catalyst for FTS. A catalyst prepared by peptization with 9% citric acid is suitable for scaling up to industry. INFRA Technology developed an industrial process for catalyst production based on the reported results.

Acknowledgement. This work was supported by funding from the Ministry of Education and Science of the Russian Federation (Project No. 3553).

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OP-I-5

Catalysts based on the Mg, Ni and Li-Containing Layered Double Hydroxides for Furfural Hydrogenation

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The development of economically efficient and environmental friendly technologies to transform lignocellulosic biomass into fuels and chemicals generates interest. Biomass derived furfural is considered as a potential platform for biofuels and chemicals, such as furan, furfuryl alcohol, tetrahydrofurfuryl alcohol, 2-methyl furan, 2-methyl tetrahydrofuran, and tetrahydrofuran. All these products are industrially important [1]. The development of new catalysts with a high activity in hydrogenation and selectivity of valuable products has a great interest. Catalysts based on layered double hydroxides (LDH) are very perspective due to their moderate basicity and the possibility of its deliberate control by varying the cationic and anionic composition [2].

The aim of this work is to synthesize of Mg(Ni,Li)Al-LDH by different methods, to investigate their structural and textural properties and to establish the relationship between nature of hydrogenating metal (Pd, Ni), support basisity (MgAl- and LiAl) and catalytic properties of hydrogenation catalysts, based on corresponding LDH.

Mg(Ni,Li)Al-LDHs were prepared by two different methods: traditional coprecipitation method and mechanochemical activation with subsequent aging in water. Catalysts with nickel as hydrogenating metal were prepared by Ni(Mg)Al-LDH calcination at 550 °C (mixed oxide, Ni(Mg)AlO$_x$) and following reduction at various temperatures (550 and 600 °C). Catalysts with palladium as hydrogenating metal were made by interaction of $[PdCl_4]^{2-}$ complexes with Mg(Li)Al-LDH or Mg(Li)Al-mixed oxides. The content of metals in the solid samples (after their dissolution) was determined by atomic emission spectrometry with inductively coupled plasma (ICP-AES) on a Varian 710-ES instrument. The structural properties of the synthesized LDH were examined using X-ray diffraction analysis (XRD), D8 Advance (Bruker). Textural properties of mixed oxides (LDH calcined at 550 °C) were examined by the low-temperature nitrogen adsorption, ASAP-2020 (Micromeritics). Liquid-phase hydrogenation of furfural (99%, Sigma–Aldrich) in the presence of synthesized catalysts was examined using a 180 cm^3 steel autoclave. The reaction conditions were T = 90 ˚C, P = 2 MPa, furfural concentration 5.5. wt.%, solvent – water. The products of furfural hydrogenation were identified by ^{1}H NMR, ^{13}C NMR (Bruker Avance-400) and GC–MS (Agilent 5973N/6890N).

MgAl-LDHs with Mg/Al = 2, 3 and 4, NiAl-LDHs with Ni/Al = 2, 3 and 4, MgNiAl-LDHs with M^{2+}/Al = 3 and Ni/(Ni+Mg)=0.3, 0.5, LiAl-LDH with Li/Al = 0.5 were synthesized. According to XRD data, all synthesized samples have the hydrotalcite structure with a typical set of reflections on the diffraction pattern. Mixed oxides prepared by LDH calcination at 550 °C were characterized by significant specific surface area (150 – 200 m^2/g). Li-containing mixed oxide are characterized by smaller pore diameter and total pore volume compared with MgAl- and NiAl analogs. Furthermore, bimodal pore size distribution with maximum at 3 and 30 nm was observed for $MgAlO_x$, whereas unimodal pore size distribution with maximum at near 9 and 5 nm was observed for $NiAlO_x$ and $LiAlO_x$, respectively. Furfural hydrogenations over $Mg(Ni,Li)AlO_x$ catalysts were characterized by high furfural conversion and furfuryl alcohol and tetrahydrofurfuryl alcohol formation only (Table 1). Herewith, $NiMgAlO_x$ catalysts were showed greatest furfural conversion up to 99%.

Table 1. Furfural conversion, selectivities on furfuryl alcohol and tetrahydrofurfuryl alcohol for $Ni(Mg)AlO_x$ catalysts.

Sample	Furfural conversion, %	Selectivity, %	
		Furfuryl alcohol	Tetrahydrofurfuryl alcohol
$NiAlO_x$, Ni/Al=2*	39	84	13
$NiAlO_x$, Ni/Al=3*	43	84	11
$NiAlO_x$, Ni/Al=4**	93	70	25
$NiAlO_x$, Ni/Al=3**	75	71	21
$NiAlO_x$, Ni/Al=4**	98	52	27
$NiMgAlO_x$, Ni/(Ni+Mg)=0.3**	99	65	31
$NiMgAlO_x$, Ni/(Ni+Mg)=0.5**	90	54	25

* - samples, reduced at 550 ˚C

** - samples, reduced at 600 ˚C

Furfural hydrogenation with 1.5%Pd/$MgAlO_x$ catalysts were characterized by formation of three main products: tetrahydrofuran, furfuryl alcohol and tetrahydrofurfuryl alcohol. Furfural conversion and selectivity of formation of listed products were determined not only by Mg/Al ratio in support but also by mode of palladium complexes anchoring.

Acknowledgement. We thank Suikova O., Vysotskii S. for their help with catalytic experiments. The work was carried out with the financial support of the FASO Russia, projects No. AAAA-A17-117021450095-1, AAAA-A17-117021450099-9.
The work was performed using facilities of the Omsk Regional Shared Equipment Center SB RAS.

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OP-I-6

N-Methylation of Amines over the Catalysts Based on Cu-Layered Double Hydroxides

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Introduction

N-alkylation of primary amines to secondary and tertiary amines is the important reaction for the synthesis of N-alkylamines, which can be used for production of pharmaceuticals, agrochemicals, and fine chemicals [1]. The usual synthetic method for the synthesis of amines is amination of aryl/alkyl halides. However, this method has some drawbacks, such as the need for activation of aryl/alkyl halides, the toxicities of the alkylating agent. In recent years the new process for the synthesis of the secondary amines based on N-alkylation of amines by alcohols is developed [2]. Metal catalysts can enable effective N-alkylation.

Layered double hydroxides (LDHs) can be used as the catalysts in N-alkylation of primary amines. The LDHs can be represented by general formula: $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot mH_2O$. In this formula M^{2+} (e.g. Mg^{2+}, Ni^{2+},…) and M^{3+} (e.g. Al^{3+}, Fe^{3+}, Cr^{3+}…) are divalent and trivalent cations, which cationic radius is not too different from that of Mg^{2+}. The pure LDH phases can be obtained when $0.2 < x < 0.33$, where x is a ratio of $M^{3+}/(M^{2+}+M^{3+})$, resulting in the M^{2+}/M^{3+} ratios of 2 – 4 being reasonably stable. The conventional synthesis method of LDHs is co-precipitation of metal nitrates with a precipitating agent such as a mixture of NaOH and Na_2CO_3 [3].

The aim of the work is investigation of Cu-LDHs in N-methylation of primary amines by methanol. The influence of the synthesis parameters of LDHs and reaction conditions on catalytic activity was investigated.

Experimental

CuAl-layered double hydroxides with the molar Cu:Al ratio of 2 – 4 were synthesized by co-precipitation method at pH 9.0 ± 0.2 and temperature of 70°C. The appropriate amounts of metal nitrates were precipitated by mixture of NaOH and Na_2CO_3 with different concentrations. The aging of the samples was carried out at 70°C for 4 hours. The samples was washed with distilled water, dried and calcined at 450°C for 4 hours.

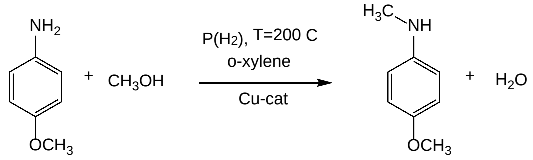
N-alkylation of amine by methanol was conducted in autoclave. The reaction mixture consisted of amine (0.1 mole/l) and methanol (0.1 – 0.9 mole/l) in o-xylene (10 ml) and n-decane as internal standard. Reaction was carried out at 180 - 200°C and H_2 (or N_2) pressure of 2 – 6 bar. Reaction products were analyzed by GC-MS.

OP-I-6

Results

According to X-ray diffraction, a well-crystalline phase which resembles the hydrotalcite-like compounds (ICDD PDF-2 #00-046-0099) was observed in all samples dried at 110°C. Increase the calcinations temperature up to 450°C results in decomposition of hydrotalcite structure and formation of two phases, CuO or $CuAl_2O_4$, depending on the synthesis parameters of layered double hydroxide. The data obtained is in well agreement with TG-DTA analysis which shows that the main weight loss occurs up to temperatures of 400 – 450°C. There are three endothermic peaks at 60 – 80°C, 180 – 190°C and 240 – 300°C which correspond to removal of physically adsorbed water, interlayer water in the hydrotalcite structure, dehydroxylation and decarbonation, respectively.

Several catalytic tests were performed using CuAl-LDH with the molar Cu:Al ratio of 2 to find the optimal conditions for N-methylation of primary amine.



Prior to reaction the catalyst was reduced in H_2 flow at 300°C. The reaction does not occur in nitrogen atmosphere regardless of temperature which was varied in the range of 160 – 200°C. Changing the reaction atmosphere to hydrogen promotes formation of the desired product. Increase temperature from 180 to 200°C results in increase of amine conversion from 6% to 16%. It is worth to note that catalyst is reduced during reaction. The conversion is the same for the pre-reduced catalyst (32%) and for the catalyst which is reduced during reaction (31%). The selectivity to secondary amine reaches 99.5%. Therefore it is not necessary to reduce catalyst before reaction. Besides, the excess of methanol in reaction media can lead to further increase of amine conversion to 99% with the selectivity to secondary amine of 97%. The optimum pressure of H_2 for the N-alkylation of amine by methanol is 4 bar. The lower pressure is not enough for the reduction of the catalyst, and the higher pressure results in shifting the equilibrium to methanol formation. The optimal conditions for the reaction are 200°C, 4 bar in H_2 atmosphere. The CuAl-LDH with the higher molar Cu:Al ratios and CuAl-LDH substituted with Zn were investigated in the reaction. However, tCuAl-LDH with the molar Cu:Al ratio of 2 showed the higher catalytic activity.

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OP-I-7

Novel CuAl and CuFeAl Ceramometal Catalysts for WGS Reaction

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Water-gas shift (WGS) reaction is one of the primary industrial steps of hydrogen production. The WGS catalysts are usually comprised of Cu, Zn and Al oxide composites prepared by coprecipitation or impregnation. One of the main problems of the low temperature WGS reaction is a low activity of the conventional granulated CuZnAl catalyst per the unit volume of the catalyst bed due to a low loading density and a poor access of reagents into the bulk of granules due to internal diffusion limitations. A possible way to increase such a volume activity is the use of ceramometal catalysts with enhanced real and loading density possessing also a developed system of transport macropores and mesopores. Such catalysts could also prevent emergence of temperature gradients within the catalytic layer [1] due to a high thermal conductivity provided by the presence of metal particles in their bulk.

Preparation procedure includes the mechanical alloying (MA) of powdered precursors from metal powders (Cu,Fe,Al). At this stage different types of intermetallics are formed with nanocomposite structure depending upon the MA conditions and metal powder blend content. The second stage is hydrothermal treatment followed by calcination. This stage leads to partial oxidation of metal particles and their cementation into a porous monolith. XRD, NMR, TEM and SEM with mapping, Differential dissolution and XPS were used to examine the structure and microstructure of powdered precursors and porous ceramometals CuAlO/CuAl and CuFeAlO/CuFeAl. Catalytic properties in WGS were characterized for fine and coarse fractions of the composite catalyst. The textural features were evaluated as well.

It was found that the microstructure of initial cermets has an egg-shell character (Fig. a) with metallic phases in cores randomly distributed in the oxide matrix forming oxide egg-shell. For CuAlO/CuAl system the amount of Al_4Cu_9 intermetallide was found to pass through the maximum at MA time 9 min. For CuFeAlO/CuFeAl system this amount gradually diminishes with MA time. Non-monotonous variation of the specific surface area (SSA), pore structure and crushing strength with the time of preliminary MA was revealed. Correlation of specific activity with Al_4Cu_9 content for similar types of ceramometals was found. Catalytic activity of ceramometals in WGS reaction estimated for their fine fractions and expressed as the efficient first-order rate constant is lower than that for CuZnAl oxide catalyst due to a lower (by an order of magnitude) specific surface area of ceramometals. Specific activity of ceramometals expressed as specific rate constant related to the unit surface area of metallic copper exceeds that for CuZnAl oxide catalyst. The presence of ultramacropores with the size up to tens of microns (Fig. a,b) as well as enhanced density was shown to be typical for ceramometals, while in oxide catalysts these macropores are absent (Fig. c). As a result, the activity of granulated ceramometal catalysts in WGS reaction is higher than that of granulated CuZnAl oxide [2].

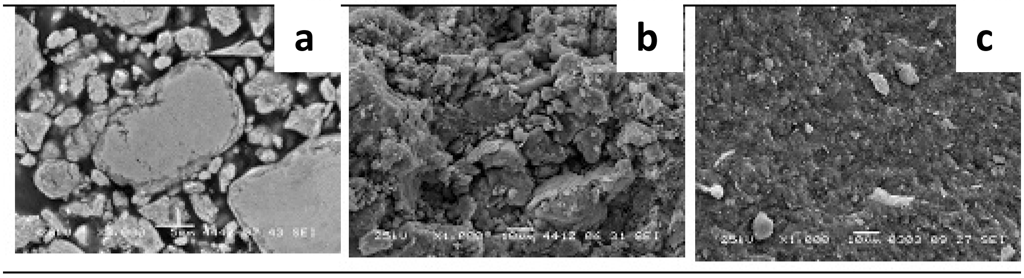

Fig. SEM images of polished CuFeAl cermet (a), surface of CuAl sermet (b) and surface of CuZnAl-oxide catalyst (c).

Acknowledgement. This work was conducted within the framework of budget project No. 0303-2016-0013 for Boreskov Institute of Catalysis SB RAS.

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OP-I-8

Investigation of Ag- and Co_3O_4-Impregnated Strontium Titanium Ferrite in Methanol Steam Reforming

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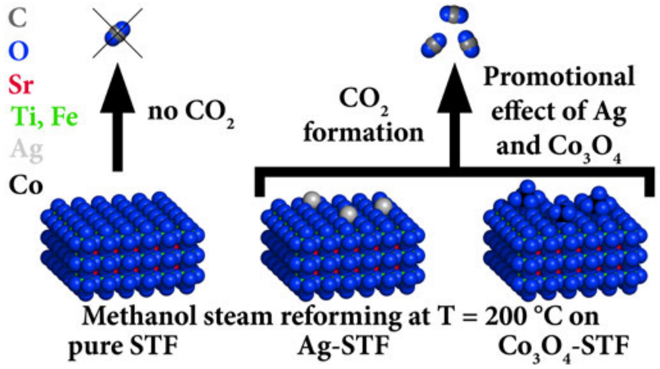

Facing the advance of climate change humanity needs to gradually withdraw from fossil fuels for energy generation and turn to renewable sources. An issue that has to be resolved regarding the use of alternative energy sources like photovoltaics and wind power is the problem of energy storage and distribution.[1] A possibility of chemical storage would be the conversion of CO_2 into methanol, which is liquid at ambient temperature and pressure and exhibits a high hydrogen-to-carbon ratio. To release the stored energy, methanol can either be used itself in a direct methanol fuel cell (DMFC) or converted to H_2 utilizing methanol steam reforming (MSR) prior to introduction to a proton exchange membrane fuel cell (PEMFC), generating electrical energy.[1,2]

Since the activation of water, a crucial factor for a CO_2 selective MSR catalyst, has been reported to be possible on strontium titanium ferrite (STF),[3] this perovskite seems to be a suitable choice as the support of such a catalyst. Additionally, cobalt oxides are often employed as catalysts in MSR, displaying a strong dependence of the activity on the ratio of the different oxidation states of the metal cation (Co^{2+}/Co^{3+}).[4] As both materials exhibit desirable properties, we investigated whether STF with the ability to supply lattice oxygen by forming vacancies as a support material could influence the balance of the oxidation states of cobalt and, thus, affect the performance in MSR. Silver, on the other hand has become important in many oxidation reactions,[5] being able to interact with oxygen by formation of molecularly adsorbed species or subsurface oxygen.[6] Thus, a synergistic effect of a support material like STF, due to its capability of supplying oxygen to the supported phase, can be envisioned.

Therefore, we prepared two systems consisting of Co_3O_4 or Ag supported on STF ($SrTi_{0.7}Fe_{0.3}O_{3-\delta}$) and chose MSR as the model reaction for their catalytic characterization.[7] Both supported catalysts strongly promote the evolution of CO_2 at around 170 °C, whereas the carbon dioxide formation on pure STF starts at about 220 °C. The catalytic profile of Co_3O_4-STF is characterized by a temperature-dependent transition between methanol steam reforming, methanol dehydrogenation and the water-gas shift equilibrium.[7] Considering the Ag-STF system, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) investigations suggest that the metallic phase is covered by a thin Ag_2O layer after peroxidation in oxygen at 600 C, which vanishes upon prereduction in hydrogen at 400 °C. If the reaction is started from the preoxidized state, Ag lowers the activation barrier for the total oxidation of methanol to carbon dioxide.[7] This effect can be explained by the supply of lattice oxygen from STF toward Ag via the perovskite-metal phase boundary. Furthermore, this Ag-STF system might be utilized as an anode material in a solid oxide fuel cell, where a continuous electrochemical replenishment of the lattice oxygen is provided and, thus, long-term total oxidation of methanol to CO_2 should be possible without deactivation by coking.[7]

Acknowledgment: The work was financially supported by the Austrian Science Foundation (FWF) via SFB projects F4501-N16 and F4503-N16 within the SFB “Functional Oxide Surfaces and Interfaces” (FOXSI) and performed within the framework of the platform Materials- and Nanoscience and the special Ph.D. program “Reactivity and Catalysis” at the University of Innsbruck.

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OP-I-9

Pretreatments of Carbon Nanotubes: Effects on Their Physicochemical Properties and Catalytic Performances in the Oxidative Steam Reforming of Methanol

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The work was dedicated to the investigation of the effects of oxidative and thermal treatments on the properties of CNT and CNT-supported catalysts. The carbon samples were treated using concentrated HNO_3 (to introduce oxygen functionalities), by heating in Ar atmosphere (to eliminate their presence) and via oxidation followed by heat treatments at 400 and 800°C (to adjust the amount of oxygen species). Their properties were investigated using FTIR, TGA, BET and TPD-NH_3 techniques. The copper (20wt%) catalysts supported on pristine and treated MWNCTs were prepared by incipient wetness impregnation technique using aqueous solution of copper nitrate (II) as a metal precursor. The reducibility of obtained catalysts was investigated by TPR-H_2 method and their catalytic performance was studied in the oxidative steam reforming of methanol. The activity tests were performed in the temperature range from 200 to 300°C under atmospheric pressure in a flow quartz tubular reactor. The ratio of the reactants in the test reaction was $CH_3OH:H_2O:O_2 = 1:1:0.4$

According to the obtained results, both oxidation and heat treatments were found to increase the specific surface area of CNTs. The highest surface value of 355 m^2g^{-1} was observed for oxidized-heated (400°C) sample. Acid treatment of CNTs resulted in intensive formation of oxygen-containing groups which was confirmed using TGA and TPD-NH_3. Their presence resulted in significant degradation of thermal stability and increased surface acidity of carbon nanomaterial. The recorded temperature-programmed reduction profiles showed two overlapped reduction peaks in the temperature range 100 – 420 °C which are associated with stepwise reduction of CuO via formation of Cu_2O intermediate to metallic Cu. The sample treated by oxidation-heating (800°C) was characterized by the lowest reduction temperature with its maxima at 216 °C.

The activity results (Fig.1) revealed that even the elimination of the insignificant amounts of oxygen containing groups on CNT surface as well as mild oxidation can significantly modify the catalytic properties of CNT-based catalysts. Generally, the copper catalysts supported on heated and oxidized-heated carbon nanotubes exhibited higher activity (above 78% at 250°C and about 100% at 300°C) than the other catalyst samples. The highest methanol conversion at 250°C was ~ 84% and was observed for 20%Cu/CNTs-oxid.-heat.(400°C). Interestingly, oxidation treatment of carbon nanotubes did not have a positive effect on the activity of supported catalyst. The 20%Cu/CNT-oxidized catalysts showed the lowest values of methanol conversion, 59 and 90% at 250 and 300°C respectively.

OP-I-9

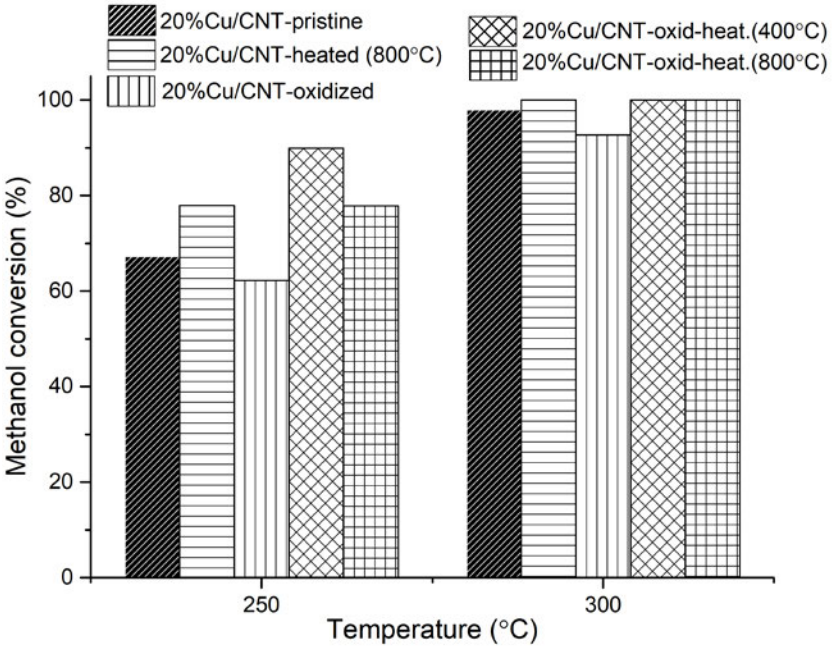

Figure 1. The catalytic activity of 20%Cu/MWCNTs catalysts in the oxidative steam reforming of methanol.

Acknowledgement: The partial financial support of this work by the FMN grant (Fundusz Młodych Naukowców, Grant No. W-3D/FMN/5G/2017) is gratefully acknowledged.

OP-I-10

Deactivation and Methods to Improve of the Active Phase Stability in VMoNbTe Oxide Catalysts for Ethane Oxidative Dehydrogenation

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VMoNbTe oxide catalysts show unsurpassed (compared to the other knows heterogeneous catalysts) activity and selectivity in the ethane oxidative dehydrogenation (ODE), selective propane oxidation to acrylic acid and propane ammoxidation to acrylonitrile processes. These processes require oxidative atmosphere, intermediate temperatures (450°C and below) and utilize cheap and widely available light alkanes (ethane and propane) to obtain valuable for chemical industry products. However, the perspective of the industrial implementation of these processes is limited due to the instability of the active phase – a so-called phaseM1. [1]. One of the most significant disadvantages of the MoVTeNbO catalysts is the Te loss causing structural instability of the M1 phase. The goal of the present work is to establish the structural transformations during the deactivation of the M1 phase and to increase its stability e by the introduction of Bi cations.

The catalytic testing showed that severe catalysts deactivation occurs after treatment in the "reducing" mixture at 460°C ($C_2H_6/O_2 = 3$). The unpromoted sample was the least stable to deactivation: the ethylene yield dropped almost twice - from 47 to 26%. XRD showed that deactivation was accompanied by the loss of the crystallinity degree from 74% to 46%. That observation correlated well with the increase in the specific surface after reaction. TEM showed appearance of cavities, pores, and a large amount of fine particles covering the M1 phase crystallites were observed after deactivation of the unmpomoted catalyst. XPS analysis showed that the significant decrease in the Te/Mo ratio on the surface of the deactivated catalysts without Bi.

Doping of VMoNbTe oxide catalyst by Bi (Bi/Mo<0.05) results in the activity increase in the ODE reaction as well as stability of the catalysts under severe reaction conditions [2]. The main reason for the enhancement of catalyst stability is hindering of the Te segregation along the 6-membered channels owing to the bismuth insertion, which leads to a decrease of Te losses from the M1 structure and its subsequent stabilization. Also, the defect concentration and dispersity of M1 crystallites increase. In combination with possible Bi participation in the active sites, this could be considered as a reason of increased activity and selectivity to ethylene.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 17-03-20073.

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OP-I-11

Trimetallic Naphtha Reforming Catalysts. Properties of the Metal Function and Influence of the Order of Addition of the Metal Precursors on Pt–Sn–Zr/γ-Al_2O_3–Cl

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The reforming catalysts are based on the Pt/γ-Al_2O_3 system. The metallic function is virtually always promoted by the introduction of metals, for example, Sn, Re, Ge, Ir and others. The main positive effects caused by the presence of a promoter include the weakening of platinum particles sintering in the process, a decrease in deactivation by coke, and an increase in selectivity for the reformate. Many patents involve catalysts with three elements in the metal function, e.g. Pt–Sn–In [1] and Pt–Ir–Sn [2].

The goal of our work was to elucidate the effect of the order of addition of the metal precursors on physicochemical and catalytic properties of trimetallic Pt–Sn–Zr/γ-Al_2O_3–Cl reforming catalysts.

The support used was a commercial high-purity spherical γ-alumina, γ-alumina with 0.2 wt.% Sn and γ-alumina with 0.5 wt.% Zr (Sasol Germany GmbH). Mono- and bimetallic systems were prepared as a comparison catalysts. Zirconium nitrate $ZrO(NO_3)_2*2H_2O$, tin (IV) chloride $SnCl_4*5H_2O$ were used as metal oxide precursors.

The catalysts were synthesized by introducing the calculated amounts of Pt and Cl precursors ($H_2PtCl_6*5H_2O$ and HCl) by impregnation in excess solution onto alumina promoted with metals in order to obtain 0.25 and 1.2 wt.% Pt and Cl, respectively. Supports and catalysts were characterized by TGA, XRD, the nitrogen adsorption-desorption method, NH_3-TPD, H_2-TPR. Catalysts were tested in a model reaction of n-heptane reforming.

The work was carried out with the financial support of the Federal Agency of Scientific Organizations of Russia in accordance with the Program of Fundamental Scientific Research of the State Academies of Sciences for 2013-2020 in the direction V.46, project № V.46.2.4 (AAAA-A17-117021450095-1).

Acknowledgement. Study of physic-chemical characteristics of the objects of research conducted with the use of the instrument base Omsk regional Centre of Collective Usage SB RAS.

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OP-I-12

Hydrothermal Synthesis of Platinum and Chrome Oxidation Catalysts on Metallic Support

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Bimetallic catalysts consisting platinum and non-ferrous metal are perspective as electrodes for fuel cells and catalysts for deep oxidation of hydrocarbons. Earlier [1], the decomposition reactions of binary complexes $[Ni(NH_3)_6][PtCl_4]$ and $[Co(NH_3)_5Cl][PtCl_4]$ in hydrothermal conditions were studied. The reaction products are black powders including metallic platinum particles on non-ferrous metal oxides. The catalysts obtained from binary complexes exhibit high catalytic activity in the hydrogen peroxide decomposition and propane combustion. Also [2] the catalysts including $Pt\text{-}Cr_xO_y$ phases on the chips of stainless steel were produced by autoclave thermolysis $[Pt(NH_3)_4]CrO_4$. Their properties in the propane combustion reaction are superior those of monometallic platinum catalysts. Chrome has the oxidation degree from +5 to +3 in oxides formed during the decomposition of the chromate ion. We guess only the oxide Cr_2O_3 should be formed from the binary complex $[Cr(NH_3)_5Cl][PtCl_4]$, as well as from binary complexes Pt-Ni and Pt-Co.

The aims of this work were research of tetrachloroplatinate (II) chloropentamminechromium (III) $[Cr(NH_3)_5Cl][PtCl_4]$ hydrothermal decomposition, the obtain of powdered and supported catalysts from it and study their properties.

The binary complex was synthesized by the ion exchange reaction from the corresponding simple complexes. Decomposition of the binary complex was carried out in an aqueous solution with a pH of 8-9 at 190°C. The reaction products and the obtained catalysts were examined by scanning electron microscopy and energy dispersive X-ray microanalysis, and by atomic force microscopy.

The catalytic properties of the obtained powdery samples were studied in the hydrogen peroxide decomposition reaction. The catalytic activity was determined from the rate of oxygen formation.

Also, Pt-Cr supported catalysts were formed in autoclave conditions. We used oxidized chips of stainless steel as the support.

The catalytic properties of the supported catalyst were studied in the propane combustion reaction. The activities of the catalysts from the complex $[Pt(NH_3)_4]CrO_4$ and the binary complex $[Cr(NH_3)_5Cl][PtCl_4]$ are compared.

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OP-II-1

Revealing the Active Sites of a Pd/Zr Intermetallic Precatalyst in Dry Reforming of Methane by ex- and in-situ Methods

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Intermetallic Pd-Zr precatalysts show strongly improved activities in dry reforming of methane (DRM) relative to pure Pd. In addition to or as a consequence of its high activity and relatively low onset temperature, the “carbon behaviour” is one of the most interesting aspects of this catalyst. On the one hand, carbon formation is a major aspect to create an active DRM catalyst but on the other hand, the carbon “blow-off” reaction has to be sufficiently quick to prevent deactivation by coking. The Pd/Zr catalyst shown here fulfills both and is therefore an interesting material to produce useful syngas out of two climate-relevant greenhouse gases. The present work gives mechanistic insights in a carbon tolerant Pd/Zr catalyst system for the DRM reaction. Catalytic investigations on chemical-vapor-deposition-prepared $Pd/Zr^0/ZrO_xH_y$ inverse model catalysts and Pd/Zr intermetallic compound systems in DRM are presented [1,2].

As crucial steps of this reaction, the CH_4-induced carbon nucleation and growth, which are only possible upon starting from the initially intermetallic Pd-Zr state, versus the carbon clean-off reaction by CO_2 are identified. Starting from a fully oxidised ZrO_2 state (e.g. by preceeding O_2 oxidation in UHV) or from clean Pd does not allow for graphene/graphite nucleation under reaction conditions, and the catalyst remains inactive.

For structural and chemical characterization, different methods are used, namely scanning tunnelling microscopy (STM), in situ and ex situ X-ray photoelectron spectroscopy (XPS), in situ X-ray diffraction (XRD) and transmission electron microscopy (TEM). For catalysis testing, a combined ultra-high-vacuum (UHV)/high pressure setup is used. The major aspect of this setup is the direct connection of an UHV chamber to a batch reactor with on-line GC-MS detection. The ambient-pressure batch reactor enables catalytic studies from room temperature up to 1300 K whereas the UHV chamber is used for model catalysts preparation and surface characterization via XPS and low-energy ion scattering (LEIS) [3].

Acknowledgement. The work was performed within the platform “Material- and Nanoscience” at the University of Innsbruck and the Institute of Applied Physics at the Vienna University of Technology. Financial support of the SFB project FOXSI F4503, F4505 and F4501, funded by the Austrian Science Fund and the doctoral program “Reactivity and Catalysis” funded by the University of Innsbruck is greatly acknowledged.

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OP-II-2

Model Bimetallic Pd-Me/HOPG (Me=Ag;Cu) Catalysts: Preparation and STM/XPS Study

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Bimetallic systems attract attention of many scientific groups due to their ability to significantly improve catalytic properties compared to monometallic catalysts [1-3]. Among these systems, the Pd–Au catalysts are the most frequently studied systems because they exhibit improved catalytic performance in a number of industrially important reactions, such as direct formation of hydrogen peroxide from H_2/O_2 [4], oxidative acetoxylation of ethylene [3], etc. Nevertheless the other bimetallic systems such as Pd-Ag or Pd-Cu are promising for the reactions of selective alcohols oxidation or olefins epoxidation [5-6] and selective hydrogenation of acetylene to ethylene [7]. Despite to a large number of publications devoted to study of bimetallic Pd-Ag (Pd-Cu) systems published in recent years, the reasons of synergistic effects in different catalytic reactions have not be rationalized.

One of the most evident proposals, which have been supported by many researchers, is the key role of surface composition of bimetallic particles. It is well known that not only the ratio of the introduced metals, but also temperature of calcination will affect the surface composition causing the difference between Ag(Cu)/Pd atomic ratios in the bulk and surface. It is also evident that surface composition can be varied under the influence of reaction mixture due to enrichment of the surface with one of the metals. Thus the detailed study of surface structure and composition of bimetallic Pd-Ag (Pd-Cu) catalysts is necessary to understand the nature of active sites and help to optimize the catalyst composition for the best activity, selectivity and stability.

Success in such a study is impossible without development of procedures for synthesis of bimetallic Pd-Ag (Pd-Cu) catalysts with controlled particle size and Ag(Cu)/Pd ratio. Furthermore, low loading of the active component (< 1-2wt. %) and complex composition of the noble metal on high surface area supports in “real” supported catalysts limits the application of surface sensitive techniques. Using of model catalysts, where metal particles deposited on the planar support, could help to solve those problems and get more reliable information concerning surface structure and chemical composition of active metals depending on different treatments [8-10].

In the present work we have studied the regularities of two different bimetallic Pd-Ag and Pd-Cu catalysts preparation using the combination of scanning tunneling microscopy (STM) and X-Ray photoelectron spectroscopy (XPS). The procedure described in our recent work concerning the preparation of Pd-Au/HOPG model catalysts [10] was used for Pd-Ag(Cu)/HOPG preparation. This procedure includes four stages: (1) - Surface defect formation on the HOPG surface via low energy Ar^+ etching; (2) – Pd deposition; (3) - Defects annealing (mainly interlayer defects) at 300°C in UHV and final stabilization of the monometallic system; (4) - deposition of Ag or Cu on Pd nanoparticles supported on HOPG matrix. The XPS and STM investigation shows that using this procedure a set of bimetallic Pd-Me/HOPG (Me=Ag or Cu) samples with various particle density, size distribution and Pd/Me atomic ratio were prepared.

Investigation of the Pd-Me/HOPG sample during heating from RT to 500°C in ultra high vacuum conditions was performed at RGL station (Berlin synchrotron radiation centre HZB, BESSY II). The key issue of the experiment was an application of XPS with variable energy of exciting radiation that allows us to get the information not only about chemical states of the elements, but also about their depth profiles in the nanoparticles. It has been shown that annealing the model catalysts at a temperature range of 350-450°C leads to formation of Pd-Ag(Cu) alloyed particles. Increasing of heating temperature above 450°C results in sintering of bimetallic nanoparticles. Contribution of different parameters controlling the properties of Pd-Ag(Pd-Cu) alloyed particles has been discussed.

Acknowledgement. This work was supported by the RFBR grant 17-03-01378.

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OP-II-3

In situ XRD and XPS Study of the Reduction Process of Mixed Mn-Zr and Mn-Co Oxide Catalysts of CO Oxidation

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Mn-containing oxides can effectively catalyze the gas-phase oxidation of hydrocarbons or chlorcarbons. On manganese oxides, oxidation reactions are known to proceed through the Mars van Krevelen mechanism, according to which in the first step lattice oxygen oxidizes the substrate which is accompanied by generation of an oxygen vacancy, and in the second step the reduced catalyst is reoxidized by gas-phase molecular oxygen. Under these considerations, the catalytic activity is significantly determined by the oxidation-reduction properties of the oxides. Cooperative utilize of Mn and another oxide leads to synergetic effect – increase in catalytic activity as compared with simple oxides. In double metal oxide catalysts, not only simple compounds are present in system, but the formation of mixed oxides (solid solutions) is possible. Mn cations can enter the lattice of ZrO_2 with the formation of solid solutions $Zr_{1-x}Mn_xO_2$, in which lattice oxygen possesses sufficiently high mobility and hence high reactivity. On the other hand, some authors suppose that the active species in oxidation reactions is mobile oxygen that is incorporated in disperse MnO_x rather than lattice oxygen of the solid solution. Moreover, in a reducing atmosphere, a segregation of manganese with the formation of dispersed MnOx is possible on the surface of the solid solution $Zr_{1-x}Mn_xO_2$. For Mn-Co catalyst, the formation of mixed oxide based on spinel structure is typical, appearance of this phase increase the activity in oxidation reactions.

The purpose of this work was to elucidate influence of redox properties of solid solutions (interaction between simple oxides) on the catalytic performance. A series of catalysts based on mixed Mn-Zr and Mn-Co oxides with different molar ratios of cations have been prepared by coprecipitation and characterized by X-ray diffraction and N_2 adsorption techniques. Reduction mechanism of Mn-containing catalysts with hydrogen was studied by a temperature-programmed reduction technique, in situ XRD, and near ambient pressure XPS. It was shown, that there are differences in redox properties of Mn cations in Mn-Co and Mn-Zr oxide matrix. Correlations between the redox properties and the catalytic activity in the CO oxidation reaction have been found.

Acknowledgement. The reported study was funded by RFBR according to the research project № 18-33-00542 and the framework of the budget project for Boreskov Institute of Catalysis.

OP-II-4

Na_2WO_4-Mn_xO_y/SiO_2 Mixed Oxide Catalyst: Insight into the Nature of the Reactive Oxygen

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The oxidative coupling of methane (OCM) is an alternative route for the natural gas transformation to the value added products, such as light olefins. Among various OCM catalysts the Na_2WO_4-Mn_xO_y/SiO_2 mixed oxide was repeatedly reported to be the most efficient and to give the highest C_2 yields. At the same time, despite the substantial research efforts, the nature of the active sites and the relationship between the catalytic activity and the exact structure of the components of the Na_2WO_4-Mn_xO_y/SiO_2 system remain unclear [1,2]. One of the features of the catalyst of interest is the presence of two elements able to change their oxidation state within the catalytic cycle. Earlier, by using the combination of temperature programmed desorption (TPD) and thermal gravimetric analysis (TGA) we revealed the existence of two forms of the reactive lattice oxygen [3]. The "strongly-bonded" oxygen can be reversibly removed at the reduction of the catalyst by methane and hydrogen at the temperatures above 600 °C, while the "weakly-bonded" oxygen releases at temperatures above 600 °C. Based on the results of sequential O_2/CH_4 pulse experiments it was demonstrated that both forms of oxygen were responsible for the methane activation, whereas the "weakly-bonded" had much greater impact. Therefore, the purpose of the present work is to get insight into the phase composition and the structure of the catalyst which include or exclude the "weakly-bond" oxygen form.

The as-prepared, thermally treated (the catalyst sample was gradually heated in a He flow up to 900 °C to remove the "weakly-bonded" oxygen) and re-oxidized Na_2WO_4-Mn_xO_y/SiO_2 catalysts were investigated by the X-ray diffraction (XRD) and the scanning electron microscopy (SEM) combined with the X-ray energy dispersive (EDX) spectrometry which shows the local elemental composition of the sample.

According to the XRD analysis, the main phase in all the samples was α-cristobolite SiO_2. Considering the supported components, the XRD data showed the presence of Na_2WO_4 and Mn_2O_3 phases in the as-prepared and re-oxidized catalysts, whereas only $MnWO_4$ phase was detected in the thermally treated sample. The results allowed us to assume the occurrence of the following reaction describing the reversible removal of the "weakly-bonded" oxygen:

$$2Na_2WO_4 + Mn_2O_3 \leftrightarrow 2MnWO_4 + 1/2\ O_2 + 2Na_2O,$$

whereas the real physicochemical interactions might be much more complicated.

The SEM micrographs of the studied catalysts are shown in Fig.1 and the obtained results do not oppose the XRD data. The backscattered electron detector was used to allow the components with different composition to be imaged as different (greyscale) contrast.

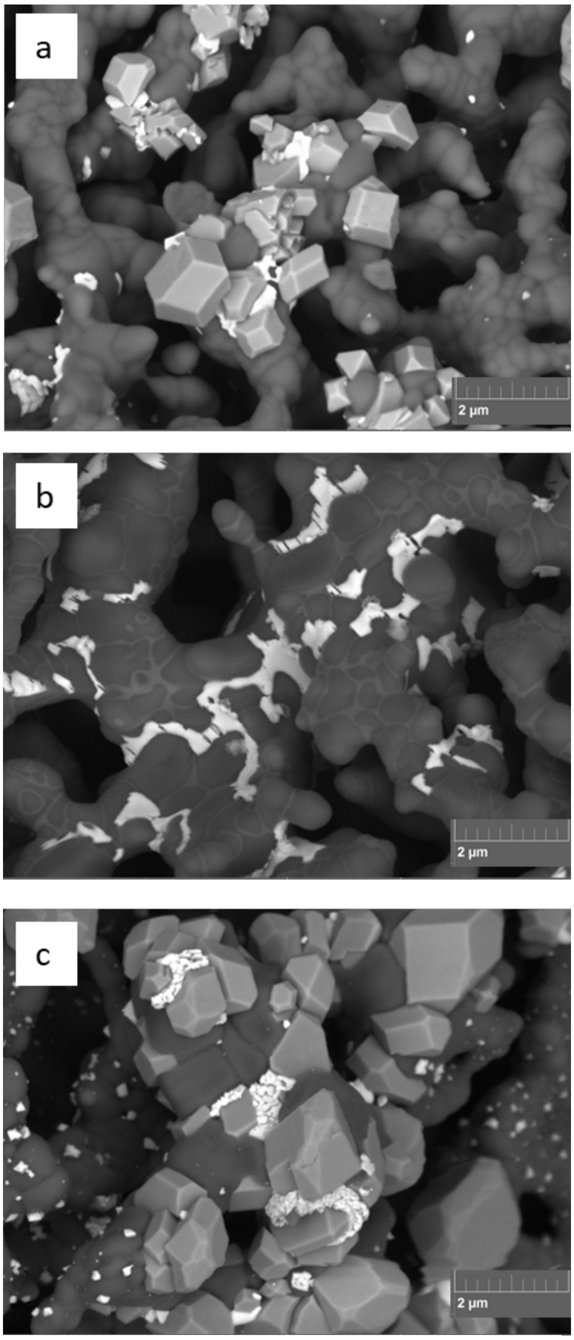

Fig.1. SEM images of the as-prepared (a), thermally treated (b) and re-oxidized (c) Na_2WO_4-Mn_xO_y/SiO_2 catalysts.

One can see that silica support is composed of conglomerated spherical particles. The large crystals with the sizes ranged from 0,2 to 2 μm, which are seen in Fig 1 (a, c), correspond to the Mn_xO_y oxide, as it was evidenced from the EDX analysis. The light contrast phase includes the heavy element, *i.e.* tungsten. It was also found that in the case of the initial and re-oxidized catalysts, this phase contains Na and W, while Mn and W are the metal components of the bright light phase in the thermally treated sample (Fig.1 b). These observations are in a good agreement with the XRD data.

The most interest evokes the matter located at the grain boundaries of silica particles. The EDX analysis of this thin layer (amorphous for XRD) revealed the presence of Mn, Na, O, and Si. Apparently, at the high temperature heating, both melting of Na_2WO_4 (m.p. 698 °C) and recrystallization take place. The latter process seems to involve the Mn_2O_3 phase, which was detected by XRD. At the same time, re-oxidation of the sample results in the similar visual picture with a slight difference in the special and particle-size distributions of the Na_2WO_4 phase.

To sum up, the obtained results reveal the chemical nature of the component interaction and the phase transformations occurring in the OCM redox circle.

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OP-II-5

In situ XAS and XRD Study of CuFeAl-Composite Catalysts of CO Oxidation

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Catalytic oxidation of gasification products of solid fuels is allows utilizing low-grade fuels such as lignite, peat, and firewood as well as various industrial wastes. At the same time catalytic combustion produces a significantly lower amount of harmful emissions then "traditional combustion" of fuels. CuFeAl-composite catalysts demonstrate high activity and stability in catalytic oxidation of gasification products of solid fuels. Moreover, the catalysts are inexpensive and ecologically clean. In this contribution we present our first results of in situ investigations of the catalyst state in reaction conditions. Since carbon monoxide is the main product of gasification of solid fuels we performed investigation CuO, Fe_2O_3, and CuFeAl-composite catalysts in CO and $CO+O_2$ mixture in a wide temperature range. We applied three methods: XANES, EXAFS, and XRD. XANES is very useful for identification of different chemical states of copper and iron and allows us to study the chemistry of the catalysts under reaction conditions. X-ray diffraction techniques allow us to study the phase composition, but, unfortunately, the technique cannot identify nanoparticles and amorphous phases. This shortcoming can be eliminated by EXAFS which may clarify the structure of local environment of copper and iron atoms even when their concentration is extremely low.

In situ XAS experiments were performed at the Structural Materials Science station at Kurchatov Center for Synchrotron Radiation. The spectrometer is equipped with high temperature chamber that allows collecting XAS spectra within temperature range from RT to 600°C in the gas mixture at atmospheric pressure [1]. *Operando* XRD/MS experiments were carried out at the "High Precision Diffractometry II" station at "Siberian Synchrotron and Terahertz Radiation Center" and at lab Bruker D8 Advance diffractometer (Boreskov Institute of Catalysis). The both diffractometers are equipped with XRK 900 reaction chambers (Anton Paar GmbH) that allow observing the diffraction patterns within temperature range from RT to 900°C in the reactant mixture at atmospheric pressure [2].

We found that fresh CuFeAl-composite catalysts consist of CuO, Fe_2O_3, and Al_2O_3. In a CO flow, the reduction of copper from Cu^{2+} to Cu^{1+} and Cu^0 started at temperature about 200°C; at 600°C copper is mainly in the metallic state. At the same time the reduction of iron started at temperature about 400°C and at 600°C about 20% of iron is in the metallic state. *Operando* XRD study allows us to determine the phase transition of iron-containing phase during the reduction in a CO flow. The reduction process occurs in the next manner: Fe_2O_3 -> Fe_3O_4 -> FeO and Fe^0. In $CO:O_2 = 2:1$ mixture, the reduction of copper from Cu^{2+} to Cu^{1+} started at temperature about 400°C and at 600°C about 50% of copper is in the Cu^{1+} state, whereas iron is slightly reduced to Fe^{2+} state at 600°C. The following increase the partial pressure of O_2 leads to shift initial reduction temperature to high temperature range.

Thus, the use of complimentary methods (XANES, EXAFS, and XRD) allows us to determine the chemical state of copper and iron, phase composition in the catalyst during the oxidation of CO. The data presented can facilitate to clarify the mechanism of oxidation of CO.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 17-73-20157.

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OP-II-6

The Local Structure Pt-Doped CeO_2 Catalysts Studied by PDF and EXAFS Methods

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Pt/CeO_2 system is a key component of three-way catalysts for neutralization of exhaust gases. Although these catalysts have been widely studied, the nature of Pt active center is still debated. According to recent literature, Pt ions plays important role in many oxidation reactions [1,2]. Many researchers point out that ionic form of Pt enters in ceria lattice, which enhances the catalytic activity. However, the structure of Pt-CeO_2 solid solutions has not been studied yet. Therefore, the aim of this work is detailed analysis of structure of Pt-CeO_2 solid solution.

The catalysts with different platinum loading (1-30$\%_{wt.}$) were prepared by coprecipitation method. This method allows obtaining samples with a wide range content of Pt ions in ceria structure. Samples were synthesized from solutions of platinum and cerium nitrate, followed by calcination at various temperatures ranging from 450 to 800°C. All samples were studied using set of methods: XRD, XPS and HRTEM. The local structure of Pt-CeO_2 solid solution was analyzed by Pair Distribution function (PDF) method. The diffraction data for the PDF were obtained using synchrotron radiation with $\lambda=0.177$Å at ID22 station of the ESRF. For studying of Pt local environment, EXAFS was applied. XAFS measurements were conducted at Pt L3-edge at the XAFS beamline of the Elettra Synchrotron. Also, the catalysts were investigated by TPR-CO method, which allowed us to examine the reactivity of the catalyst oxygen towards carbon monoxide and to elucidate the main species.

The XRD data indicate that all samples at calcination temperature below 800 °C are single CeO_2 phase. Metallic Pt or its oxides were not detected. The increase of the calcination temperature at 800 °C leads to the formation of metallic Pt. XRD data are fully confirmed by HRTEM, which revealed that the initial samples do not contain any extended platinum species. Moreover, EDX microanalysis data indicate that platinum is distributed uniformly within entire ceria particles. The lattice parameter of the fluorite phase increases with increase of Pt loading, while the fluorite particle size decreases. According to XPS data the main platinum state in all samples is Pt^{2+}. Pt4f spectrum for 1$\%_{wt.}$ Pt-CeO_2 catalysts shows only single Pt^{2+} state, while for other samples there are two states: Pt^{2+} and Pt^{4+}states. It can be attributed to platinum in $Pt_xCe_{1-x}O_{2-\delta}$ solid solution.

According to PDF data Pt-CeO_2 solid solutions exhibit the main features of a fluorite structure on the local level. The increase of Pt loading leads to the formation of additional peaks on the PDFs. These distances can be attributed neither to metallic Pt, nor to platinum oxides. The increase Pt loading above 8%$_{wt.}$ leads to formation additional 3,09 Å and 3,48 Å distances. They can be ascribed to Pt-Pt dispenses, which are similar Pt-Pt distances in Pt_3O_4 [3] and $Pt_{3.4}O_4$ [4].

The EXAFS spectra show the Pt-O distances in first coordination sphere, which can be corresponded Pt^{2+} in square planar coordination and Pt^{4+} in cubic coordination in Ce positions. The additional distances in the second coordination sphere is formed with Pt loading above 1%$_{wt}$. They can be attributed to Pt^{4+}-Ce distances, when Pt^{4+} replaces Ce position in fluorite structure. At Pt loading above 8%$_{wt.}$ the additional short distances in second coordination sphere are observed. According to all obtained data, 8%$_{wt.}$ Pt-CeO_2 catalysts represents a saturated solid solution. Therefore, the short additional distances could be attributed to Pt-Pt distances in PtO_x clusters on the surface of catalysts. More detailed modeling of solid solution structure and PtO_x clusters was performed.

The TPR-CO data show the strong CO absorption below 150 °C in the samples with Pt loading above 8%$_{wt}$. We suggest that this strong CO absorption is due to Pt^{4+} presence in solid solution structure and/or in PtO_x clusters.

Acknowledgement. The reported study was funded by RFBR according to the research project № 17-03-00754. TPR-CO analysis was conducted within the framework of budget project for Boreskov Institute of Catalysis.

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OP-II-7

In Situ EMR and Dynamic Light Scattering Studies of Liquid Phase Hydroxylation of Phenol to Dihydroxybenzenes in the Presence of FeO$_x$/Siral Catalysts

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The mesoporous Siral type materials with different SiO_2/Al_2O_3 ratios (1:1; 1:10 and 1:40) and immobilized FeOx structures were used as catalyst for direct hydroxylation of phenol to dihydroxybenzenes in the presence of hydrogen peroxide. The tested support materials (aluminous/siliceous) characterized with high surface area, well-defined regular structure and narrow pore size distribution of mesopores, and are suitable supports for the active components. Until today the nature of active sites and the mechanism of this reaction are discussed [1-3]. In the present report in situ and ex-situ electron magnetic resonance (EMR), dynamic light scattering (DLS), and electron absorption spectroscopy in UV/Vis region are used to monitor the state of catalyst and liquid phase products of the hydroxylation of phenol with H_2O_2 in the presence of FeO_x/Siral catalysts. The magnetic, electronic and dispersed states of the catalytic system as a function of temperature are monitored by EMR, UV/Vis spectroscopy and DLS, respectively. The composition of reaction products is determined by Fourier transform infrared (FTIR) spectroscopy and GC/MS. The stable and intermediate magnetic species within room temperature - 343 K are identified. In the table dynamic light scaterring data on the evolution of these liquid phase catalytic system are given. The nature of active sites are studied and the activity of the FeO_x structures with superpara/ferromagnetic properties for this hydroxylation reaction based on the obtained data are discussed. Perhaps this is the first direct experimental evidence for in situ detection of nano- and micro-sized structures in catalytic systems for hydroxylation of phenol to dihydroxybenzenes in liquid phase. It was shown that in situ, real time monitoring of catalytic system by DLS provides useful information on the formation of particles and dynamics of their size and concentration in liquid phase and allows to evaluate the size of particles.

Table. DLS data on the catalytic system based on the FeO_x/Siral catalyst (Here sample 1 is the liquid solution of phenol in benzene; 2,3- the liquid phase catalytic system before and after reaction, accordingly)

Sample	Diameter of particles in liquid system, nm					Span	Diffusion Coefficient, $E^{-13}m^2/s$.
	Diameter for 10, 50, 90 % of particles			Mean	Mode		
	10	50	90				
1	1,7	2,2	2,7	2,1	2,3	0,52	3798,9
2	123,9	434,7	808,6	445,6	624,2	1,61	1,48
3	142,1	474,5	918,8	502,5	713,7	1,64	1,32

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OP-III-1

Computational Study of Fe Containing Porous Catalysts for Selective Methane Oxidation

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The selective conversion of methane to methanol in one step is considered one of the greatest challenges of catalysis [1]. Cu and Fe-containing single-site catalysts are among the most attractive chemocatalytic systems for the low-temperature methane activation. Hutchings et al [2] and Gascon et al [3] reported on the possibility of highly efficient conversion of methane to methanol with H_2O_2 in aquous media over Fe-containing ZSM-5 zeolite and MIL-53(Al) metal-organic framework (MOF) materials, respectively. The origin of the unique catalytic behaviour of these porous catalysts remained moot until now.

In this study we conducted a detailed periodic DFT study of the reaction mechanism of methane oxidation to methanol over the above mentioned catalysts. Our computational analysis included besides the actual mechanism of the catalytic conversion of CH_4 to CH_3OH such crucial processes as the active site formation, the overoxidation reactions, and the competing H_2O_2 decomposition. For both types of catalysts, we assumed the dimeric Fe(III)-oxo species as the reactive site model based on the earlier experimental and computational characterization of the materials [3,4]. In Fe-MIL-53(Al) Fe is incorporated in the inorganic part of the framework by substituting the Al ions, while in Fe/ZSM-5 an extraframework Fe complex is stabilized as a counterion to the lattice anionic $[AlO_2]^-$ site. In both systems however all Fe species are in an octahedral weak ligand field that renders them uniquely similar to the related biological systems capable of the selective methane oxidation such as methane monooxygenase enzyme [5].

Our calculations reveal a highly complex reaction network underlying aqueous-phase methane to methanol oxidation with H_2O_2. There are many feasible possiblities for the paths resulting in the generation of the actual active site as well as for the subsequent methane conversion. The C-H bond cleavage process over a single dimeric Fe site can follow homolitic and heterolitic mechanisms with comparable probability. Furthermore, we also identified reaction paths resembling the Fenton type chemistry. The simultaneous optimization of all these reaction channels is impossible and this represents one of the key challenges for further development of the zeolite- and MOF-based methane oxidation catalysts. Besides, our calculations show that the overoxidation of methanol is very thermodynamically favourable and proceed with low activation barriers. However, our calculations also show that the overoxidation cannot take place in a concequtive manner, which leaves the possibility of methanol product accumulation in the catalytic system. Another intrinsic problem of the systems considered is that the same active site provide catalytic paths for the almost barrierless decomposition of H_2O_2 towards O_2 and H_2O rendering this oxidant unsutiable for this reaction. The computational results presented provide crucial fundamental insights necessary for further design and optimization of practical heterogeneous catlaysts for the selective oxidation of methane to methanol.

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OP-III-2

Arene C-H Bond Oxidation by Iron(V)-Oxo Intermediates Bearing Aminopyridine Ligands

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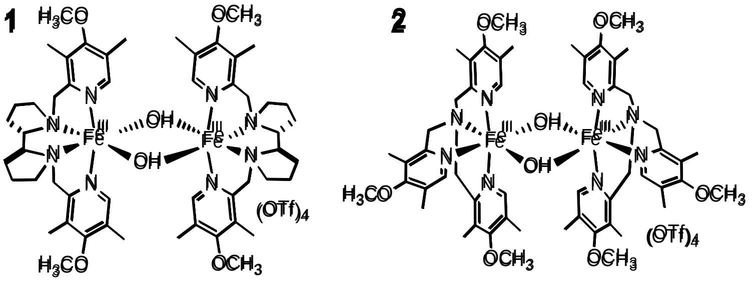
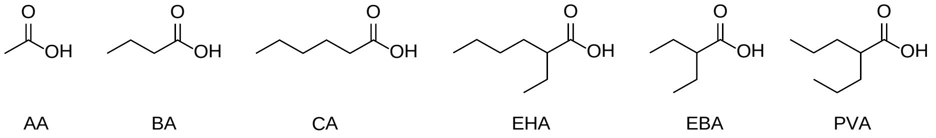
Aromatic hydroxylation is a challenging catalytic reaction because of a very strong C-H bond of a substrate. Several enzymes in nature conduct aromatic hydroxylation using Fe^{V}=O or Fe^{IV}=O species as the key oxidizing intermediates. Examples of synthetic iron-based catalyst systems capable to conduct catalytic selective aromatic hydroxylation are very rare.

In this work the direct data on the reactivity of the nonheme iron(V)-oxo intermediates towards substituted benzenes at –70 °C were obtained. The intermediates were generated in the catalyst systems **1**(**2**)/CH_3CO_3H/RCOOH. It was found that the only one type of the iron(V)-oxo intermediates **1a**^{RCOOH} with proposed structure $[(PDP^*)^{\bullet+}Fe^{IV}{=}O(O(O)CR)]^{2+}$ (g_1 = 2.071, g_2 = 2.007, g_3 = 1.960) is observed for complex **1**, whereas for complex **2**, two types of the iron(V)-oxo intermediates **2a$_1$**^{RCOOH} (g_1 = 2.071, g_2 = 2.004, g_3 = 1.963) and **2a$_2$**^{RCOOH} (g_1 = 2.076, g_2 = 2.01, g_3 = 1.964) (presumably, $[(TPA^*)Fe^{IV}{=}O(^{\bullet}O(O)CR)]^{2+}$ and $([(TPA^*)^{\bullet+}Fe^{IV}{=}O(O(O)CR)]^{2+})$ can be detected.



Bioinspired iron catalysts used in this work.



Various linear and branched carboxylic acids (RCOOH) used in this work.

When RCOOH is linear carboxylic acid, the intermediate **2a$_2$**^{RCOOH} predominates in the reaction solution. When RCOOH is branched carboxylic acid, concentration of **2a$_1$**^{RCOOH} can be much larger, than concentration of **2a$_2$**^{RCOOH} at the beginning of experiment, then **2a$_1$**^{RCOOH} rapidly converts into **2a$_2$**^{RCOOH}. The reactivity of the iron-oxo species found toward substituted benzenes increases in parallel with the growth of the substrate nucleophilicity. The aromatic hydroxylation reactivities of the observed intermediates are settled down in the following order **2a$_1$**^{RCOOH} < **2a$_2$**^{RCOOH} < **1a**^{RCOOH}.

PDP* = (*S*,*S*)-1,1'-bis((4-methoxy-3,5-dimethylpyridin-2-yl)methyl)-2,2'-bipyrrolidine, TPA* = tris((4-methoxy-3,5-dimethylpyridin-2-yl)methyl)amine.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 17-13-01117.

OP-III-3

On the Mechanism of Aldehydes Condensation over Sn and Zr-BEA zeolites

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Recently, zeolites with metal sites incorporated into the framework position triggered considerable interest. Many metal cations, such as Ti^{4+}, Sn^{4+}, Zr^{4+} and Hf^{4+} were successfully incorporated in to zeolite BEA lattice positions [1]. This M-BEA materials exhibits strong Lewis acidity due to electron accepting properties of isolated metal sites. On the other hand, hydrophobic system of siliceous zeolite channels protects Lewis acid sites from poisoning in aqueous media. This fact causes widespread application of M-BEA catalysts in biomass-derived oxygenates conversion in water.

Aldol condensation is one of the most important synthetic routs leading to C-C bond formation. This reaction is of great importance for the conversion of bio-derived carbonyl compounds in valuable chemicals. Lewis acid-base M-O pairs were found to activate aldehydes towards condensation via bifunctional "soft-enolization" mechanism [2]. Recently, some authors report the possibility of pure Lewis acidic catalysis over Zr and Ti-doped BEAs due to reduced basicity of lattice oxygen [3]. Apparently the type of framework heteroatom strongly affects the mechanism of aldol condensation. In this regard, the goal of present study was to elucidate the effect of heteroatom type on mechanism of aldehydes activation and their further reaction over M-doped BEA zeolites.

To achieve this goal we used isotopic exchange methods. Zeolite lattice oxygen was labeled with O^{18} isotope prior to aldehyde adsorption. After aldehyde admission, the progress in exchange was followed by FTIR spectroscopy by monitoring $\nu(C{=}O^{16})$ and $\nu(C{=}O^{18})$ carbonyl groups stretching. To study H/D exchange pulses of D_2O were added to aldehyde flow during aldol condensation. The appearance of D-containing aldehydes at the reactor outlet was monitored by on line mass-spectrometry. Finally, the kinetics of aldol condensation of various C1-C4 aldehydes was studied in continuous flow to determine formal reaction order and rate constants.

The results points that O-exchange between zeolite lattice and carbonyl group proceeds selectively at M-O-Si bridges and depends on the nature of M^{4+} cation. For example, Sn^{4+} induces strong basicity of nearest oxygen, so adsorbed ethanal exchanges already at 298K. Doping with Zr^{4+} leads to less basic lattice oxygen and no exchange was detected. The use of larger aldehyde reveals that van-der-Waals interactions of alkyl chain with zeolitic environment may facilitate O-exchange.

The formation of surface enolic species does not limit overall condensation rate, so enol being in equilibrium with adsorbed butanal. In case of ethanal the apparent reaction rate is totally governed by rate of enolization. Our results allow establishing pathways of aldehydes activation and reaction, not yet illuminated. For the first time, we show the size-dependent oxygenate chemistry in zeolite porous network Also Lewis acidic properties of metal cation were directly dependent on the size of the aldehyde as a consequence.

Acknowledgement. Authors thank the Russian Science Foundation for the financial support (grant 14-23-00094). P.A. Kots and A.V. Yakimov gratefully acknowledge Haldor Topsøe A/S for PhD fellowship.

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OP-III-4

The Overlooked Problem in Negishi Coupling

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Cross-coupling reactions allow for an easy, predictable, and reliable construction of carbon frameworks. One of the widely exploited cross-coupling approaches is based on the procedure introduced by Negishi that provides a very efficient route to form new C-C under mild conditions. Although Negishi coupling is based on the utilization of air- and moisture-sensitive organozinc reagents (RZnX), this approach has been proven highly versatile and practical in various synthetic applications [1].

Despite years of intense studies on the mechanism of the Negishi coupling, the common mechanistic proposals are centered on a single ("main") catalytic cycle. However, the formation of M-Zn-intermetallic species is often overlooked when constructing mechanistic proposals even with this simplistic single-cycle model (Figure 1). Pd catalysts are the classic choice in the case of the coupling reactions, and Ni catalysts seem a promising cheaper and more abundant alternative [2]. Zinc halides (ZnX_2) are the main by-product formed as a result of the transmetallation stage. In this work, we use DFT modeling to show that ZnX_2 can react with the key Ni- and Pd-catalytic species in Negishi couplings thus altering the normal catalytic process.

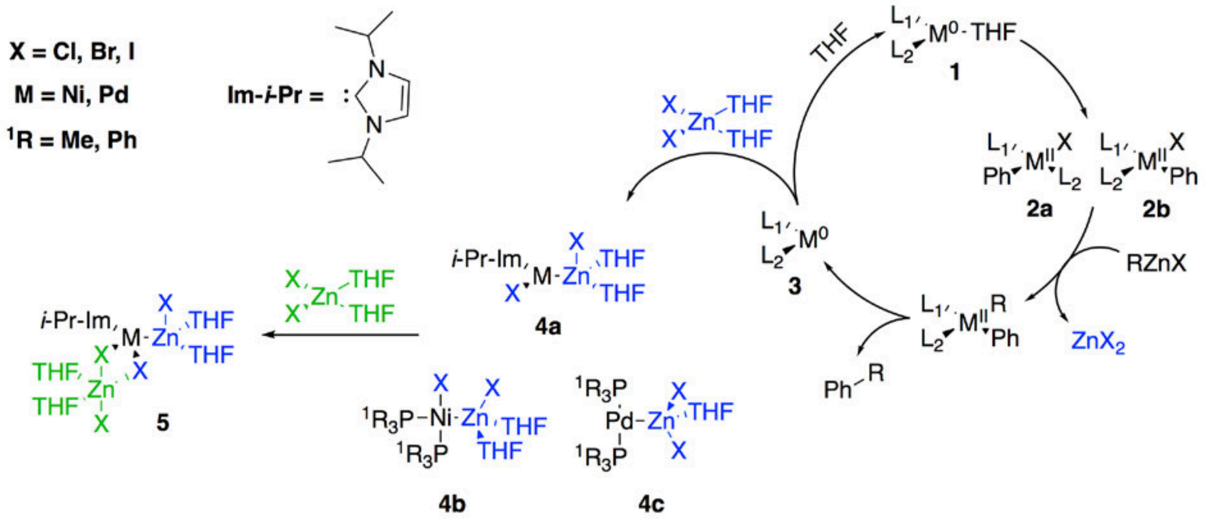
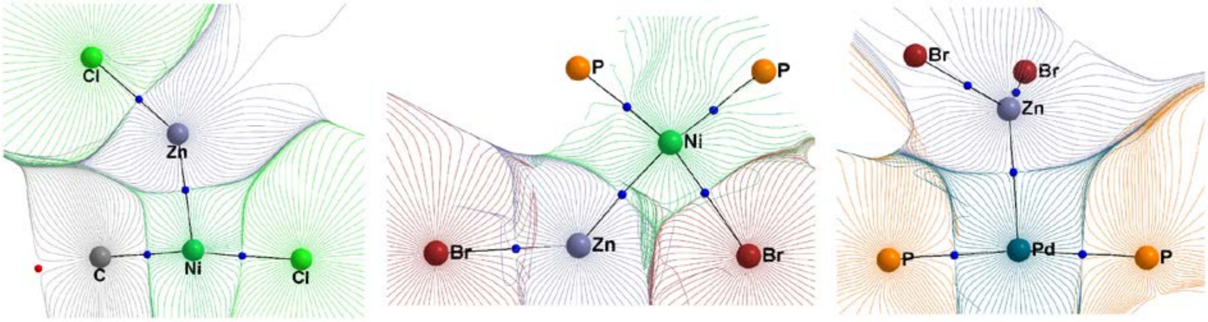


Figure 1 – The formation of M-Zn-intermetallic species in Negishi cross-coupling.

The formation of **4a-c** intermediates was found to be highly exothermic with the corresponding reaction energies $\Delta E_{3 \rightarrow 4a(4b)}$ varying from -56.2 to -19.9 kcal/mol and the reaction free energies $\Delta G_{3 \rightarrow 4a(4b)}$ varying from -40.4 to -3.0 kcal/mol (computed with B97-3c method). The M-Zn-clusters **4a-c** formation leads to the oxidation of the catalytic species **3**, and in the case of Ni catalytic systems with imidazolic NHC-ligands, the Ni-Zn bonding is so strong that non-catalytic Ni-Zn-intermediate **4a-c** formation blocked the catalytic cycle if X = Cl.

We used QTAIM theory to assess the nature M-Zn-intermetallic bond (M = Ni, Pd, Figure 2), and it may be classified as the donor-acceptor interaction. We use a fast and precise approach to QTAIM analysis in this work and suggest this approach for routine studies in transition metal catalysis.



4a **4b** **4c**

Figure 2 – Basin gradient paths of representative M-Zn-cluster electron density distributions. Bond critical points are blue spheres, ring critical points are red spheres.

ORCA program (ver. 4.0.1) was used to perform all computations. Reaction energies were computed with the B97-3c method and at RI-TPSS-D3(BJ)/def2-SVP-gCP level of theory (with def2/J auxiliary basis set). Vibrational frequencies were calculated numerically. Solvent effects were accounted by the explicit inclusion of THF molecules as well as by using C-PCM implicit solvation model. All-electron ZORA computations at RI-TPSS/ZORA-def2-TZVP level of theory (with SARC/J Coulomb fitting basis set) were performed for QTAIM analysis with AIMAll program (version 17.01.25).

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OP-III-5

Strong Experimental Evidence for Fast Oxidative Addition of Aryl Halides to Pd(0) in Direct C-H Arylation of Indoles

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Direct C-H arylation of heteroaromatic compounds is very attractive synthetic methodology allowing obtaining new C-C bonds without any pre-functionalization (in comparison with related cross-coupling reactions). However, due to this field has been studied intensively for several years only, a lack of fundamental knowledge about proceeding of these processes including information about elementary steps is observed.

It is well-known that the first step of the catalytic cycle of indole C-H arylation is oxidative addition of aryl halide to Pd(0). Previously, when cross-coupling processes were studied, it was assumed that such oxidative addition (opening cross-coupling catalytic cycles also) can be the rate-determining, especially when non-reactive aryl bromides and chlorides were used. It should be noted that such conclusion was frequently formulated using Hammet plots of competing reactions that really cannot give any information about rate-determining steps per se [1]. We suggested the approach for reliable establishing of the nature of fast and rate-determining steps of complex catalytic reactions by the analysis of integral kinetic curves of consumption of two competing substrates. It was demonstrated that if the substrates compete in a fast elementary step, acceleration at the kinetic curve of less reactive substrates should be observed at the moment when more reactive substrate is virtually consumed [1]. Another situation when consumption of less reactive substrate does not appear points to the participation of the competing substrates in slow steps of the catalytic cycles (however, this conclusion must be verified by competing experiments using other pairs of competing substrates).

We have revealed that under competition of *p*-iodoacetophenone and iodobenzene in the indole arylation using ligandless Pd catalytic system at the kinetic curve of consumption of iodobenzene acceleration were observed when more reactive *p*-iodoacetophenone consumed. Also this effect was registered at the kinetic curve of *p*-iodotoluene consumption under competition with *p*-iodoacetophenone in the indole arylation. The data obtained indicate that oxidative addition of aryl iodides is fast step of the indole direct C-H arylation.

It is possible to expect more hampered oxidative addition in the reaction with less reactive aryl bromides. However, when indole was competitively arylated by *p*-bromoacetophenone and bromobenzene, at the kinetic curve of the latter consumption acceleration was observed and coincided with the moment when the former virtually consumed. This result unambiguously points to the participation of aryl bromides in the fast step of the catalytic cycle. So, even non-reactive aryl bromides are used in the direct C-H arylation of indoles, oxidative addition cannot be the rate-determining step.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 16-29-10731.

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OP-III-6

Kinetics of Liquid-Phase Hydrogenation of Nitrobenzene Using Ru-Containing Catalyst

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The process of catalytic hydrogenation of nitrobenzene is the most important chemical and technological process to receive aniline which is used as a semi-product in the synthesis of polyurethane, rubber, various pharmaceuticals, pesticides and herbicides (the scheme of nitrobenzene hydrogenation is presented in fig. 1). The process of gas-phase nitrobenzene hydrogenation usually is carried out using Ni or Cu-containing catalysts, in the hydrogen atmosphere at a pressure 0.1 – 0.5 MPa and at reaction temperatures 250-300 °C [1-4]. When using Pt- and Pd-containing catalysts, a liquid-phase process is carried out at a pressure 1 - 5 MPa and temperature 50 - 100 °C using various solvents and without them [5]. This work is devoted to the study of kinetic regularities of nitrobenzene hydrogenation process using Ru-containing catalyst.

Hydrogenation of nitrobenzene was carried out in a batch high-pressure stainless steel reactor Series 5000 Multiple Reactor System (MRS). The experiments were carried out in the presence of a catalyst of 3% Ru/MN-270 on the base of hypercrosslinked polystyrene MN-270 type (Purolite Ltd, UK). Samples of the reaction medium were taken every 10 minutes. Product analysis was performed by gas chromatography using gas chromatograph Crystallux-4000M (Russia, Meta-Chrome) with PID detector.

For a study of kinetic of nitrobenzene hydrogenation process a number of experiments was carried out varying the following parameters: temperature 160 to 190 ºC with a step 10 ºC, pressure (0.2, 0.5, 1, 2, 3 MPa), the mass of the catalyst (0,05 g, 0,15 g, 0,2 g). The obtained temperature dependences of nitrobenzene conversion to aniline are presented in fig. 2. The increase in temperature leads to the increase of conversion, while selectivity doesn't change and remains equal 97-98%.

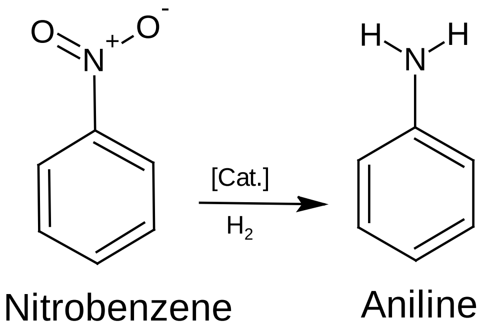

Fig. 1 Scheme of nitrobenzene hydrogenation

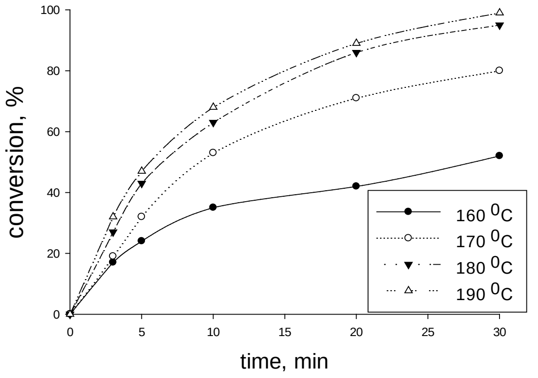

Fig. 2 Dependences of nitrobenzene conversion on time at various temperatures

The obtained experimental data have formed the base for mathematical modeling of kinetic of selective hydrogenation of nitrobenzene. The method of the back integration was applied for the calculation of more than ten mathematical models. The mathematical model which well describes the experimental points of the kinetic curves has been chosen. On the base of the chosen mathematical model there were calculated: a speed constant of nitrobenzene hydrogenation reaction, parameters of the Arrhenius equation and the apparent activation energy.

During the work optimal parameters of nitrobenzene hydrogenation to aniline have been chosen: temperature 180 °C, reaction time 30 minutes, hydrogen pressure 0.2 MPa, the mixer turn speed 1100 rpm, solvent isopropyl alcohol, nitrobenzene concentration 0.24 mol/l, catalyst mass (3%-Ru/MN-270) 0.05 g. These conditions allow achieving 98% selectivity to aniline and 95%conversion.

Acknowledgement. This work has been performed within the project 16-38-00-342 financed by the Russian Foundation for Basic Researches.

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OP-III-7

Aerosol Synthesis of Single-Walled Carbon Nanotubes with Tailored Characteristics

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Single-walled carbon nanotubes (SWCNTs) are a class of materials characterized by a wide range of characteristics. Depending mainly on structure, morphology, and purity SWCNT can provide either metallic or semiconducting properties. This opens a bright opportunity for development of a various materials and devices with advanced characteristics: from thin film transistors to transparent electrodes for flexible electronics, from charge carrier of the cathode of Li-ion battery to window layer of flexible solar cell. However, each application requires SWCNTs with characteristics optimized for this particular case, thus, emphasizing the synthesis of nanotubes with tailored properties to be a key factor to enhance materials research.

During the last 25 years, the interest of scientific community to SWCNTs has resulted in a number of methods – laser ablation, arc discharge, different modifications of the catalyst chemical vapor deposition (hot-wire, plasma enhanced, fluidized bed, substrate, microwave assisted *etc.*). So-called aerosol CCVD – an application of the floating catalyst approach with low catalyst concentration – allows synthesizing individual SWCNTs instead of unentangible bundles provided by fluidized bed technique, while covering a wide range of substrates of low thermal stability to collect nanotubes when compared to substrate CVD. Moreover, aerosol CVD can be integrated with roll-to-roll technique resulting in continuous technology for SWCNT growth.

In the present work we have performed a classic catalytic study of the process - varying reaction conditions (temperature, contact time, carbon source and promotor concentration), catalyst nature and collecting technique (filtering, themophoretic deposition) we have studied the structure and properties of SWCNT films by a comprehensive set of study methods: HRTEM, SEM, AFM, Raman and UV-vis-IR spectroscopy, optic microscopy, analysis of differential mobility of aerosol particles, conductivity studies *etc.* The results obtained are in agreement with classical nucleation theory allowing us tuning the properties of both individual SWNCTS (diameter and chirality distribution, length, defectiveness) and thin film morphology. The SWCNT films obtained show a state-of-the-art conductivity facilitating the development of flexible electronics.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 17-19-01787.

OP-IV-1

Ferrosilicate-Based Heterogeneous Fenton Catalysts: Influence of Crystallinity, Porosity, and Iron Speciation

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The removal of organic contaminants from both gas and aqueous phase is an ever growing need due to stricter environmental regulations [1]. It is in this context that Advanced Oxidation Processes (AOPs) are nowadays considered to be one of the most effective methods to remove organic contaminants. Fenton and photo-Fenton oxidation are two AOPs showing greatest potential [2,3]. Earlier we have shown that Fe-ZSM-5 is an effective heterogeneous Fenton catalyst in total hydrogen peroxide oxidation of a series of organic substrates [4,5]. In order to develop suitable heterogenous catalysts which act under Fenton conditions in liquid phase, in this study we have prepared different ferrosilicate samples with varying degrees of crystallinity, porous texture, and speciation of the Fe sites by both hydrothermal and sol-gel procedures: Fe-silicalite-1 with microcrystals (2–10 μm) and nanocrystals (180 nm), Fe-containing composite material consisting of silicalite-1 and amorphous silica, and two samples of mesoporous Fe-containing amorphous silica Fe-SiO_2. The resulting solids have been tested for their potential as organic pollutants removal under Fenton-like conditions in heterogeneous catalytic wet oxidation of phenol and clarithromycin lactobionate (CL) by hydrogen peroxide with registration of CO_2 and O_2 evolving during the process (Fig. 1). The main results of our study are as follows:

- Crystallinity, texture and acidity of Fe-containing materials effect on the adsorption of phenol. Adsorption of phenol is monolayer on Fe-silicalite-1 samples and polylayer on samples containing amorphous phase mainly due to the surface defectiveness of last mentioned. Lower acidity of Fe-containing samples is more favorable for the adsorption of phenol being a weak acid and the reaction between ferric sites and phenol with the formation of iron-phenolate complexes.
- Inhibition effect of intermediates on the catalytic activity was observed for all Fe-containing samples under phenol oxidation by hydrogen peroxide, however there is no one in clarithromycin lactobionate oxidation probably due to the absence of iron complexing agents among them. Active sites of crystalline sample are more stable for blocking by intermediates, apparently resulting from the protective function of zeolite framework.
- The decrease of Fe-silicalite-1 crystal size results in the better access of organic substrates to active oxidative particles, enabling the higher mineralization, especially of large molecules.

- Amorphous Fe-SiO_2 without sulfur admixtures was characterized by the most effective oxidant consumption in the oxidation of clarithromycin lactobionate despite of lower catalytic activity compared with crystallized samples.

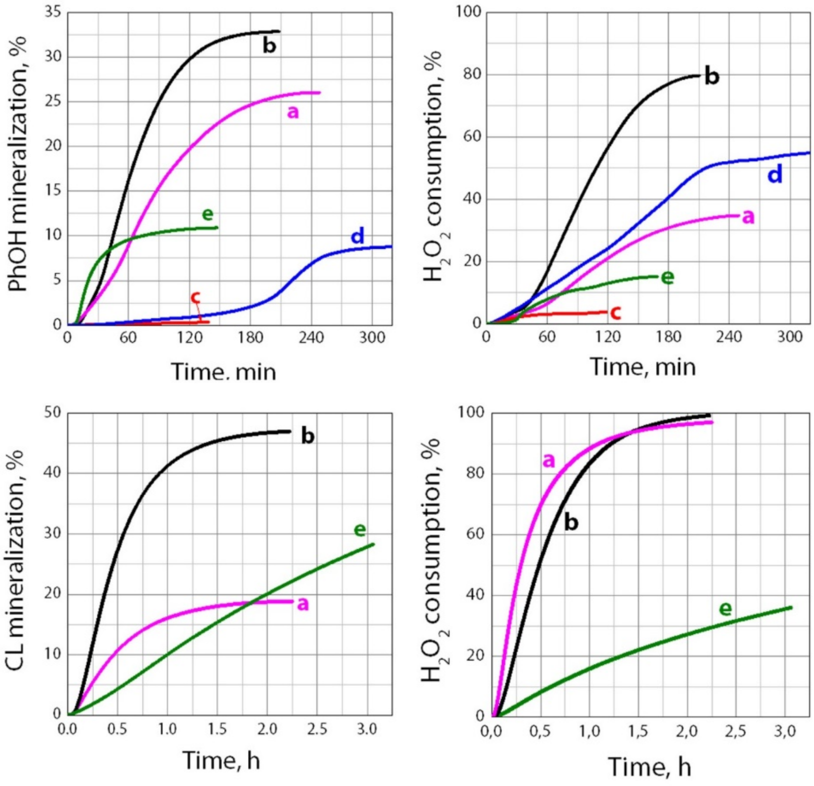

Fig. 1. Kinetic curves of phenol (upper) and CL (bottom) oxidation by H_2O_2 over Fe-containing samples according to CO_2 (left) and O_2 (right) evolving: Fe-silicalite-1 microcrystals (a); Fe-silicalite-1 nanocrystals (b); Fe-composite (c); Fe-SiO_2 sample 1 with sulfur admixtures (d); Fe-SiO_2 sample 2 without sulfur admixtures (e). Experimental conditions: for phenol – $[H_2O_2]_0$ = 1 M, $[PhOH]_0$ = 0.5 g/L, [cat] = 20 g/L, T = 30 °C, for CL – $[H_2O_2]_0$ = 1.5 M, $[CL]_0$ = 0.3 g/L, [cat] = 20 g/L, T = 40 °C.

- Amorphous Fe-SiO_2 without sulfur admixtures was characterized by the most effective oxidant consumption in the oxidation of clarithromycin lactobionate despite of lower catalytic activity compared with crystallized samples.

- Our results indicate that crystallinity, texture and acidity show a strong interplay towards the abatement of pollutants in liquid phase. Thus, samples with high crystallinity and sufficient acid character show an improved performance in the oxidation of organic contaminants over amorphous samples in which the Fe speciation is very well controlled.

Acknowledgement. The authors thank A.V. Polukhin for his help in carrying out catalytic experiments and N.A. Rudina for SEM analyses. This work from Russian side was conducted within the framework of State contract with Ministry of Education and Science if the Russian Federation No. 14.604.21.0159. The authors from Spanish side thank the Spanish Ministry of Economy and Competitiveness (MINECO), Generalitat Valenciana and FEDER (CTQ2015-66080-R MINECO/FEDER and PROMETEOII/2014/010) for financial support. J.G.A. thanks the Spanish Ministry of Economy and Competitiveness (MINECO) for his fellowship (BES-2013-063678), the presentation is supported by PJSC Gazprom Neft project.

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OP-IV-2

Ag/CeO$_2$ as Promising Catalysts for Total Oxidation of Harmful Compounds

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Nowadays, the problems of emission of harmful compounds from industrial plants and motor vehicles in crowded urban areas are getting more and more attention and new solutions for air cleaning are urgently required.

The catalytic full oxidation of organic pollutants to CO$_2$ and water is the most effective way to solve this problem. However, a significant part of the developed catalysts cannot be used under real conditions due to high cost (noble metals such as palladium, platinum, gold are used with a loading of 2-10 wt.%). Therefore, the development of high-performance affordable and stable catalysts for low-temperature total oxidation of harmful compounds is still challenging. Efficiency and cost of catalysts based on noble metals are associated with the correct selection of the type of active component, support and preparation method. Enhanced catalytic activity of such catalysts can be achieved by using reducible metal oxides as supports and by controlling the metal support interaction in order to provide synergistic effect between active sites of the support and noble metal. For this reason, Ag/CeO$_2$ is a promising heterogeneous catalyst for total oxidation of harmful organic compounds thanks to its high activity and relatively low cost [1]. The aim of this work is to study the structural properties, nature of oxygen species, chemical composition and oxidation state at the surface of Ag/CeO$_2$ catalysts, prepared by different techniques, and to find their influences on the catalytic properties in deep oxidation of harmful organic compounds.

Ceria was used as a support due to oxygen storage capacity and its ability to adjust the oxygen concentration at the catalyst surface under reaction conditions. Several strategies have been developed to control the metal–support interaction. It was shown that the distribution of active components on the support surface and their interaction depend on the preparation method. Ag/CeO$_2$ catalysts (Ag loading was 10% wt.) were prepared by three different techniques: impregnation (Ag/CeO$_2$(imp)), impregnation of pre-reduced CeO$_2$ (Ag/CeO$_2$(red-imp)) and co-deposition precipitation (Ag/CeO$_2$(co-DP). It was found that Ag/CeO$_2$(co-DP) had strong metal–support interaction, expressed in epitaxy of silver on the ceria surface (confirmed by TEM HR), and significantly increased reducibility of ceria in the presence of silver (TPR-H$_2$ results). Weak interaction of silver clusters with ceria support was observed for Ag/CeO$_2$(imp). Ag/CeO$_2$(red-imp) was showing the most homogeneous distribution of Ag nanoparticles. Oxygen vacancies on CeO$_2$ play the key role in the metal–oxide interaction [2] and influence the catalytic properties. A morphology-dependent interplay between oxygen vacancies and Ag–CeO_2 interaction was found for the Ag/CeO_2 catalysts. According to Raman and XPS results, the presence of silver in CeO_2 leads to significant growth of defectiveness of CeO_2 particles. High amount of oxygen vacancies was observed for Ag/CeO_2 (co-DP) and Ag/CeO_2 (red-imp) catalysts. The catalysts were tested in CO oxidation and combustion of soot. The catalytic properties of Ag/CeO_2 catalysts in CO oxidation were studied under 0.5% CO+4.4% O_2+ 95.1% He with a flow rate of 300 ml/min and heating of 10 deg/min. Figure 1 (a, b) shows the temperature dependence of the reaction rate and activation energy. CO conversion started at room temperature for all Ag-containing catalysts. The Ag/CeO_2 (co-DP) catalyst was the most active in CO oxidation and the activation energy for CO conversion, in a temperature region corresponding to conversions from 4 to 20%, was 29.3 kJ/mol with a reaction rate at 100 °C of 7.7×10^{-8} mol/m^2×s (fig. 1 a, b). The lowest catalytic activity was observed for Ag/CeO_2 (imp) (E_a = 42.6 kJ/mol and W = 3.89×10^{-8} mol/m^2×s). To study the catalytic activity of the samples in soot oxidation a simultaneous thermal analysis (STA-TGA) was used. Soot oxidation over Ag/CeO_2 catalysts was observed in a temperature range of 230-640°C with T_{max} = 390 °C for Ag/CeO_2(red-imp) and T_{max} = 415 °C for Ag/CeO_2(co-DP), respectively. Over Ag/CeO_2(imp) soot oxidation occurs between 300-680°C with T_{max} = 460°C. Based on the so far reported results, it emerges that the activity of the Ag/CeO_2 catalysts in CO and soot oxidation mainly depends on the metal–support interaction. Enhanced Ag–CeO_2 interfacial interaction in Ag/CeO_2(co-DP) and Ag/CeO_2(red-imp) catalysts provides an increased activity in low-temperature CO oxidation and soot combustion.

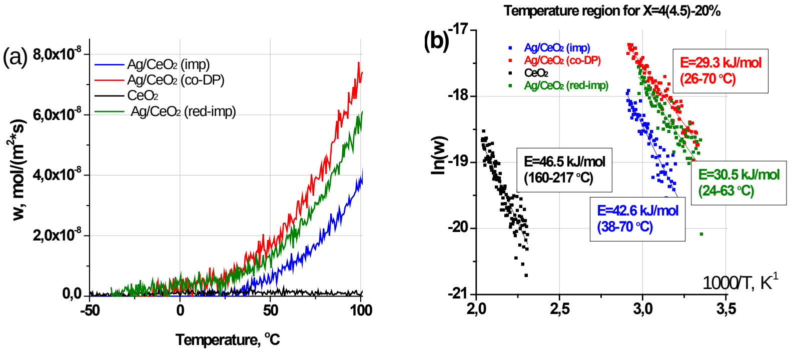

Figure 1. The temperature dependence of reaction rate (a) and energy of activation (b) of samples.

In conclusion, we have shown that the control of Ag–CeO_2 interaction can be used as a powerful tool to design promising catalysts for pollution control at low-temperature.

Acknowledgement. This work was supported by the grant of the President of the Russian Federation (МК-2015.2017.3) and Tomsk State University competitiveness improvement program.

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OP-IV-3

Crucial Role of Catalyst Stability in Hydrotreatment of Biomass Pyrolysis Oils

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Use of renewable energy resources attracts much attention as the oil reserves are gradually depleting, and the necessity to lower the carbon footprint becomes obvious due to increased buildup of CO_2 in the atmosphere. The use of biomass derived fuels is attractive, since biomass is the only renewable carbon resource with a sufficiently short reproduction cycles. Among all biomass conversion methods, the thermochemical conversion by fast pyrolysis is considered one of the most promising, being relatively simple and cost effective [1]. Nevertheless, pyrolysis liquids (PL) still contain a large amount of oxygen, and an upgrading step to reduce / remove these oxygen is deemed required. Hydrotreatment (hydrodeoxygenation, HDO) process is a viable option for downstream upgrading of such liquids, eventually to produce liquid transportation fuels [2]. A crucial step is to develop catalysts, with reduced costs and sufficiently high activity and high stability in hydroprocessing such aggressive and unstable pyrolysis liquids.

Numerous studies have shown that the main reasons of catalysts deactivation are coke deposition onto the catalyst surface, poisoning by PL impurities (S, N, K, Cl, etc.), leaching of catalyst components, structural degradation in the presence of H_2O, and sintering [3]. Deactivation associated with poisoning, leaching and sintering usually appears as irreversible and presents the main causes of the catalyst's replacement. A robust catalyst that withstands the impact of aggressive feed and can be regenerated easily without losing too much activity is highly desired in the treating of pyrolysis liquids, hence might allow application on an industrial scale.

Here we present the results of a detailed study of sol-gel catalysts with high Ni loading stabilized by SiO_2 in batch and continuous hydrotreatment of pyrolysis oil (supplied by BTG, The Netherlands). The reaction temperature in both cases was 210-230 °C, which corresponds to the effective stabilization of highly reactive species in pyrolysis oil (aldehydes, furanics, etc). For additional important details, the reader is referred to Table 1.

It was shown that the introduction of Mo into NiCu-SiO_2 increases activity and stability of the catalyst in PL hydrotreatment. One of the direct indicators for this was the amount of hydrogen consumed. The highest H_2 consumption was observed for the catalyst 15-NiCuMo-SiO_2. Increased Mo content in the case of 30-NiCuMo-SiO_2 negatively affected the observed activity, probably due to smaller active surface based on CO chemisorption data.

Table 1: Catalysts formulation and operating conditions

Catalyst	**Active component**				**T reduc, °C**	**Reactor**	**Operating conditions**
	Ni	**Cu**	**Mo**	**P**			
NiCu-SiO_2	88	12	-	-	400	Continuous flow, fixed bed	210-215 °C, 7.5 MPa, 4 kgs(PL)/kgs(cat)·h, V(H_2)/m(PL) = 250 nL/kgs·h
15-NiCu**Mo**-SiO_2	75	10	15	-	500		
30-NiCu**Mo**-SiO_2	62	8	30	-	500		
2-NiCuMo**P**-SiO_2	75	9	14	2	650	Batch (autoclave)	230 °C, 3 hours, 2000 rpm, 24 kgs(PL)/kgs(cat), V(H_2)/m(PL) = 200 nL/kgs
5-NiCuMo**P**-SiO_2	73	8.5	13.5	5	650		
8.5-NiCuMo**P**-SiO_2	71	8	12.5	8.5	650		

H_2 consumption profiles were in good agreement with those of CH_4 and CO_2. Thus, the highest yield of CO_2 was obtained in the presence of the least active catalyst, NiCu-SiO_2, due to thermal transformations (e.g. decarboxylation), which contribution increased with a low catalyst efficiency. According to TEM and CO chemisorption studies, the main reason of catalysts deactivation was sintering of metallic Ni phase, however it was less pronounced for Mo-modified samples (see Fig. 1). Positive effect from Mo was associated with the formation of NiMo(Cu) solid solutions and coordinatively unsaturated forms Mo^{x+} on the catalyst surface (based on a detailed study by CO and H_2 chemisorption, XRD and XPS, etc).

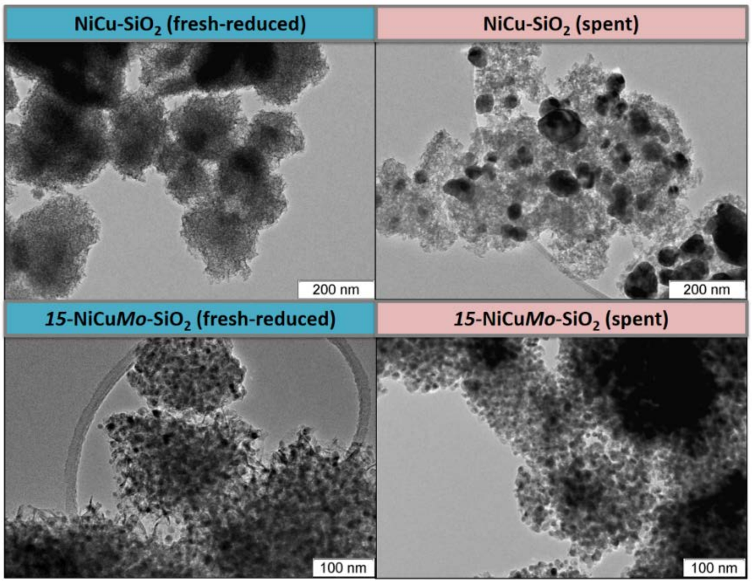

Figure 1. Micrographs of catalysts NiCu-SiO_2 and 15-NiCuMo-SiO_2 before and after PL hydrotreatment.

Further catalyst modification by phosphorus decreased the yield of gaseous products by a factor of 1.5 (mainly CH_4), as well as the formation of coke deposits. This observation was associated with the incorporation of phosphorus (along with Mo and Cu) into the active phase by the formation of phosphides. Thus, it helped to increase the distance between Ni centres known to be active in structure sensitive methanation and coke formation reactions. Based on XRD and CO chemisorption data, modification of 15-NiCuMo-SiO_2 catalyst by P allowed almost to exclude the problem of insufficient thermal stability, being one of the key reasons for irreversible catalyst deactivation. The XRD pattern of 8.5-NiCuMoP-SiO_2 catalyst remained practically unchanged after the reaction, due to the presence of thermally stable phosphide particles (Ni_3P).

Additional investigation of the catalysts stability in an acidic medium simulating aggressiveness of PL was carried out using boiling 1 M solution of acetic acid at 100 °C for 3 hours. Prior to this treatment, the catalysts were reduced in H_2 followed by passivation in a He flow with 2 vol.% of O_2. It was shown that Mo significantly increased the catalyst stability to corrosion (the mass of the residue increased from 63% to 77-80%) due to the formation of solid NiMo solutions. Further addition of P to 15-NiCuMo-SiO_2 improved the corrosion resistance even more efficiently. Thus, 100% mass retention was achieved for 8.5-NiCuMoP-SiO_2, the best catalyst in terms of stability and activity in the considered series.

Acknowledgement. This work was conducted within the framework of the budget project AAAA-A17-117041710075-0 for Boreskov Institute of Catalysis. Additional financial support from Russian Foundation for Basic Research (RFBR, Grant No. mol_g-18-33-10011) is gratefully acknowledged.

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OP-IV-4

MO_x-$Ce_{0,8}Zr_{0,2}O_2$ (M = Cu or Mn) Prepared by Template Methods for CO or Soot Oxidation

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Ceria-zirconia-based oxide systems are promising catalysts for the oxidation of carbon monoxide and soot particles due to high oxygen capacity and resistance to sintering [1]. This work focuses on CO and soot oxidation over Ce-Zr double oxides, both pristine and modified with MnO_x or CuO, which were prepared by co-precipitation method without any templates (CP), and in the presence of the biologic or organic template.

$Ce_{0.8}Zr_{0.2}O_2$ and MO_x-$Ce_{0.8}Zr_{0.2}O_2$ (M = Cu, Mn) biomorphic systems were prepared by soaking of Scotch pine (*Pinus sylvestris*, SD) or whitewood (*Picea excels*, SD') sawdust (0,25 – 0,50 mm) in the aqueous solution of the metals salts with further drying at 120°C and calcination at 500°C for 3.5 h. Similar systems were synthesized by co-precipitation method using NH_3(aq) as a precipitant (CP) or in the presence of the organic template - cetyltrimethylammonium bromide (CTAB). Detailed description of synthesis techniques is presented in [2, 3]. The molar Ce:Zr ratio was about 4:1 in all samples. Mn and Cu loadings were 8 wt.% and 25 mol.% in relation to CZ, respectively.

Soot oxidation activity was evaluated on the base of a decrease in a mass of the sample at linear heating (10 C/min) in air flow (60 ml/min) during TGA experiments (STA 449C, Jupiter, NETZSCH, Germany) at 30 – 800°C. Soot:catalyst weight ratio was 1:20. 'Loose' (**L**, gentle stirring with a spatula for 1 minute), and 'tight' (**T**, strong grinding in a mortar by a pestle for 3 minutes) contacts were used for soot/catalyst mixtures. Catalytic properties in CO oxidation were tested in the fixed-bed microcatalytic set at pulse feeding of the reaction mixture (2 vol.% CO, 1 vol.% O_2 in He) in the temperature range from 100 to 400°C. The reaction products were analyzed by GC.

The XRD diffraction patterns of all prepared samples comprise cubic Ce-Zr oxide phase reflexes. Separate CuO phase is present in Cu-containing samples. No diffraction peaks attributed to the phase of MnO_x were found for Mn-CZ indicating that Mn oxide is highly dispersed or particle size of these phases is too small to be defined by XRD. However, the presence of Mn^{3+} was detected by the XPS method. The values of the specific surface area of almost all systems was 80 – 95 m^2/g, with two distinction which were found for CZ (SD) (S_{BET} = 45 m^2/g) and CZ (CTAB) (S_{BET} = 165 m^2/g). Advanced oxygen mobility is characteristic for biomorphic samples in comparison with CP and CTAB-templated, as it was demonstrated on the base of O1s XPS spectra, TPR data and the Raman spectra. In addition, according to XPS and SEM-EDA data, all biomorphic samples comprise significant amounts of K and Ca as ash impurities, inherited from initial sawdust. It is known that K and Ca can promote the catalytic activity in the oxidation reactions [3, 4].

OP-IV-4

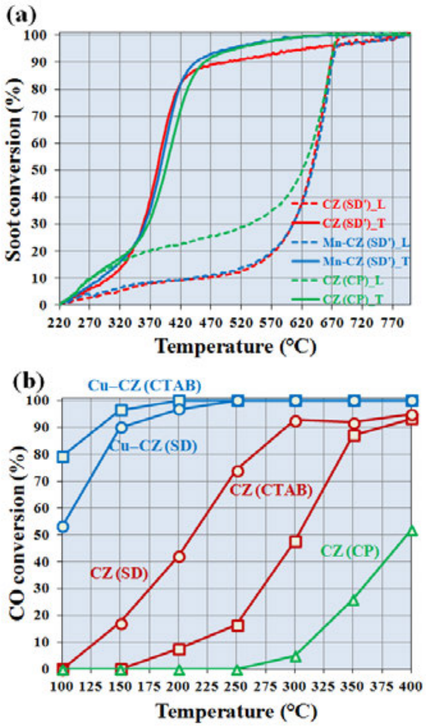

Figure 1. Soot (a) and CO (b) conversion (%) *vs* reaction temperature

The graphs of soot conversion *vs* reaction temperature are shown in Fig. 1 (a). For all systems, the soot oxidation starts at 220°C. The enhancement of the soot-catalyst contact leads to a significant increase of soot conversion at 220 – 670°C. Modification by MnO_x for systems with 'loose' contact provides no improvement of catalytic properties, but at 'tight' contact an improvement of conversion at 420 – 770°C is visible. Low content of Mn ions embedded in the lattice of CZ was detected by EPR. The weak interaction of MnO_x with CZ does not provide the formation of highly defective structure. Interesting, that CZ (CP) system with 'loose' contact containing no Mn is the most effective, but at 'tight' contact it is a bit less effective at (330 – 470°C) than Mn-CZ (SD').

In contrast, templating provides significant improvement of catalytic efficiency in CO conversion (see Fig. 1 (b)). CZ (SD) exhibits much higher activity over the investigated temperature range than CZ (CTAB). Such results can be caused by the difference in oxygen mobility and the presence of K and Ca in biomorphic samples. Modification by CuO leads to a significant improvement of low-temperature catalytic activity of templated systems, due to the involvement of additional redox pair Cu^+/Cu^{2+} into catalytic cycle, and the formation of mixed Cu-Ce-Zr oxide phases. CuO-modified biomorphic sample works a bit less effectively than the CTAB-templated counterpart due to lower CuO loading.

We can conclude that the additional modification and the use of template synthesis methods allow improving conversion in the investigated temperature range in the case of CO oxidation, but the notable increasing of the activity is not observed for soot oxidation.

Acknowledgement. This work was maintained in part by Lomonosov Moscow State University Program of Development.

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OP-IV-5

Study of Modified Cu-Containing Catalysts in the Hydrogenation of Furfural

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The development of cost and energy efficient processes to produce motor fuels and chemicals is required for the sustainability of modern society. Search for new high-octane additives and other useful products as well as the technologies for their production from non-food raw materials is one of the important tasks today. Furfural is a good raw material for the conversion to useful products. It can be obtained via the acidic hydrolysis of hemicellulose and can be converted to furfuryl alcohol via the catalytic hydrogenation. Furfuryl alcohol may be used in chemical industry as follows: a solvent and film-forming agent in petrochemistry and paint and varnish production; in the production of glass fibers, polymer concrete, etc., and in the synthesis of different derivatives of furan. In addition, furfuryl alcohol can be used as a high-octane additive. In the latter case, stabilizing additives should additionally be used to suppress the reactions of alcohol polymerization [1].

The copper-chrome systems are commonly used for the conversion of furfural [2]. The process is carried out under liquid-phase conditions at 90-120 °C and a hydrogen pressure of 5-6 MPa. The main disadvantage of the copper-chrome catalysts is the toxicity of chromium compounds. The catalysts based on noble metals may also be used [3], but they are very expensive and have a low selectivity towards furfuryl alcohol. Therefore, the non-toxic and stable catalysts with a low cost and a high activity resulted in increased yield and selectivity towards furfuryl alcohol are to be developed.

In this study, the promoted copper-based systems, Cu/SiO_2, $CuCa/SiO_2$ (impregnation), $CuCa/SiO_2$ (sol-gel), Cu-Fe-Al, were used for the selective hydrogenation of furfural. The process was carried out in an autoclave under the following conditions: the temperature is 100 °C, the total pressure is 6.0 MPa, the isopropyl alcohol: furfural ratio is 55.8:4.2 (ml/ml), 5 g of catalyst, the reaction time is 3.5 h. The introduction of calcium into the monometallic copper catalyst (i.e. $CuCa/SiO_2$ samples) was shown to allow for the increase in the furfural conversion from 88 to 98 mol. % and the increase in the yield of furfuryl alcohol from 88 to 96 mol. %. The calcium as a structural promoter increased the dispersion of copper particles, which allows for a decrease in the agglomeration of crystal copper particles and, as a result, an increase in the stability of whole catalyst [4]. The XRD and XPS analyses of the in the initial catalysts revealed the metals in the form of copper (II) and calcium (II) oxides. In contrast, no oxidized forms of copper was observed for the copper-iron-aluminum catalyst prepared by melting of metal salts. As a result, the total conversion of furfural with a 100% yield of furfuryl alcohol was observed for that catalyst. An increased activity of copper catalyst prepared via melting method can be explained by the formation of phase containing copper (II) and iron (III) compounds [5], which have high dispersion and activity in the hydrogenation reactions.

Therefore, the promotion of monometallic copper-catalysts with other metals (Ca, Fe, and Al) may improve the hydrogenation of furfural and increase its conversion and selectivity towards the furfuryl alcohol up to 100%.

Acknowledgement. The work was supported by Ministry of education and science of Russian Federation: project № 14.575.21.0171, identification number of the project is RFMEFI57517X0171, the title is “Development of methods for processing of products of non-food plant raw materials conversion into furanic high-octane additives for motor fuels and into other high-value chemical products”.

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OP-V-1

Zirconia-Based Materials as Alternative-Type Catalysts for Non-Oxidative Dehydrogenation of Light Alkanes: Factors Influencing Catalyst Performance

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Despite Pt- and CrO_x-based catalysts are widely used for large-scale non-oxidative dehydrogenation (DH) of light alkanes to the corresponding olefins, they face challenges such as high cost of platinum and toxicity of chromium [1]. Moreover, such catalysts and known alternatives are materials possessing supported catalytically active metal or metal oxide species on their surface. In general, performance of supported catalysts is determined by the fine structure of active species and their interaction with the support, which may, however, change under severe reaction conditions. To address the above challenges, we have introduced and experimentally verified a novel concept for designing alternative-type catalysts for DH of light alkanes [2]. According to this concept, catalytically active sites are defects on the surface of bulk metal oxide possessing high oxygen mobility, with ZrO_2 being one of such materials. Coordinatively unsaturated zirconium cations (Zr_{cus}) and neighbouring O^{2-} were concluded to be responsible for alkane dehydrogenation. Their importance for the DH reaction was experimentally proven by catalytic tests with gas-phase additives blocking such sites. For example, the presence of small amounts of O_2, H_2O or CO_2 in the propane DH feed resulted in up to 15 times lower catalyst activity because such molecules reacted with either Zr_{cus} or O^{2-} sites.

We also investigated how the concentration of Zr_{cus} sites can be tuned. They are formed upon catalyst reduction above 550°C or/and through doping of zirconia with low valent metal oxides. Increasing the temperature of reductive catalyst treatment led to an increase in the concentration of oxygen vacancies and therefore of Zr_{cus} sites as proven by O_2-pulse titration experiment in the temporal analysis of products (TAP). A good correlation between

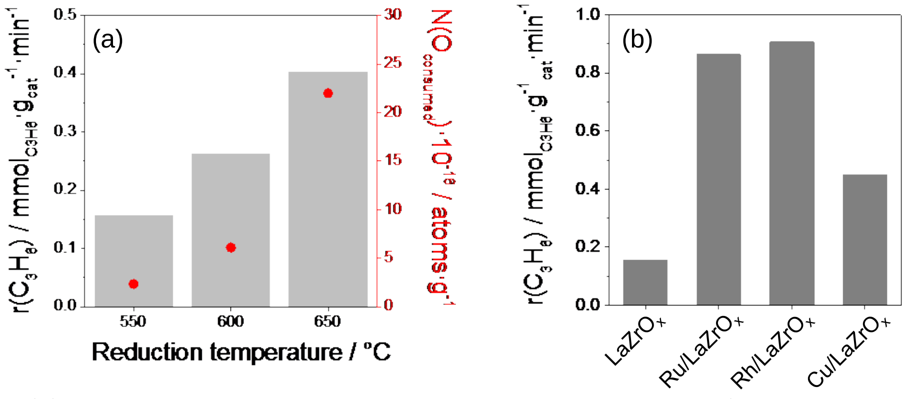

Figure 1: (a) Influence of temperature of reductive treatment of $LaZrO_x$ (ZrO_2 doped with ~ 10 wt.% La_2O_3) on the rate of C_3H_6 formation at 550°C (grey bars) and on the number of oxygen atoms consumed during O_2-pulse titration experiment (red symbols); (b) C_3H_6 formation rate determined at 550°C over $LaZrO_x$ without and with 0.05 wt.% of Ru, Rh or Cu after reduction in a H_2 flow at 550°C for 1h.

catalyst activity and the number of oxygen atoms removed upon catalyst reduction was obtained (Figure 1 (a)). The higher the reduction temperature, the higher was the concentration of anion vacancies and the higher was the rate of propene formation. The presence of tiny amounts of hydrogenation-active metal (Ru, Rh, Cu) was also found to positively affect catalyst activity (Figure 1 (b)). This was explained by fact that the metal promotes removal of lattice oxygen during reductive catalyst treatment thus resulting in the formation of additional Zr_{cus} sites.

In order to investigate the influence of metal oxide dopant on ZrO_2 physicochemical and alkane DH properties, several samples composed of ZrO_2 and about 10 wt.% of MO (M = Ca^{2+}, Mg^{2+}) or M_2O_3 (M = La^{3+}, Y^{3+}, Sm^{3+}) were synthesized, characterized by XRD, BET, NH_3-TPD, O_2-pulse titration method and Raman spectroscopy, and tested in DH of propane, n-butane and isobutane. Selected properties of the catalysts are listed in Table 1. It was found that different dopants influence not only the number of active sites but also their intrinsic activity. Moreover, the presence of dopant changes reaction pathways of product formation. Thus, coke formation could be significantly suppressed over doped ZrO_2-based materials.

Practical relevance of ZrO_2-based catalysts was demonstrated in a series of propane and isobutane DH and regeneration cycles. The catalysts showed good durability and high productivity compared to those of commercially like Pt- and CrO_x-based catalysts.

Table 1. Specific surface area (S_{BET}), amount of oxygen atoms consumed by reduced catalysts during O_2-pulse experiment ($N(O_{consumed})$), density of acidic sites determined from NH_3-TPD test with reduced samples (D(a.s)), apparent activation energies of C_3H_6, n-C_4H_8 and iso-C_4H_8 formation over reduced catalysts.

Sample	S_{BET}, $m^2 \cdot g^{-1}$	$N(O_{consumed}) \cdot 10^{-16}$, $atoms \cdot g^{-1}$	D(a.s), $N(sites) \cdot nm^{-2}$	$E_a(C_3H_6)$, $kJ \cdot mol^{-1}$	$E_a(n\text{-}C_4H_8)$, $kJ \cdot mol^{-1}$	$E_a(iso\text{-}C_4H_8)$, $kJ \cdot mol^{-1}$
ZrO_2	38.3	0.30±0.04	1.32	133±6	142±14	144±8
$LaZrO_x$	84.2	6.1±1.4	1.06	133±7	121±10	137±7
$YZrO_x$	73.9	19.0±3.9	0.87	121±8	105±8	128±3
$SmZrO_x$	59.5	0.8±0.5	0.75	135±6	114±10	143±6
$CaZrO_x$	95.3	BDL*	0.44	179±5		
$MgZrO_x$	37.9		0.67	213±12		

*BDL – below detection limit

In summary, a novel concept for designing of alternative-type catalysts for DH of light alkanes has been introduced. ZrO_2-based catalysts prepared on this basis showed attractive performance in comparison with Pt- and CrO_x-based catalysts currently used in industry. Fundamental factors influencing the performance of such catalysts were also identified.

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OP-V-2

Metal Catalysts Supported on Halloysite Nanotubes for Partial Oxidation of Aromatic Compounds

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The selective catalytic oxidation of simple aromatic hydrocarbons has a great significance in modern industry as it allows to gain a number of valuable products such as aromatic acids, benzaldehyde or maleic anhydride.

The catalysts used for oxidation of aromatic compounds may be divided into two types: supported noble metals, mainly Pd and Pt, and supported or bulk oxides of such metals as Co, Fe and Cu. It is important to note that though the latter type shows less catalytic activity, it is economically more favorable due to its lower price and larger active surface. To enhance the catalytic performance metal catalysts are deposited in different carriers, such as γ-Al_2O_3, ZrO_2, TiO_2 and CeO_2. The nature and properties of the supports significantly affect their catalytic activity. Today the use of nanomaterials as catalytic carriers is of a great research interest. Halloysite nanotubes are ones of the promising naturally occurring nanotubes due to their unique multiwall tubular structure and mesoporous lumen that vary from 15 to 50 nm. The low price and biocompatibility of halloysite make it much more interesting for the industry than expensive synthetic nanomaterials like carbon nanotubes. Due to the combination of unique chemical properties and small diameter of the tubes the material demonstrates prospective results as a catalysts carrier.

In this work, various metal (Co, Cu, Ru) catalysts deposited on halloysite nanotubes were obtained using wet impregnation method. Chemical, textural and structural properties of the samples were studied using transmission electron microscopy (TEM), X-ray diffraction (XRD), N_2-adsorption-desorption isotherms and temperature programmed reduction (H_2-TPR).

Catalytic activity of the samples was tested in the reactions of partial oxidation of benzene, toluene, o- and p-xylene. Experiments were conducted in stainless steel 40 ml Parr batch reactors in the presence of water at different temperature (150-180^{o}C) and pressure (0,5 - 4,0 MPa).

The possibility of using halloysite as carriers of aromatic oxidation catalysts was shown. The dependence of substrate conversion on time and reaction temperature was studied.

Acknowledgement. This work was supported by the Ministry of Education and Science of the Russian Federation (Unique ID of the work (project) RFMEFI57717X0239; agreement number 14.577.21.0239).

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OP-V-3

One-Pot Synthesis of Secondary Aromatic Amines over Supported Copper Catalysts in a Flow Reactor

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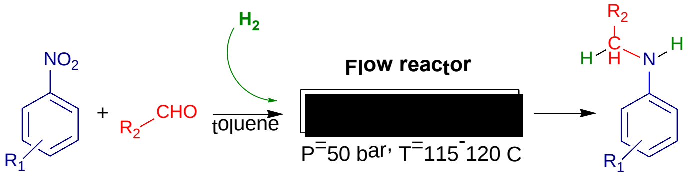
One-pot reductive amination of aldehydes with nitroarenes over heterogeneous catalysts using molecular hydrogen or other “green” reducing agents is an atom-economical and environmentally attractive method for the synthesis of secondary aromatic amines [1–4]. This process involves three cascade reactions: hydrogenation of nitroarene into primary aromatic amine, reversible condensation of primary amine with aldehyde to imine, and hydrogenation of imine to the desired secondary amine. Generally, the reaction is realized in the presence of noble metal-based catalysts (Pd, Pt, Au, Ir and Ag) [1-3]. However, the high price and limited availability of these precious metals have spurred interest in heterogeneous catalysis utilizing more earth-abundant metal alternatives [4]. Herein, we report the synthesis of functionalized secondary aromatic amines by one-pot reductive amination of aldehydes with nitroarenes over supported copper catalysts using molecular hydrogen as a reducing agent in a continuous flow reactor.



Supported copper catalysts were prepared by impregnating the support (γ-Al_2O_3, θ-Al_2O_3, SiO_2 and TiO_2-SiO_2) with an aqueous solution of copper (II) nitrate followed by drying at 70 °C under vacuum and calcination in air at 300 °C for 3 h.The investigation of the catalytic properties was performed in an H-Cube Pro™ setup (Thalesnano, Hungary) equipped with packed-bed reactors CatCart®30 (length of 30 mm, inner diameter of 4 mm). Before each catalytic run, the catalyst was reduced in a mixture of hydrogen with tolueneat T = 120 °C and P =50 bar for 1 h. The catalytic tests were carried out at 110–125 °C, 50 bar of hydrogen pressure, liquid and hydrogen feed rates of 0.35 and 60 $cm^3 min^{-1}$, respectively.

It was found that Cu/γ-Al_2O_3 catalyst provides the highest yield of the secondary amine in the reductive amination of aldehydes with nitroarenes in a flow reactor. Various secondary amines were synthesized over the Cu/γ-Al_2O_3 catalyst with a yield up to 97% using toluene as a solvent. Aliphatic aldehydes give higher yields of secondary amine in the reaction with nitroarenes as compared with benzaldehyde derivatives. The introduction of electron-donating substituents in the *para*- and *meta*-positions of nitrobenzene increased the yield of secondary amines. At the same time, in the case of nitroarenes with electron-withdrawing substituents in the *para*-position or methyl substituent in the *ortho*-position a reduction in the yield of the target products was observed under the same reaction conditions. According to obtained results, the yield of secondary amine is determined by the rate of imine formation.

Investigation of the reaction mechanism allowed us to assume that the reaction begins with preferential adsorption of nitroarene through the nitro group on Lewis acid sites of the γ-alumina located at the perimeter of the copper particles. Further hydrogenation of the nitroarene results in the formation of a primary aromatic amine which can react with the aldehyde on the Lewis acid sites of γ-Al_2O_3 as well as in the absence of any catalyst in the reaction medium. The hydrogenation of the aldehyde in a side reaction takes place only after the conversion of the greater part of nitroarene.

The time-dependent investigation of the Cu/γ-Al_2O_3 showed a slight deactivation of the catalyst with time-on-stream, which can be explained by the formation of carbonaceous deposits on the catalyst surface. The activity of the spent Cu/γ-Al_2O_3 catalyst could be recovered after washing with a mixture of toluene/isopropanol followed by oxidative treatment in air.

Acknowledgement. This work was conducted within the framework of project No.0303-2016-0006 (Boreskov Institute of Catalysis).

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OP-V-4

Hypercrosslinked Polystyrene as a Support for Ligandless Catalysts of Suzuki Cross-Coupling: Means of Optimization of Catalyst Properties

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Suzuki cross-coupling reaction is one of the most widely used and environmentally friendly methods of carbon-carbon bond formation for the synthesis of various chemicals including APIs, crop protection agents and polymers [1].

Despite the diversity of ligandless catalysts of Suzuki cross-coupling synthesized using inorganic (activated carbon, oxides, zeolites, magnetic nanoparticles (NPs)) or organic (CNT, graphenes, nanostructured polymers) supports, polymer-based catalysts can be considered as the most promising ones [2, 3] due to the possibility to control NP growth and prevent their aggregation. The variety of polymer properties (presence of functional groups, degree of crosslinking, hydrophilicity or hydrophobicity, etc.) allows the opportunity to influence the process of NP formation [4]. In this work we investigated the hypercrosslinked polystyrene (HPS)-supported mono- (Pd, Au) and bimetallic (Pd-Au) catalysts of Suzuki cross-coupling. Pd/HPS catalysts were synthesized at variation of HPS type, metal precursor nature, metal loading, and reduction method. It is noteworthy that HPS is highly thermally and chemically stable polymeric network in which "pores" are formed spontaneously during polymer synthesis. Thus the HPS consists of relatively rigid "nano-pores" serving as one of possible mechanisms for control of NP growth [5, 6] (see Fig. 1, rout 2).

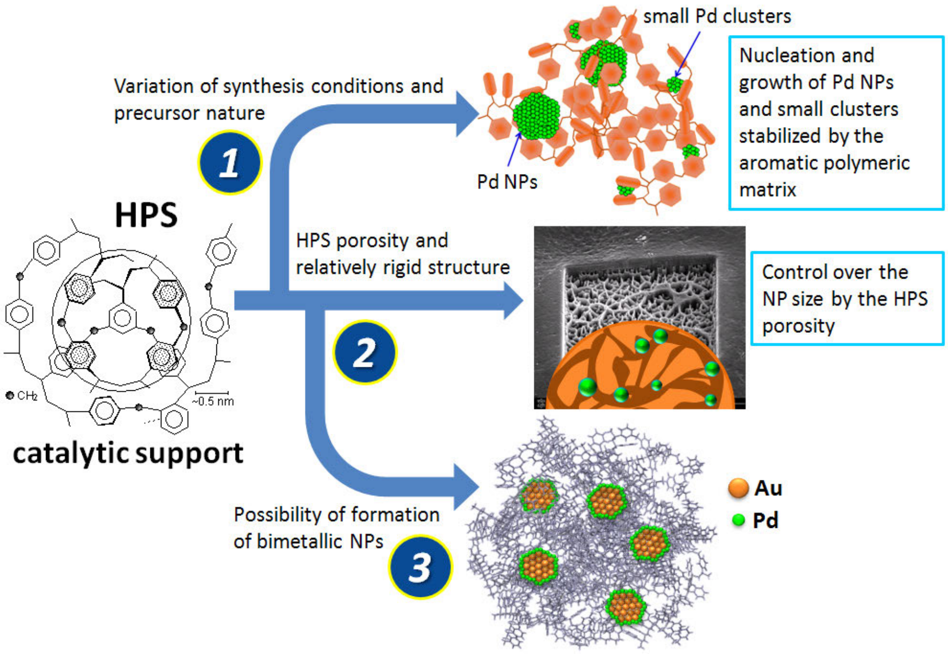

Fig. 1. Advantages of the use of HPS as catalytic support

The Suzuki cross-coupling of 4-bromoanisole and phenylboronic acid was carried out as described elsewhere [7] at ambient pressure while using EtOH/water mixture as a solvent at variation of reaction temperature and type of base.

It was shown [8] that proper combination of Pd precursor nature and the HPS type is extremely important and allows influencing Pd NPs sizes and size distributions (Fig. 1, rout 1). Best results were obtained for the catalyst synthesized while using $PdCl_2(CH_3CN)_2$ as the precursor. In this case, the use of HPS as a support allowed achieving more than 98% conversion of aryl halide for less than one hour of reaction duration at mild reaction conditions (60^oC, NaOH, solvent EtOH/water mixture (5:1)) and at the absence of phase transfer agents. However, independently of the precursor nature, Pd(II) was assumed to be the direct source of the main catalytically active form of Pd (Pd clusters formed *in situ*) in the case of unreduced Pd-containing sample [9]. For the samples, which were preliminarily reduced in hydrogen flow, the use of the HPS as a support allowed formation of a large number of Pd NPs as well as of Pd_n clusters (shown by the XPS method), and the latter were found to be responsible for the observed high activity of reduced Pd/HPS catalysts.

In the case of reduced Pd-containing catalysts, the influence of the second metal (gold) addition was studied (Fig. 1, rout 3). It was found that bimetallic Pd-Au catalysts in comparison with monometallic ones allow noticeable increase of catalytic activity (more than in two times) and stability at multiple reuses. It was revealed that synthesized HPS-based catalysts can be reused four times without essential loss in activity.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 15-19-20023.

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OP-V-5

Structure Features and Evolution of Cobalt Catalyst Supported on Carbon Nanotubes in Fischer-Tropsch Synthesis

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The increase of the cost of oil extraction makes the conversion of natural gas, coal, and biomass into hydrocarbons, alcohols and ethers one of the main trends in natural fuel processing industry. This process, also known as Fischer-Tropsch synthesis (FTS), is based on the catalytic conversion of synthesis gas into more valuable hydrocarbons, alcohols and ethers on iron or cobalt-containing catalysts. Comparing to iron catalysts, the advantages of cobalt systems are their increased time stability and lower process pressure and temperature. The properties of carbon nanotubes (CNTs) favour their use as a catalyst support for FTS. The chemical inertness of CNTs, their structural rigidity, high thermal conductivity, tuneable surface properties and localization of catalyst particles distinguish them from oxide or other carbon-based supports [1].

In this work we investigate the FTS on cobalt catalysts supported on CNTs and transformations of metal and support at different stages of catalyst life cycle: fabrication, reduction and catalytic reaction. For this purpose, pristine CNTs were functionalized to the different degrees with oxygen-containing groups. It was found that the stability of catalysts to sintering is determined by the geometry of the support surface, while the homogeneity of both Co distribution and its dispersion depends on the degree of functionalization of the support [1-3]. TEM, XPS, Raman spectroscopy, and low temperature nitrogen sorption were used to control the structure of both supports and catalysts.

The activity of Co/CNT catalysts loaded with 15 wt.% of Co linearly depended on the metal dispersion in the d_{Co} range of 4–25 nm, which confirms the absence of interaction of the catalyst with the support, even in the case of CNTs containing a large number of functionalities. Despite the selectivity to C_{5+} hydrocarbons was found to be lower for samples with d_{Co} of about 4 nm than that for the catalysts with d_{Co} larger than 5 nm, the highest yield of this fraction was observed in the case of smaller particles. Thus, the total amount of surface Co plays a more significant role in the formation of condensed hydrocarbons than the quality of the active centres. At the same time, in the case of simultaneously low Co content and a high degree of surface functionalization, the formation of metal particles smaller than 3 nm with the amorphous structure was observed revealing the metal-support interaction at the stage of catalyst preparation. Further studies showed the absence of FTS activity over this catalyst and the formation of carbon shells around amorphous Co particles. TEM images of Co catalyst supported on oxidized CNTs are shown in Fig.1.

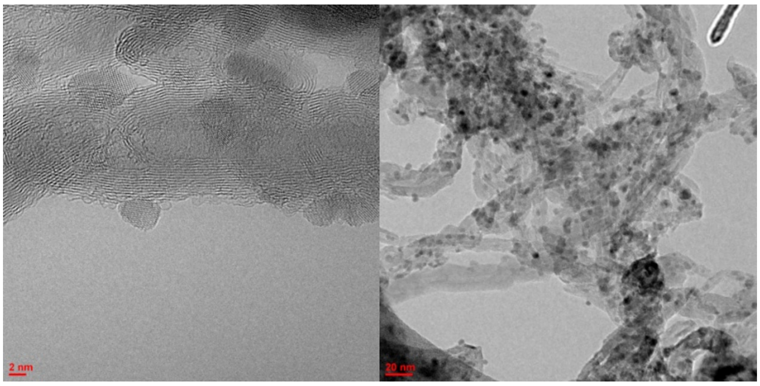

Fig.1. TEM images of the reduced Co catalyst supported on oxidized CNTs.

To investigate the support evolution Co was washed from the catalyst after annealing, reduction and FTS. It was found that the annealing and reduction significantly change the structure of CNTs which results in the increase of the S_{BET} and total pore volume. The change in the composition and content of functional groups was thoroughly studied It was found that about 70% of oxygen had been removed by the beginning of the FTS. The methanation of CNTs during reduction was demonstrated by TEM (Fig.2). Nitrogen-doped CNTs were also studied as a support for Co catalysts in the FTS.

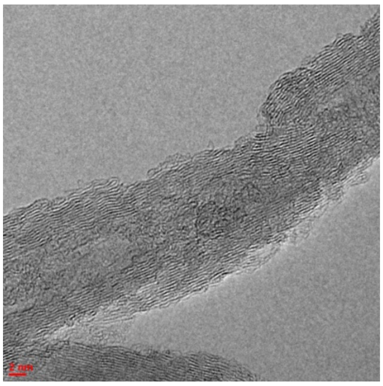

Fig.2. TEM image of the CNTs after catalyst reduction.

Acknowledgement. The reported study was funded by RFBR according to the research project № 18-33-00390.

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OP-V-6

The Effect of Zeolite Addition into Skeleton Cobalt-Based Fischer–Tropsch Catalyst

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Cobalt is an active component for catalysts for commercially available Fischer–Tropsch (FT) synthesis [1]. FT synthesis is the main stage of the technology of high-quality fuel production from carbon containing feedstock. Hydrocarbons produced on Co sites active in FT synthesis can be involved in various transformations in the presence of zeolites. The surface acid sites of zeolites are known to exhibit selectivity towards lighter and branched products through reactions of cracking, alkylation and isomerization.

Catalysts on the basis of skeletal cobalt can be an alternative to traditional impregnated catalysts for FT synthesis. It provides high thermal conductivity, which is particularly important for FT synthesis due to strong exothermal nature of FT reactions [1, 2]. Catalysts of low thermal conductivity tend to get overheated during the synthesis, which may cause enlargement of the Co crystallites and decrease activity and selectivity of the process.

Deposition of Co on zeolite leads to the formation of catalysts, which combine features of metallic and acidic contacts [3].

The aim of this work was to study the effect of acidic zeolite addition into thermally conductive pellets of skeleton Co-based FT catalysts. The combination of skeleton Co and HBeta in the catalyst composition may lead to a catalyst with high thermal conductivity that will allow producing hydrocarbons of controlled composition.

Table 1. Catalyst paste composition

Paste composition, wt.%				HB/Co ratio
Al metal	Boehmite	HBeta	Skeleton cobalt	
50	30	0	20	0
50	25	5	20	0.25
50	20	10	20	0.5
50	20	15	15	1
50	20	20	10	2

The catalysts were prepared by extrusion of paste. The composition of the paste is presented in Table 1. All samples contained 50 wt.% of dispersed Al metal powder. The content of other components was varied as follows: 20–30 wt.% of binder and 5–20 wt.% of zeolite HBeta. The reference sample was zeolite-free.

Aluminum powder and skeleton Co represent a uniform heat-conductive system (Fig. 1). One can observe transportation pores and shiny pieces of Al metal evenly distributed across the field. Fig. 1b shows large particle of skeletal cobalt (Co), which is surrounded by shiny pieces of Al metal (Al) and small spherical particles of HBeta zeolite (HB).

FT synthesis was carried out in a fixed-bed reactor. Following the activation in H_2 at 400°C, the catalyst was heated stepwise (3–10˚C steps every 6 hour) in a 2 MPa synthesis gas stream (H_2/CO=2). The temperature was raised from 170 up to 228–234˚C. Initial gas-hour space

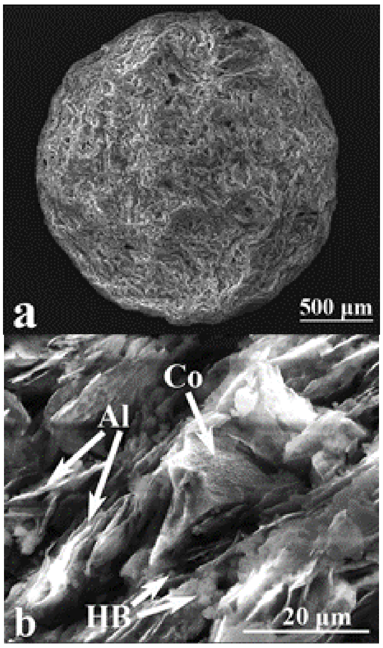

Figure 1. SEM microphotographs of a catalyst sample at 500 (a) and 20 µm scale (b)

velocity (GHSV) of 1000 h^{-1} was applied. The temperature was raised and optimized at that GHSV. Then the temperature optimization was done for every GHSV from 1000 up to 5000 h^{-1} to optimize the productivity.

Fig. 2a shows, that maximal CO conversion (70%) and the highest productivity (540 g/kg/h) corresponds to a catalyst with HB/Co = 0.25. The increase of HB/Co ratio leads to significant decrease of productivity, the lowest one (339 g/kg/h) was achieved in the presence of catalyst with HB/Co = 2.

Introduction of zeolite leads to the decrease of n-paraffins content from 73 to 42–49 %, the increase of olefins and iso-paraffins contents from 17 to 33–38 % and from 10 to 18–20 %, consequently. The increase of zeolite content has no significant effect.

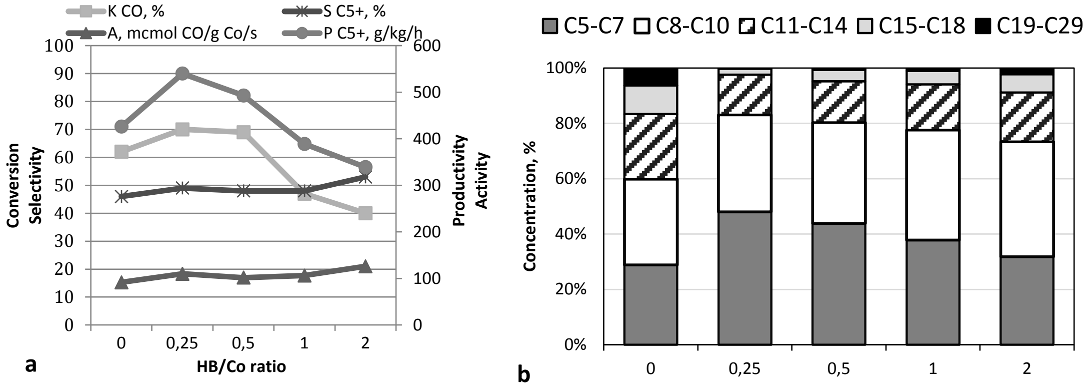

Figure 2. Process parameters (a) and product composition (b) at 5000 h^{-1}

Fig 2b suggest the opportunities to control the product fraction composition by zeolite addition. Liquid products produced in the presence of investigated catalysts are characterized by unusually high content of jet fuel fraction. The activity of such bifunctional catalysts depends on the amount of Co sites available for the formation of hydrocarbons, but in the presence of acidic sites formed hydrocarbons may participate in secondary transformations, such as cracking, isomerization and alkylation. As a result of such active site combination, the product composition is determined by the competition between metallic and acidic sites.

Acknowledgement. This work was supported by funding from the Ministry of Education and Science of the Russian Federation (Project No. 3553).

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OP-V-7

Metal Nanoparticles Immobilized in MOF UiO-66 for Selective Oxidation of Propylene Glycol

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Nowadays bio-based feedstock sources received a great importance in the chemical industry. Propylene glycol (PG), product of catalytic hydrogenolysis of bioglycerol, can be further oxidized to lactic acid (LA), which is a valuable intermediate in fine organic synthesis and biodegradable polymers production. Also, LA consumption in beauty and food industries grows rapidly. Development of effective “green” way for LA synthesis remains a challenging task.

Xu and coworkers reported that Ag/Pd bimetallic non-supported nanoparticles demonstrate great catalytic activity in selective oxidation of PG to lactic acid [1]. His group investigated that bimetallic nanoparticles with different Ag/Pd ratio and particle size show up to 98% PG conversion and up to 93.7% LA selectivity. However, an essential point for the formation of LA in this system is an alkaline medium, as a result of which LA salt is obtained. The presumable path of the reaction is the oxidation of PG to methylglyoxal, which is disproportionated in the alkaline medium through Cannizzaro reaction with the formation of lactic acid. This reaction can also take place in a neutral medium catalyzed by Lewis acids, such as Sn, Zr, Ti ions ect. [2,3]. Thus, it is actual task to create a bifunctional catalyst containing both noble metal nanoparticles and Lewis acid sites for direct production of lactic acid in the absence of alkali. In this work we immobilized Ag/Pd nanoparticles within porous zirconium terephthalate UiO-66 structure, which possess large surface area, high pore volume, high thermal, chemical and aqueous stability [4].

UiO-66 was synthesized by solvothermal method following the procedure of Cavka et al. with some modifications [4]. Obtained UiO-66 was washed with N,N-dimethylformamide and ethanol then pre-dried at room temperature and finally degassed under vacuum at 150 °C.

Bifunctional catalysts were prepared by wet impregnation method with the use of aqueous solutions of silver and palladium nitrates. Metal loading and Ag/Pd molar ratio were varied. Samples were dried at room temperature and then metals were reduced in H_2 flow at 200 °C. Obtained catalysts were characterized by XRD, FT-IR spectroscopy and low temperature nitrogen adsorption method.

Catalytic experiments were performed in 75 ml autoclave under O_2 pressure 3 bar at 80-100 °C, [PG] = 0.4 M. The amounts of PG and reaction products were analyzed by GC and HPLC methods.

Obtained UiO-66 possessed high specific surface area (about 1300 m^2/g) and pore volume (about 0.53 cm^3/g). After the impregnation process the surface area and pore volume of the catalysts decreased to 960-1220 m^2/g and 0.40-0.47 cm^3/g, respectively. Prepared catalysts preserved UiO-66 structure (Fig. 1). XRD analysis showed that metal particle sizes did not exceed 3 nm after reduction. The shape of pore size distribution curves (Fig. 2) indicated localization of nanoparticles inside large pores of UiO-66 (0.9 nm). Thus, metal nanoparticles were formed within UiO-66 pores. No formation of large nanoparticles on external surface was observed.

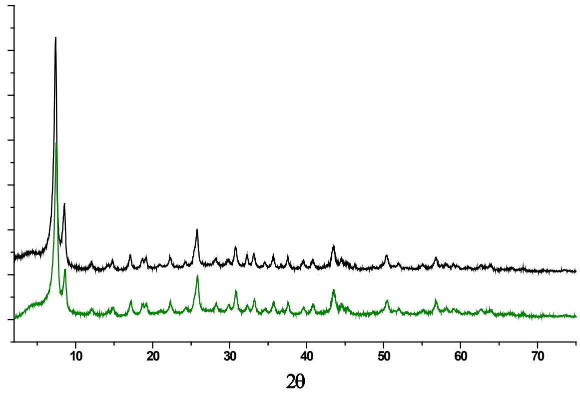

Figure1. XRD pattern of UiO-66 (black) and 1% 0.85Ag/0.15Pd@UiO-66 (green)

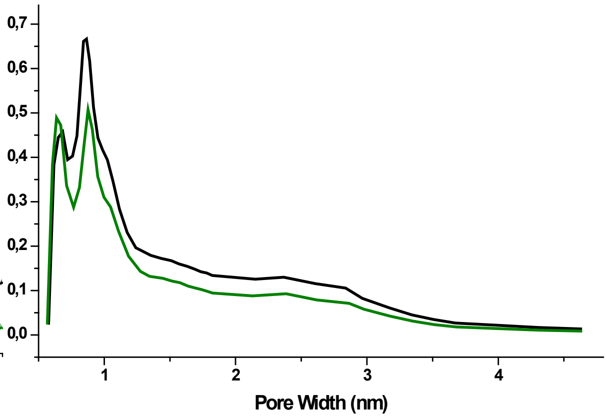

Figure 2. Pore size distribution of UiO-66 (black) and 1% 0.85Ag/0.15Pd@UiO-66 (green)

Principal formation of LA in aerobic PG oxidation over bifunctional Me/MOF catalyst without addition of any base was shown. The highest catalytic activity and selectivity towards LA (>95 % at 6 % conversion) after 7 h was obtained when 1% Ag,Pd/UiO-66 (Ag/Pd=85/15) prepared via wet impregnation method was used as a catalyst. No formation of C-C cleavage products was observed.

Acknowledgement. This work was supported by “The Tomsk State University Academic D.I. Mendeleev Fund Program” grant.

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OP-V-8

Expanded Ring N-Heterocyclic Carbene Transition Metal Complexes. Synthesis, Structure, Applications in Catalysis

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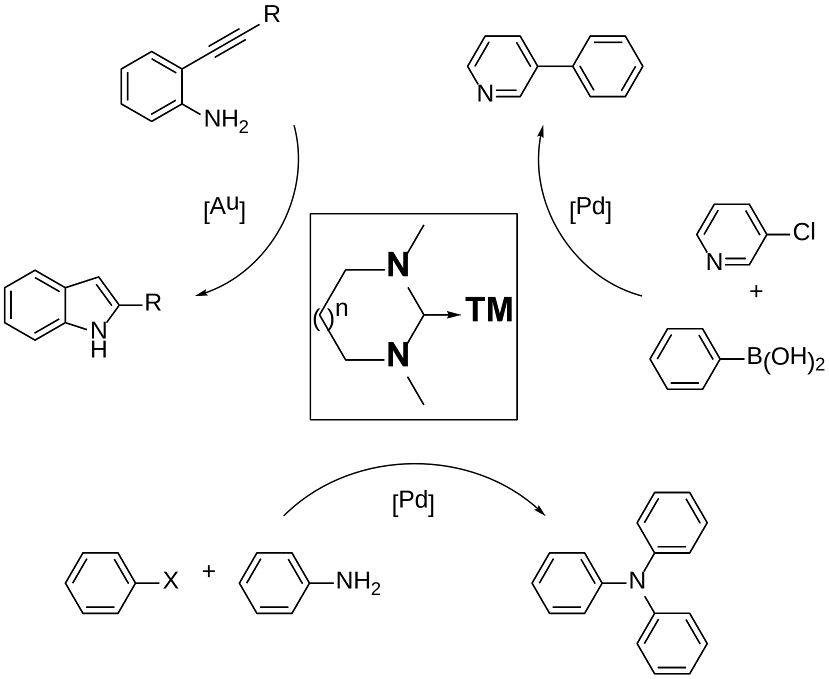
N-heterocyclic carbenes (NHCs) became widely used as organocatalysts and as ligands in transition metal catalysis. Most of NHC-metal complexes known to date are derived from five-membered ring imidazol-2-ylidene and imidazolin-2-ylidene type carbenes. In recent years, our group develops chemistry of 6-, 7- and 8-membered ring carbenes. Expanded ring carbenes (er-NHCs) exhibit superior stereoelectronic properties in comparison with five-membered ring counterparts. Expansion of the ring leads to significant increase in donor strength and sterical hindrance.

In this contribution we report our recent results on theoretical calculations of electronic structure and ligand properties of er-NHCs; efficient methods of synthesis of precursors and generation of free carbenes; synthesis of late transition metal (Cu, Ag, Au, Pd) complexes. er-NHC complexes of palladium are highly active in Suzuki-Miyaura coupling in water, and C-N Buchwald-Hartwig coupling under solvent-free conditions. Cationic gold complexes are active catalysts of addition of nucleophiles to carbon-carbon triple bonds.



OP-V-9

Hydrogenation of Butyl Sorbate Using Ruthenium Catalyst

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Leaf alcohols, namely *cis*-hex-3-en-1-ol and *trans*-hex-2-en-1-ol, are highly desirable materials in the fragrance industry. Great attention is paid to *cis*-hex-3-en-1-ol, which has a less stable *cis* configuration. Literature offers different ways to synthesize this leaf alcohol, but in many cases it is a difficult multistage procedure with small yield [1]. The easiest method of its preparation is based on cheap and available sorbic acid (hexa 2,4-dienoic acid) and sorbol (hexa-2,4-dien-1-ol) [2-3]. Sorbic acid can be selectively hydrogenated to *cis*-hex-3-enoic acid, and obtained acid can be reduced to the desired product. Selective hydrogenation of sorbol can give directly *cis*-hex-3-en-1-ol. These reactions were successfully catalysed by half sandwich ruthenium complex with the structure [Cp*Ru(sorbic acid)]CF_3SO_3 (Cp* = pentamethylcyclopentadienyl), which was successfully immobilized on smectite minerals (Fig. 1) [3].

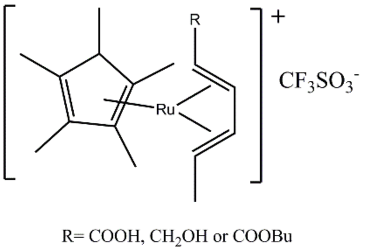

Figure 1. Cationic Cp*Ru-complexes.

This work deals with the preparation of half sandwich Ru complex [Cp*Ru(butyl sorbate)]OTf, its immobilization on various smectite minerals (hectorite, montmorillonite, bentonite) by means of ionic exchange and its use as catalyst in the hydrogenation of butyl sorbate to butyl *cis*-hex-3-enoate. This compound can be also used as an intermediate in the synthesis of leaf alcohol. Hydrogenation of butyl sorbate was performed in both homogeneous and heterogeneous arrangement. The main product was butyl *cis*-hex-3-enoate with selectivity up to 99%. Use of a heterogenized catalyst is preferable because of the simple catalyst separation from the reaction mixture and its possible reuse with no loss of selectivity [4].

The influence of solvent type (MTBE, DEE, DBE, MeOH, MTBE and DBE) on selectivity and reaction rate was studied in heterogeneous arrangement. The selectivity was not influenced by solvent and was very high in all cases (97-99%), but the reaction rate expressed as TOF (turn over frequency) was different. The best results were obtained in MTBE and therefore it has also been used when studying the effect of reaction conditions on hydrogenation.

The influence of temperature (30 - 70 ° C), pressure (0.5 - 5 MPa) and catalyst amount (3–10 wt. % of catalyst on the substrate amount) on the reaction rate and selectivity was investigated. It was found that these parameters have no influence on the selectivity.

The optimal conditions for the highest selectivity (99%) and the reaction rate were achieved in heterogeneous arrangement with MTBE as the solvent, temperature 50°C and pressure 5 MPa.

The dependence of the immobilized amount of the Ru complex on the support type and its modification was monitored. Montmorillonite was the best support. Using this smectite mineral 92 wt. % of Ru complex (15 mg / 250 mg support) was immobilized. In addition, influence of the support type on the activity and selectivity during the hydrogenation was studied. Best results were obtained using a ruthenium complex immobilized on montmorillonite. After 1 hour of the reaction the conversion of butyl sorbate was 80 % and the selectivity to the desired butyl *cis*-hex-3-enoate was 98%.

Comparing the previous up to now obtained results butyl sorbate hydrogenation proceeded with higher selectivity comparing to other 2,4-unsaturated substrates (sorbic acid, sorbic alcohol).

Acknowledgement. Financial support from specific university research (MSMT No 20-SVV/2018) is gratefully acknowledged. This work was realized within the Operational Programme Prague – Competitiveness (CZ.2.16/3.1.00/24501) and "National Program of Sustainability" (NPU I LO1613) MSMT-43760/2015).

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OP-V-10

Determining of Activation Energy and Reaction Order of Hydrogen Transfer Reactions of Menthone Catalyzed by Skeletal Nickel

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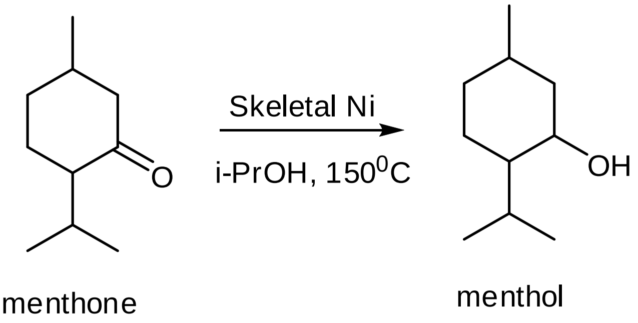
Hydrogenation is one of the most important processes widely using in both laboratory and industrial practice. Molecular hydrogen or metal hydrides are commonly used as hydrogen donors. It is well-known they are explosive and flammable therefore their using requires extra caution. Hydrogen H_2 and hydrides could be replaced by other H-donors or reductants, for example, lower alcohols, formic acid and its salts. This type of reactions is known as hydrogen transfer reactions (HTR) or transfer hydrogenation.

In the most cases, HTR are mainly catalysed reactions in which both homogeneous and heterogeneous catalytic systems should be used. The most important direction of research of HTR is a synthesis of enantiomerically pure compounds catalysed by transition metal complexes. Homogeneous catalysts usually show high activity and selectivity. On the other hand, homogeneous catalysis has very important disadvantage – difficult and/or multi-step separation of catalyst from reaction mixture. Heterogeneous catalysts are less active but more selective and can be separated easily.

HTR of menthone and some other organic compounds have been studied. Lower alcohols (methanol, ethanol and isopropanol) were used as hydrogen donors. Skeletal nickel was a heterogeneous catalyst. Skeletal nickel was shown to demonstrate catalytic activity in HTR, almost 100% of conversion of menthone was achieved at 150°C and 5 h. Activation energy of this process was 58 kJ/mol that indicates the kinetic controlled reaction. Recycle runs of skeletal nickel will be also presented. It was shown that the conversion of menthone decreased to 60% after 5th recycle run. After washing with 20% aqueous KOH, conversion increases up to 80% but then drops down to 50%. It also has been shown that HTR of menthone on skeletal nickel is of first order.



Acknowledgement. This work was supported by Federal Agency of Scientific Organizations (project № 0303-2016-0001).

OP-V-11

Study of the Aromatic Substituent Structure Influence on Catalytic Activity of Fluorinated Organic Compounds of Boron

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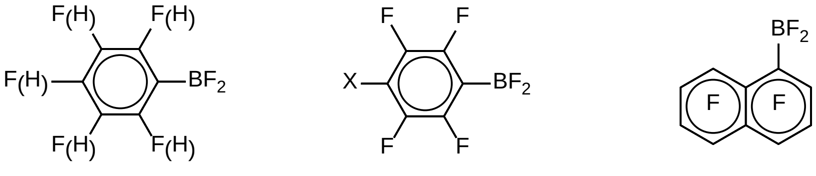
Nowadays, in spite of considerable practice experience and a large number of studies in the field of acid catalysts there are a number of actual problems in this area.

In particular, one of the problems is a necessity of creation homogeneous “soft” Lewis acids and catalytic systems based on them. This is due to the fact that using these systems opens up an opportunity to control the reaction selectivity, this being especially important for polyfunctional and polynuclear compounds. Moreover, their use interferes with the deactivation of active sites associated with the formation of heavy reaction products. Application of catalysts based on homogeneous “soft” Lewis acids will allow to expand the range of solvents suitable for carrying out the reaction, and also to avoid partial asphaltization of the reaction mixture associated with problems of mass and heat transfer.

One of the promising ways of solving the above tasks is the use of fluorinated organic compounds of boron (organofluoroboranes). This is due to the fact that the variation of the organic substituent structure makes it possible to control the electrophilic properties of the active site and the sterical availability of this. Thus, a change in the structure of the organic substituent makes it possible to control the acidity of the catalyst and the selectivity of the process, which is especially important for the processes of alkylation of polynuclear aromatic substrates. Also, these compounds are remarkable in that they are readily soluble in nonpolar and weakly polar solvents.



X = $^{-}$OPh, $^{-}$OC$_6$H$_{11}$

Fig. 1. Examples of fluorinated organic compounds of boron.

Purpose of this work is a developing convenient methods of preparation of organoflouroboranes with different structures and studying the influence of electronic effects of the aromatic substituent on the active site catalytic properties.

In the course of this work, a series of fluorinated organic compounds of boron have been prepared by carrying out a ligand cleavage reaction of potassium fluoride from the corresponding organofluoroborate by the action of 1-buthyl-3-methylimidazolium halide-aluminum chloride ionic liquids and an extracting solvent.

In addition, the acid properties of the resulting compounds using NMR-spectroscopy and their catalytic properties in selective alkylation of aromatic compounds reactions have been studied.

OP-V-12

Homogeneous Manganese Catalysts for the Efficient Hydrogenation of Esters

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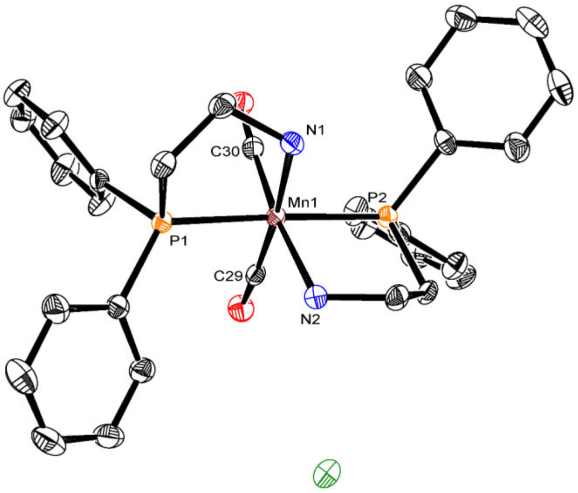
Reduction of carboxylic acid derivatives such as ketones, carboxylic acid esters and nitriles is a fundamental process in the production of fragrances, flavours, pharmaceuticals and fine-chemicals. Catalytic hydrogenations are considered a sustainable and efficient alternative to unselective and wasteful inorganic metal hydride reagents.[1] In a drive to replace scarce and toxic noble metals such as ruthenium, osmium, and iridium, several groups have reported hydrogenation catalysts based on iron, cobalt, and more recently, manganese.[2 - 5]

Potential catalysts were identified by high-throughput screening of a library of metal precursors and ligands known for their activity in catalytic hydrogenation reactions. This approach resulted in the identification of two novel homogeneous Mn catalysts bearing cooperative P,N or NHC ligands, which show high reactivity in ester hydrogenation under mild conditions.[6] Pre-catalysts for the aminophosphine-system were synthesised by reaction of $Mn(CO)_5Br$ and one or two equivalents of the P,N-ligand. Complexes **1** and **2** and were extensively characterised by $^1H/^{31}P$-NMR, ESI-MS, FTIR, elemental analysis, and single-crystal XRD.



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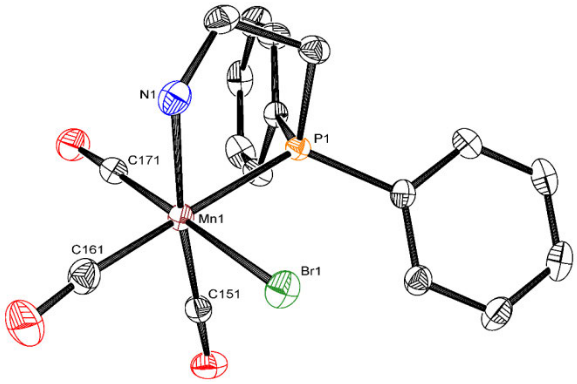
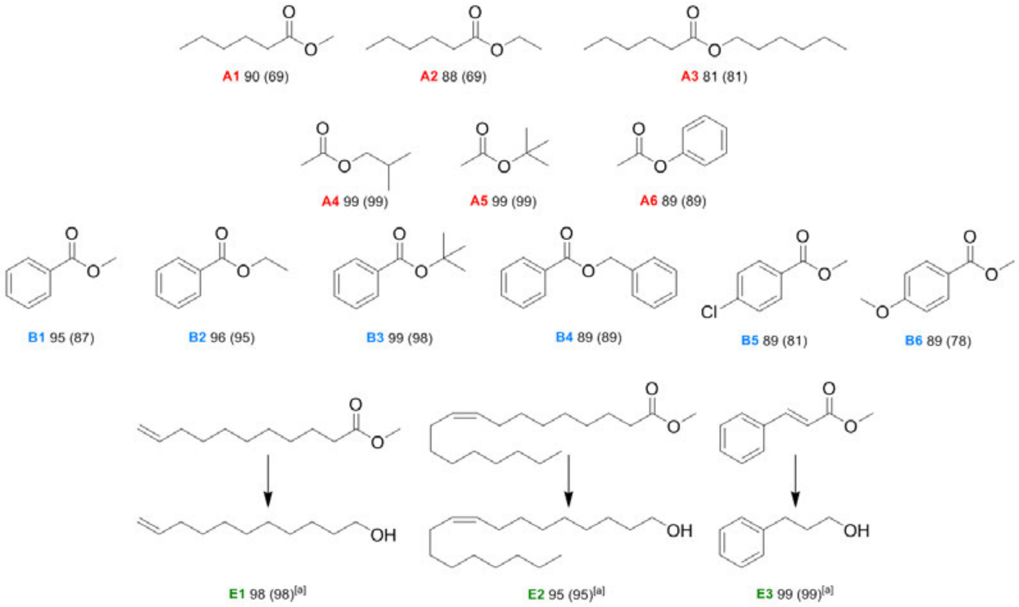


2

Reported catalysts operate at significantly reduced catalyst loading of 0.1 mol%, facilitating quantitative acyl alcohol yields within 24 hours. Reaction progress was highly dependent on base quantity in the case of Mn P,N-catalysts **1** and **2**, while this trend was not observed for the Mn NHCs under study.

OP-V-12

Under optimised conditions, hydrogenation of a variety of aromatic and aliphatic esters was efficient and produced product alcohols in quantitative yield (scheme below). Interestingly, substrates containing internal or terminal alkene functionalities were selectively and quantitatively reduced to the corresponding unsaturated alcohols when the alkene functionality was distant from the ester moiety. Methyl cinnamate (E3), however, was quantitatively reduced to hydrocinnamyl alcohol.



Dedicated kinetic experiments and computational studies were performed to study the critical role of base in the P,N-system. On basis of complementary experimental and computational results a plausible reaction mechanism was proposed that points to inhibition by small alcohols as the primary cause for the observed base requirement. Herein, base was found to be required to regenerate catalytically active metal-amide species via base-assisted alkoxide elimination.

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OP-V-13

Effect of Zeolite Content on Activity and Selectivity NiW/Y-ASA-Al_2O_3 Hydrocracking Catalysts to Diesel Fraction

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1. Introduction. Nowadays the increase in the capacity of heavy oil processing, growth in demand for middle distillates and transition to euro-5 standards of produced fuel take place in oil-refining industry. In addition to the above-mentioned there is an 100% import phase-out of hydrocracking catalysts on the Russian market. This led to the fact that hydrocracking has become one of the most important processes of secondary oil refining. Therefore, the study of hydrocracking catalysts is an important goal. The purpose of this work is to study the effect of the zeolite content in NiW/Y-ASA-Al_2O_3 hydrocracking catalysts on their activity and selectivity to diesel fraction.

2. Experimental/methodology. Supports 5 to 30 wt% of ultrastable zeolite Y (USY) and containing from 45 to 20 wt% amorphous silica-alumina (ASA) with Si/Al=0.9, respectively were prepared by mixing of USY and ASA sample with AlOOH, followed by drying and calcination at 550°C. Similar procedure was used for the preparation of Al_2O_3 and ASA-Al_2O_3 based catalysts. Deposition of metals was carried out by impregnation with aqueous solutions of nickel carbonate, ammonium paratungstate and citric acid. Impregnated catalysts were dried and hydrocracking catalysts were calcined at 550°C (preparation method is described in [1]). NiW/Y-ASA-Al_2O_3 catalysts contained 17 ± 0.5 wt.% W and 2.3 ± 0.1 wt% Ni. NiMo/Al_2O_3 hydrotreating catalyst involved 3.6 wt% Ni and 12.5 wt% Mo and NiW/ASA-Al_2O_3 hydrocracking catalyst – 3.1 wt% Ni and 17.3 wt% W. All catalysts were studied by nitrogen adsorption, XRD, HRTEM and TPD-NH_3.

Hydrocracking tests were carried out under 16.0 MPa, in the range of 360-410°C, using LHSV of 0.71 h^{-1} and H_2/feed ratio of 1500 (v/v). A mixture comprising straight-run VGO (69 wt%), heavy coker gas oil (22 wt%), heavy aromatic extract (7 wt%) and petrolatum (2 wt%) was used as a feed.

3. Results and discussion. The elemental analysis and HRTEM data suggest that NiW/Y-ASA-Al_2O_3 catalysts contain similar sulfided active component**.** The results of VGO hydrocracking over stacked beds containing three catalysts NiMo/Al_2O_3, NiW/ASA-Al_2O_3 and NiW/Y-ASA-Al_2O_3 are obtained. The dependence of fraction yields and net conversion on the temperature is shown in Fig. 1. The dependence of selectivity to diesel on net conversion is shown in Fig. 2.

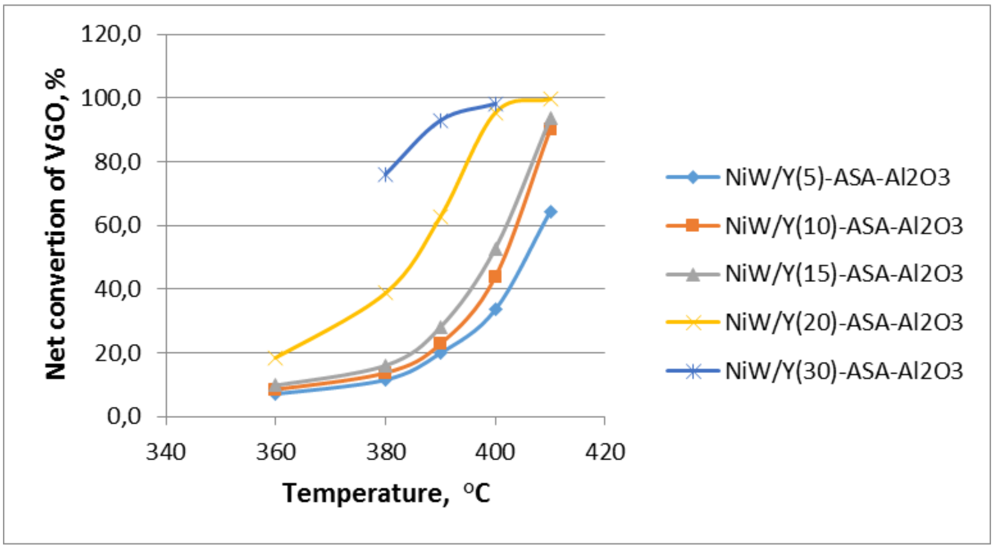

Fig. 1. Selectivity to middle distillates as a function from conversion

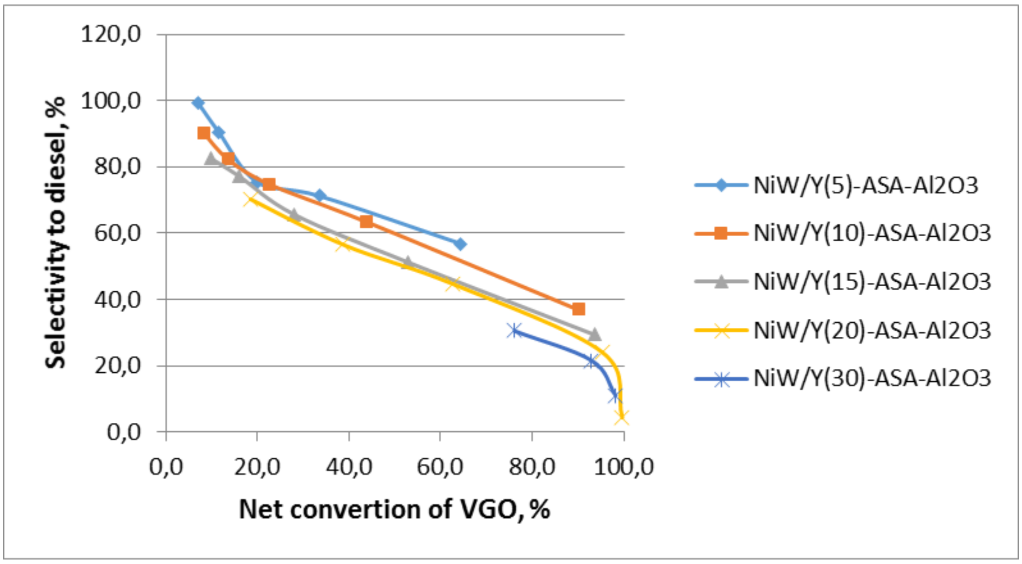

Fig. 2.Dependence of conversion on the temperature

The results show that an increase in the zeolite content in NiW hydrocracking catalyst results in a significant conversion in hydrocracking of VGO, while a significant increase in conversion with increasing temperature can be distinguished. Moreover increase in the content of zeolite in the catalysts leads to a decrease in the selectivity to middle distillates.

4. Conclusions The content of zeolite in hydrocracking catalysts affects the activity and selectivity to diesel fraction.

Acknowledgement. This work was financially supported by the Ministry of Education and Science of the Russian Federation: Project No. 14.610.21.0008, identification number RFMEFI61015X0008.

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OP-V-14

Study of Slurry-Phase Catalytic Steam Cracking of Heavy Oil in Presence of Dispersed Catalysts Formed *In Situ*

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The energy consumption growth and steady decline of light and medium crude oil reserves inevitably lead to the necessity of increasing of unconventional heavy crude oil production. Extraction and refining of heavy and extra-heavy oil are significantly more difficult in comparison with light and medium crude oils mainly due to the higher viscosity, significant content of high-molecular compounds, heteroatoms and metals, and smaller H : C ratio. Upgrading of heavy oil (HO) aimed at production low-viscous synthetic/semi-synthetic oil having improved quality. Currently, catalytic steam cracking of HO is of a strong interest as an alternative pathway to traditional upgrading approaches based on carbon rejection (thermal cracking-based processes) and hydrogen addition (hydrocracking) [1,2]. In this case, water is considered as a source of hydrogen.

The use of dispersed catalysts and processing by means of slurry-phase reactors is nowadays another fast developing approach to heavy petroleum feedstocks upgrading [3]. In the case of hydrothermal process, a suspension of dispersed catalyst, or its precursor in feedstock, and steam are fed into slurry-reactor in form of a continuous upward flow. The precursors of catalysts are decomposed directly in heavy crude or residue *in situ* under high temperature to form dispersed particles of size from a few tens of nanometers to micrometers. The aim of this work is to study the catalytic steam cracking (CSC) process of heavy Tatarstan crude oil (HCO) and vacuum residue (VR) in a slurry-type reactor with the use of dispersed catalysts based on molybdenum, iron, cobalt, and nickel being formed *in situ* in the CSC conditions.

Studies of CSC of HO and vacuum residue (VR) were carried out in a stainless steel tubular slurry-type reactor having an inner diameter of 20 mm and a length of 300 mm. Aqueous solutions of catalysts precursors ($Fe(CHO_2)_3$, $FeSO_4$, $(NH_4)_6Mo_7O_{24}$, $CoCl_2$, $Ni(NO_3)_2$) or their mixtures were introduced into the used HCO or VR via preparation of corresponding reverse emulsions. The emulsions were fed into the reactor at a rate 90 $ml \cdot h^{-1}$ (with or without additional steam supplying). CSC of the feedstocks were carried out at 425 °C and 2.0 MPa kept up by Ar delivery at a rate of 100 $ml \cdot min^{-1}$. Liquid and solid products were analyzed by various physicochemical methods (XRD, SAXS, TEM, XANES/EXAFS, CHNS-analysis, viscosimetry, ASTM-1160).

Previous studies showed that upgrading of HCO via steam cracking leads to an increase in the yield of liquid products comparing to thermal cracking. The HCO having 4.3 wt. % of S content and 48 wt. % of VR fractions ($T_{boiling}$ > 500 °C) was used for the studies. CSC of the HCO in the presence of single metal-containing – iron-, cobalt- nickel- and molybdenum-based catalysts, and bimetallic catalysts leads to an increased yield of both semi-synthetic oil (liquid products in the whole) and synthetic oil (fractions having $T_{boiling}$ < 500 °C) in comparison with steam non-catalytic cracking. It also leads to significant reduction of viscosity (by ~ 99 %) and density of the liquid products in comparison with the feedstock.

Dispersed catalysts allow to reduce diffuision limitations, which is crucially important for heavy oil and especially for vacuum residiue upgrading. The efficiency of this approach depends on a size of catalyst particles formed *in situ*. To understand the genesis of dispersed catalyst, the catalytic dispersion was studied by SAXS (small angle X-ray scattering) technique. In a case of vacuum residue dispersion, sizes of Ni- and Mo- containing particles before CSC were found to be in the range from 2 to 50 nm (Fig.) with avarage size 10 – 15 nm in VR and 7 - 8 nm in HCO. CSC of VR using Mo-containing catalyst also yielded production of semi-synthetic oil with higher content of light fractions ($T_{boiling}$ < 360 °C) as it was shown for HCO.

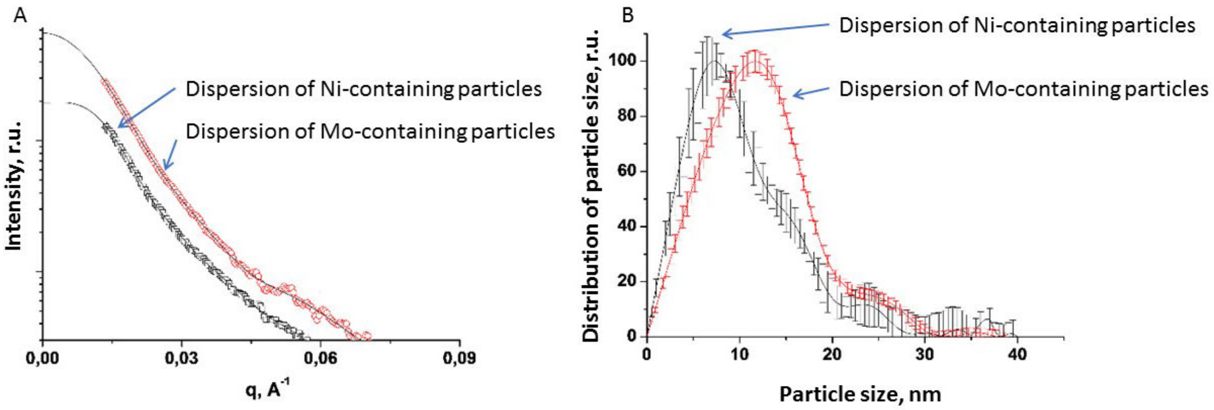

Figure. A) SAXS curves for Ni- and Mo-containing particles in vacuum residue; B) size distributions for Ni- and Mo-containing particles in coke residues.

XRD and TEM investigations of coke residues produced in the CSC of the HCO using the single metal-containing based catalysts showed a presence of MoO_2 and MoS_2, Ni_9S_8 [2, 5], Fe_3O_4 and Fe_2O_3, Co_9S_8 phases after experiments with the use the catalysts based on the corresponding metals.

Acknowledgement. The work is supported by Ministry of education and science of Russian Federation: project No 14.607.21.0172, identification number RFMEFI60717X0172

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OP-V-15

Partial Oxidation of Methane to Synthesis Gas over Structured Catalyst Based on Porous Nickel: The Influence of NiO-MgO Loading on Hot-Spot Temperature

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Addition of synthesis gas to natural gas in an amount of 10-15% leads to greater uniformity of fuel combustion in gas turbines and significant reduction in NO_x and CO emission. Stability of methane catalytic partial oxidation (CPO CH_4) in a catalytic reformer as a part of gas turbine power plant is crucial. Overheating of a catalyst near inlet (hot spot) presents the most dangerous issue because it may lead to catalyst sintering and destruction [1]. From the global kinetic viewpoint [2-4] the process of CPO CH_4 in the oxidation zone (around the hot spot) can be considered as two main parallel reaction pathways: CH_4 combustion (exothermic) and CH_4 steam reforming (endothermic). The ratio between their rates defines both the selectivity to syngas and hot spot temperature. Exothermic reaction is completely controlled by O_2 gas-solid transfer and is insensitive to kinetics. At the same time, endothermic reaction proceeds in a more complex mixed chemical-diffusive regime and is partly influenced by kinetics [2,3]. So, there exists a relation: more active catalyst (with higher endothermic apparent rate) demonstrates lower hot-spot temperature under all other identical conditions [4]. Taking into account extremely fast CPO reaction kinetics and close to thermodynamic equilibrium composition of outlet mixture, accurate measurement of hot-spot temperature may be the reliable and easy way for estimation of catalyst activity and stability under practically relevant conditions (i.e. autothermal operation, monolith catalyst, undiluted feed gas, high temperature). The previous work [5] has demonstrated the perspective of Ni/MgO catalysts based on porous nickel for CPO CH_4.

The aim of this work was study the influence of NiO-MgO loading on the apparent activity of the structured catalyst by measurement of hot-spot temperature.

We used an in-house made catalysts based on porous nickel stripes (trade mark eK0.021.742TU Type 2). The catalysts carriers were in the form of structured cylindrical monoliths formed by alternating flat and corrugated porous nickel stripes (Figure 1).

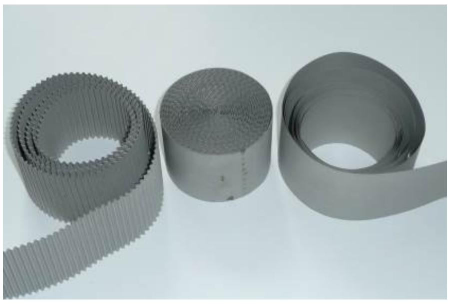

Figure 1.

The series of catalyst blocks has been prepared by wet impregnation method with $Ni(CH_3COO)_2 \cdot 4H_2O$ and $Mg(CH_3COO)_2 \cdot 4H_2O$ aqueous solution with molar ratio Ni:Mg = 1:1, followed by drying and calcination. Difference between catalysts among the series was in NiO-MgO loading that has been obtained by different number of NiO-MgO deposition cycles.

Experiments have been carried out at atmospheric pressure; excess air ratio $\alpha = O_2/(2 \cdot CH_4) = 0.3; 0.35; 0.4$; GHSV = 31200 h^{-1}. Inlet (hot-spot) and outlet temperatures of catalysts block and outlet mixture composition have been measured during experiments.

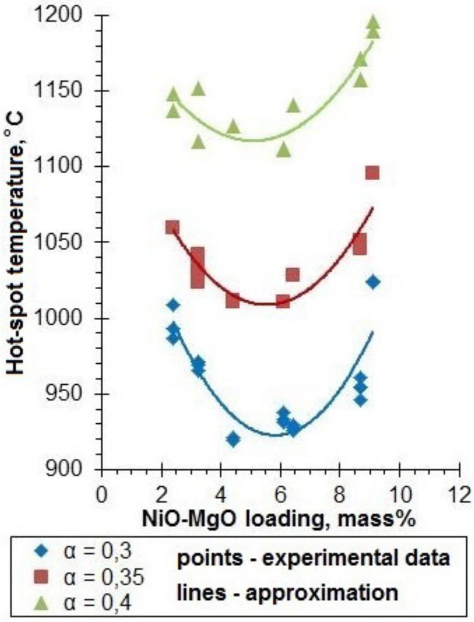

Figure 2.

According to our experimental results, the catalyst hot-spot temperature displays a minimal value at 4-7% NiO-MgO loading (Figure 2). So, the catalyst apparent rate of endothermic reaction pathway should reach its maximal value at that point. As expected, increase of NiO-MgO loading leads to monotonous rise of specific catalyst surface, that was confirmed by argon thermal desorption data. TEM data showed that mean nickel particles diameter is very close for different catalysts (8.5-8.6 nm). Thus, the rising branches of hot-spot temperature curves in Figure 2 cannot be explained by decrease of metal dispersion. Most importantly, the mercury porosimetry data clearly indicates on decreasing of transport pore volume at increasing NiO-MgO loading. Then the extremum of hot-spot temperature dependence under increasing NiO-MgO loading is easily explained as the result of interplay of two opposing factors: increase of volumetric catalyst activity and decrease of porous catalyst permeability. Falling branches on curves (Figure 2) correspond to low loadings, when the increase of volumetric activity with loading prevails over the decrease of permeability, which results in enhancement of apparent rate of endothermic reaction pathway and declining the hot-spot temperature. Rising branches on curves correspond to high loadings, when the intraporous diffusion resistance due to shrinking of transport pores along with NiO-MgO coat thickness growth begins to prevail over increase of volumetric catalyst activity. That results in decrease of apparent rate of endothermic reaction pathway and hot spot temperature rise.

Thus, an optimal NiO-MgO loading was found in this work, which provides a useful guideline for future development of structured catalysts based on porous Ni for CPO CH_4.

Acknowledgement. This work was financially supported by Russian Federation State task for Boreskov Institute of Catalysis, project № 0303-2016-0011.

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OP-VI-1

Photocatalytic Hydrogen Evolution on $Cd_{0.3}Zn_{0.7}S$: the Effect of Hydrothermal Treatment

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Hydrogen seems to be an attractive alternative to traditional energy sources, but it exists in nature in the form of compounds with other elements. Water is an ideal hydrogen source. One of the most effective ways of water splitting is photocatalysis on semiconductors, but catalytic activity in this process is quite low due to the recombination of photogenerated charge carriers on the semiconductor surface. The addition of sacrificial agents in the system reduces the rate of charge recombination and increases the rate of hydrogen evolution. One of the most commonly used sacrificial agents is Na_2S/Na_2SO_3 system [1]. CdS is considered to be one of the most well-known semiconductor photocatalyst. The photocatalytic properties of CdS could be modified by mixing with wide band gap chalcogenide semiconductors such as ZnS [2].

This research was aimed at the study of the influence of the hydrothermal treatment on the photocatalytic activity of $Cd_{1-x}Zn_xS$ photocatalysts. In this study a series of $Cd_{0.3}Zn_{0.7}S$ photocatalysts were prepared by the coprecipitation method with subsequent hydrothermal treatment at different temperatures in the range 80-160 °C in air atmosphere. To measure of the activities of synthesized samples, a water suspension with a catalyst and 0.1M Na_2S/0.1M Na_2SO_3 solution was illuminated with a 450-nm LED. The photocatalytic activities of six samples (prepared via hydrothermal treatment at various temperatures and without the hydrothermal treatment) were investigated in the hydrogen evolution under visible light.

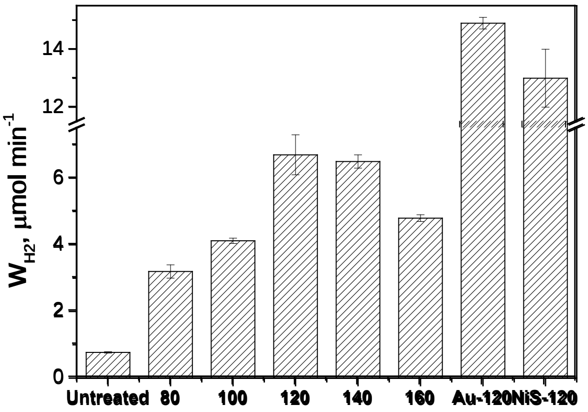

Fig. 1. Photocatalytic activities of $Cd_{0.3}Zn_{0.7}S$ samples.
Conditions: $C_0(Na_2S/Na_2SO_3) = 0.1/0.1M$, $C(cat) = 0.5$ g/L, T = 20 °C

All the photocatalysts after hydrothermal treatment have shown a higher activity than the untreated $Cd_{0.3}Zn_{0.7}S$ sample. The highest rate of hydrogen evolution, which is equal to 8 mmol g^{-1} h^{-1} was obtained for the sample treated at 120 °C. This activity is greater 8.7 times than the photocatalytic activity of the sample without hydrothermal treatment. Further, NiS and Au were deposited on the surface of this $Cd_{0.3}Zn_{0.7}S$ sample. The activities of composite samples equal to 13,0 μmol min^{-1} and 14,9 μmol min^{-1} for $NiS/Cd_{0.3}Zn_{0.7}S$ and $Au/Cd_{0.3}Zn_{0.7}S$, respectively. The results of the kinetic measurements are presented in fig. 1.

The obtained photocatalysts were characterized by XRD technique (Table 1). It was shown after the hydrothermal treatment with the $Cd_{0.3}Zn_{0.7}S$ solid solution is stratified into two phases: ZnS and $Cd_{0.6}Zn_{0.4}S$ solid solution. Also, the solid solution structure changes from cubic to hexagonal at higher temperatures.

Table 1. The properties of the synthesized photocatalysts. APD is average pore diameter, calculated from adsorption branch; ACS is crystallite size calculated using the Scherrer equation; H is hexagonal phase of $Cd_{1-x}Zn_xS$; C is cubic phase of $Cd_{1-x}Zn_xS$.

Sample	Phase content		$Cd_{1-x}Zn_xS$, ACS[1], nm	ZnS, ACS, nm	S_{BET}, m^2/g	APD, nm
As-prepared	$Cd_{0.3}Zn_{0.7}S$ (H/C)		<2	-	147	10
80 °C	$Cd_{0.6}Zn_{0.4}S$ (H/C)	ZnS (cub)	4.8	4.7	180	8
100 °C	$Cd_{0.6}Zn_{0.4}S$ (H/C)	ZnS (cub)	6.6	6.2	138	9
120 °C	$Cd_{0.6}Zn_{0.4}S$ (H)	ZnS (cub)	6.0	7.8	73	14
140 °C	$Cd_{0.6}Zn_{0.4}S$ (H)	ZnS (cub)	7.7	5.0	79	13
160 °C	$Cd_{0.6}Zn_{0.4}S$ (H)	ZnO	8.6	ZnO ~ 60 nm	68	22

Previously, it was shown that the hexagonal phase CdS was more active than the cubic phase [3], and the hexagonal phase content increases with temperature of the cubic CdS heating [4]. An improvement of H_2 evolution in the case of the treated samples likely caused by a change to a hexagonal lattice. With the addition of NiS and Au, photogenerated electrons in $Cd_{0.3}Zn_{0.7}S$ are migrated to the cocatalyst. Owing to the longer lifetime of photogenerated electrons, photocatalytic H_2 evolution rate is improved.

Acknowledgement. This work was conducted within the framework of budget project
No. 0303-2016-0016 for Boreskov Institute of Catalysis.

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OP-VI-2

4-Nitrophenol Photocatalytic Decomposition Using of Organic-Inorganic Copolymers of Poly(Titanium Oxide) Doped by Ag and Au Nanoparticles

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Nowadays, anatase TiO_2 is widely used as photocatalyst in wastewater treatment in the manufacture of dyes, in air purification systems, in the fabrication of self-cleaning glass and solar cells [1]. The photocatalytic properties of TiO_2 are result of the occurrence of UV-induced (λ ~ 350 – 400 nm) reversible single-electron transition $Ti^{4+} + e^- \rightleftarrows Ti^{3+}$.However, its quantum yield in powder TiO_2 is only ~ 15-20%. A significant increase of the charge separation degree up to 50% is achieved in the gels of poly(titanium oxide) (PTO) in alcohol medias. However, it is unstable in the air. One of the ways of increasing the effectiveness of TiO_2-photocatalysts is its doping by metals nanoparticles (NP$_S$). So the actuals task is obtaining of on solid photocatalysts basis on PTO, including modified by noble metals NPs, with high specific surface area and high quantum yield, which can be used in different regions of the spectrum.

The aim of this research was investigation and comparation of the photocatalytic properties of polymer materials based PTO doped by Au or Ag NPs and TiO_2 anatase in the reactions of 4-nitrophenol (4-NP) decomposition reaction. The new optical transparent (T ≥ 90 %) copolymers based on PTO doped by Au or Ag NPs were synthetized by polycondensation-polymerization method using $Ti(OPr^i)_4$, hydroxyethylmethacrylate (HEMA), $AgNO_3$ or $HAuCl_4$ [2]. The PTO chains in the copolymers are self-organized in clusters of average size 6 – 8 nm with a structure close to anatase, uniformly distributed in the organic polymer matrix and chemically bonded with it as it was proven by SIMS, SAXS and XPA. The average sizes of Ag and Au NPs formed in the material were 9 and 12 nm, respectively. The nanocomposites demonstrated the photochromic properties due to UV-induced transition $Ti^{4+} + e^- \rightarrow Ti^{3+}$ similar TiO_2. The quantum yield of this process in the samples was close to 1.

The copolymers and nanocomposites were studied as heterogeneous photocatalysts in the decomposition of 4-nitrophenol (4-NP) in aqueous solutions. The reaction was monitored by optical spectroscopy (Shimadzu UV-1650 PC) as change of the absorption at the wavelength of 470 nm (Fig.1a). Every sample of the material was purified after the experiment used as catalysts again. As it can be seen when copolymer HEMA-PTO was used the maximum conversion of 4-NP decomposition in 60 % was achieved during 150 min. TiO_2 –anatase powder caused the 4-NP decomposition 50% over the same time, for comparison. The copolymers of PTO doped by Au or Ag NPs exhibited higher photocatalytic activity. In this way the 4-NP concentration in the aqueous solution reduced to 30 % and 15 % in the presence of Au and Ag NPs at the same time period correspondingly.

Moreover Au and Ag NPs can absorb photons with wavelengths corresponding to its plasmon resonance - 519 – 540 nm and 400 – 430 nm respectively, and in this connection the photocatalytic properties of nanocomposites samples can take place under visible light irradiation ($\lambda > 410$ nm). Moreover, the materials with PTO doped by Ag NPs exhibited better photocatalytic properties on the contrary with Au NPs. UV-irradiation of p-NP solution for 100 min was caused only 34% conversion of its. In the case of visible light the maximum decomposition conversion of 4-NP was 94% in 12 min under using material with Ag NPs and 88% in 22 min for material with Au NPs. The calculations showed that the photocatalytic decomposition of 4-NP on the initial stages can be described by an equation of the first order. So in the experimental conditions the rate constant of p-NP decomposition were $k_{Ag} = (23.11 \pm 0.16)\cdot10^{-2}\ s^{-1}$ and $k_{Au} = (8.05 \pm 0.13)\cdot10^{-2}\ s^{-1}$ under visible light irradiation.

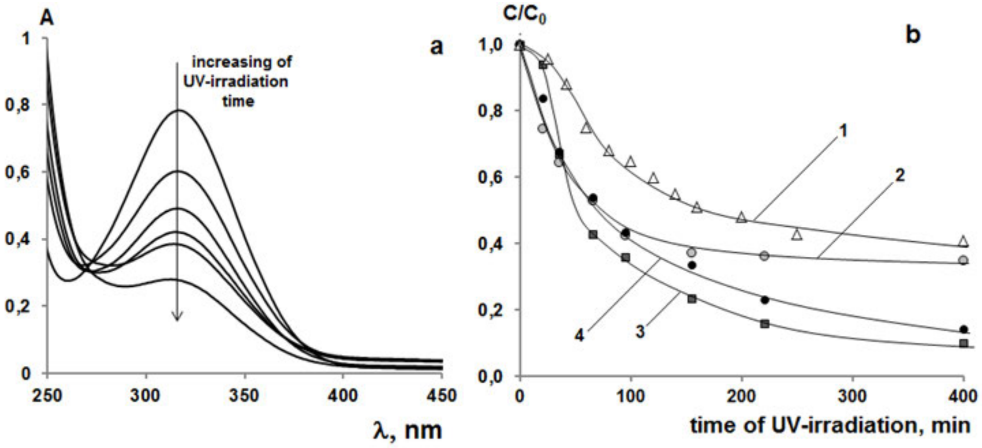

Fig. 1. The photocatytic activity of copolymers under UV-irradiation: (a) the change of absorption spectra of 4-NP in aqueous solution containing the material [HEMA]/[PTO] = 1:6; (b) the change of 4-NP concentration in solution in the presence of TiO_2 –anatase (curve 1), [HEMA]/[PTO] = 1:6 (curve 2), [HEMA]/[PTO] = 1:6 + 0.65 % Ag NPs (curve 3); [HEMA]/[PTO] = 1:6 + 0.51 % Au NPs (curve 4)

Acknowledgement. This work was supported by the scholarship of the President of the Russian Federation

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POSTER PRESENTATIONS

Section 1. Catalysts preparation

PP-I-1 ÷ PP-I-23

Section 2. Characterization and in situ studies of catalysts

PP-II-1 ÷ PP-II-20

Section 3. Mechanism and kinetics of catalytic reactions

PP-III-1 ÷ PP-III-14

Section 4. Catalysis for environmental protection

PP-IV-1 ÷ PP-IV-9

Section 5. Catalysis for fine organic synthesis, natural gas and oil processing, petroleum chemistry

PP-V-1 ÷ PP-V-36

Section 6. Catalysis for energy efficient processes, photocatalysis and electrocatalysis

PP-VI-1 ÷ PP-VI-12

Ruthenium (IV) Oxide Nanoparticles Formed in Hypercrosslinked Polystyrene as Catalysts of Levulinic Acid Hydrogenation

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At present the depletion of world's fossil fuel reserves attracts increasing attention. Thus the search of alternative approaches to energy obtaining, including transformation biomass to fuel components, is of high importance. The important advantages of biomass is its abundance, low cost and the possibility of conversion in platform chemicals [1].

Conversion of lignocellulose via catalytic hydrolysis allows obtaining levulinic acid (LA), which can be further hudrogenated to gamma-valerolactone (GVL). GVL is chemical compound that is used in cosmetic and food industries, as well as for production of "green fuel" and fuel additives [1, 2].

Various catalysts based on noble or non-noble metals supported on inorganic carriers are used for the hydrogenation of LA. According to the literature data, highest yields of GVL can be achieved using ruthenium-containing catalysts, e.g. Ru/C [3, 4]. We have shown that 98% conversion of LA can be achieved while using commercial 5%-Ru/C [4, 5].

Among the organic supports, hypercrosslinked polystyrene (HPS) is known to be successfully used as a support for catalytically active Pd, Pt and Ru nanoparticles (NPs) for different applications [6-8] due to the possibility to control the processes of NP formation. We have found that Ru/HPS (in particularly 5%-Ru/MN100) reveals higher catalytic activity in comparison with the results obtained for 5%-Ru/C in aqueous medium at the identical reaction conditions (temperature 100°C, hydrogen partial pressure 2 MPa, LA-to-catalyst ratio 100 g/g): more that 99% yield of GVL was achieved for 120 min of reaction time.

It is noteworthy that 5%-Ru/MN100 possessed high activity in the LA hydrogenation process at the absence of Ru(0) in the catalyst composition (see Fig. 1).

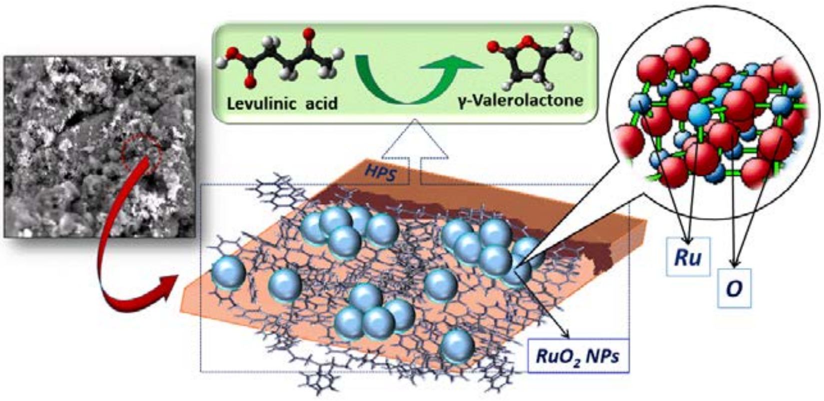

Fig. 1. Schematic representation of Ru/HPS catalyst of LA hydrogenation

The XPS data showed that the surface of 5%-Ru/MN100 contains only RuO_2 with different degree of hydration, while 5%-Ru/C contains both RuO_2 and Ru(0) [9].

The data of scanning electron microscopy (SEM) along with transmission electron microscopy for 5%-Ru/MN100 revealed the presence of small RuO_2 NPs with mean diameter of roughly 3-4 nm, which form aggregates located closer to the outer surface of the polymer (bright regions on SEM micrographs) [5, 9].

Thus, despite the fact that HPS-based catalyst contains aggregates of RuO_2 NPs as an active phase, it can compete with the commercial 5%-Ru/C and can be considered as promising for potential use in LA hydrogenation to GVL.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research (grant 15-08-01469).

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PP-I-2

Concentration of Halloysite Nanotubes from Halloysite-Containing Clay of the Chelyabinsk Region and Their Use as a Carrier for Catalysts

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When catalysts for the petrochemical industry are produced, characteristics of support materials play an important role such as bulk density, specific surface, thermal and chemical stability, etc. Another interesting question is the use of natural materials as catalyst supports.

This paper studies one of such materials - halloysite nanotubes. Halloysite is produced in China, Denmark, Belgium. The US Company Applied Minerals, Inc. is a leading global producer of halloysite clay. In Russia the deposit of halloysite-contained clay is located in Ural region but not yet developed. The investigation deals with clay from Chelybinsk district. Halloysite tubes of this clay are unique because of their characteristic - large linear dimensions, that can be used in the reinforcement of nanocomposite structures.

We used the multistage purificaton of clay for increasing the concentration of halloysite followed by the intercalation of metal ions on the halloysite surface. Results of the multistage purificaton of halloysite-containing clay are shown in Figure 1.

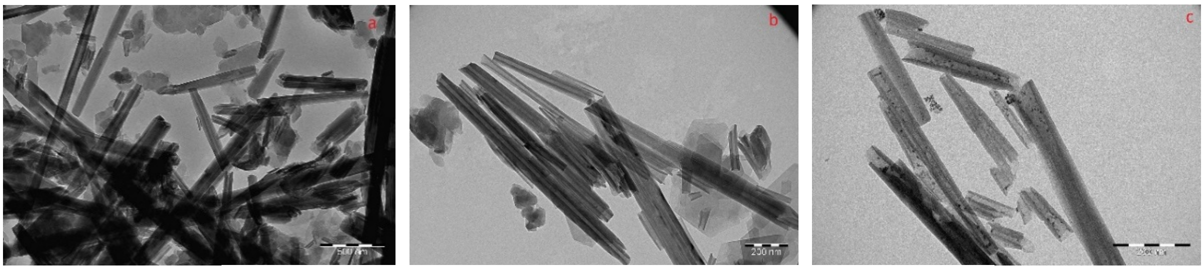

Figure 1. TEM-images of stages of preparation of halloysite.

Platinum nanoparticles were applied to the surface of halloysite. The catalyst obtained was tested in the xylene isomerization process. The experiment was carried out in plug flow reactor. The experimental results are presented in Table 1.

Table 1. The results of isomerization.

Component	Input, % wt.	Output, % wt.
o-xylene	20	32
m-xylene	50	26
p-xylene	20	38
ethylbenzene	10	4

Thus the present investigation confirms the possibility of using the Russian halloysite for catalysts synthesis. The first steps were taken in developing the methods of extracting halloysite from Chelyabinsk's clay.

Acknowledgement. This work was supported by Ministry of Education and Science of the Russian Federation, mega-grant №14.Z50.31.0035.

PP-I-3

The Influence of pH Hydroxide Synthesis on Surface Characteristics of Alumina Obtained by Thermal Decomposition

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Alumina (γ- or η-forms) is a widespread material for catalyst, carrier and adsorbent due to high specific surface area values, a wide range of acid and base centers, stability in the temperature interval corresponding to a big number of catalytic reactions. Surface characteristics regulation is an important problem to be solve by controlled variation of the synthesis parameters [1-2]. The purpose of this research is an investigation of the pH influence during synthesis on the surface characteristics of alumina obtained by thermal decomposition of precipitated hydroxides.

The sample synthesis was carried out by hydroxides precipitation while pH values were 5 and 7 (further these samples are named Al-5 and Al-7 respectively). Aluminum nitrate solution (1 M) was dropped into a reactor at the constant speed, ammonia solution (10% per mass) was dropped discretely with a relay type switch reacting to pH variation from the set value. The measurement error of pH with the electrode is ±0,1 unit. The precipitation was carried out at ambient temperature (22±3°C). After that, precipitates were filtered, wet cakes were dried at 130°C for 4 hours and powders were calcinated at 800°C for 2 hours with a heating rate equaled 400°C/h.

Alumina porosity and surface area were investigated with a method of low-temperature nitrogen adsorption with Quantachrome Nova 1200e. The specific surface area was calculated according to the BET theory; the pore size distributions were calculated from a desorption parts of the isotherms by the BJH method, an evaluation of micropores specific surface area was carried out with t-plot method. The sample degassation was carried out at 290 °C for 1 hour under vacuum. Adsorption/desorption isotherms were plotted with pressure from 0,05 to 0,99 relative to an atmospheric pressure with the pitch 0,05. The added points are 0,98 in a high-pressure field, 0,025 and 0,07 in the low-pressure field and 4 values between 0,3 and 0,5.

Figure 1a shows the adsorption/desorption isotherms. The specific surface area values of two samples are close: 172 m^2/g for Al-5 и 179 m^2/g for Al-7, while the pore size and pore shape of the samples being significantly different. The Al-5 isotherm has two hysteresis loops: one corresponds to the "ink-bottle” pores in the low-pressure field, another one corresponds to the slit-shaped pores in a high-pressure field. The Al-7 isotherm has only one hysteresis loop attributing to "ink-bottle” pores. Figure 1b shows the pore size distributions. Pore mode diameter for the sample Al-5 equals 3 nm, for the sample Al-7 – 7 nm. The micropores specific surface area values are 3 and 5 m^2/g for the samples Al-5 и Al-7 respectively.

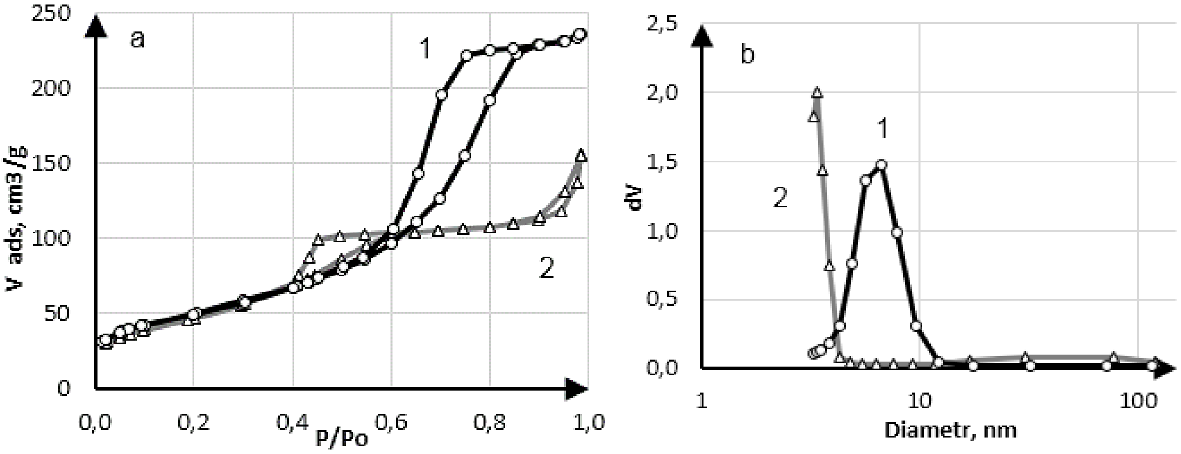

Figure 1 – a) The adsorption/desorption isotherms: Al-7 (1) и Al-5 (2),
b) The pore size distributions: Al-7 (1) и Al-5 (2).

Surface characteristics difference of the samples can be explained with the fact, that in the moment when an acidic drop of aluminum nitrate solution contacts with the reaction volume having pH=7, hydrolysis, polycondensation and formation of the electric double layer happen with higher value of OH^{-}-ion concentration compared to the sample precipitated with pH=5. This fact is a reason for visual difference of hydroxides during precipitation as Al-7 is a gel, Al-5 is a stratifying slurry. In consequence of this fact Al-7 sample pores are shaping during drying process of the gel, for the sample Al-5 they are shaping primarily during the precipitation process.

Thus, it is found, that pH precipitation significantly influences alumina surface characteristics with the oxides generated from hydroxides by means of the thermal decomposition. Hereinafter there are plans to investigate a dependence of an acid-base centers distribution on aluminum oxide surface on the pH of a hydroxide precipitation.

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PP-I-4

Influence of Various Thermal Treatments on Cu-Containing Catalysts Based on Zr-Al Oxides in Ethanol Conversion Reaction

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Copper modified oxide catalysts have been extensively used in environmental catalysis reactions such as methanol synthesis, CO oxidation, NOx reduction, alcohols dehydrogenation [1]. Recently we studied the effect of various activation methods (thermal and plasmochemical) on the catalytic activity of the copper-containing catalyst based on 5%Cu/ZrO2 in ethanol transformations [2]. This research considers the methods of reaction pre-treatment in critical temperatures in order to modify their structural properties.

Among wide variety of materials that has been developed as catalyst supports, this area is still of interest for design of good active metal support. Mixed oxide catalyst based on ceria zirconia and alumina have good structural characteristics and thermal stability and have several applications in heterogeneous catalysts [3-4].

In this study we investigate the effect of preparation method and carrier composition on catalytic performances of 5%Cu/Ce-ZrO_2-Al_2O_3 in conversion of ethanol. The samples were characterized by XRD, XPS, N_2 adsorption and SEM techniques. The experiments revealed that preparation temperature and amount of aluminium oxide strongly affects the reaction selectivity and hence the structural characteristics. We also showed the effect of various activation methods, such as critical temperatures and plasma chemical treatments.

Acknowledgement. The publication was financially supported by the Ministry of Education and Science of the Russian Federation (the Agreement number 02.a03.008).

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PP-I-5

Study of Physico-Chemical Properties of Zeolite-Like SAPO-11 Materials and Their Catalytic Performance in Hydroisomerization Reaction

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Although the production of hierarchical materials is more developed for zeolites, other similar materials such as silicoaluminophosphates (SAPOs) are also interesting due to their particular catalytic properties, especially when mild acidity is required. SAPO-11 (AEL topology) with one-dimensional, nonintersecting ten-membered ring channels and elliptical pore-apertures of 4×6 Å, was first reported by Lok *et al.* [1]. Due to its moderate acidity and suitable pore size, SAPO-11 loaded with a trace amount of noble metal has been found highly active and selective for long chain *n*-paraffins hydroisomerization to produce high quality diesel fuel and lubricants, achieving high isomerization yields and less cracking products [2]. Long chain *n*-paraffins hydroisomerization over metal loaded catalysts proceeds via a bifunctional mechanism [3]. According to Martens *et al.* [4], adsorption and reaction take place at the external surface of the crystals, i.e. at the pore mouths of medium pores molecular catalysts such as MCM-22 or SAPO-11, giving a high amount of isomerization products, especially monobranched isomers.

A number of crystalline silicoaluminophosphate SAPO-11 samples with varying silicon content were prepared using silica sol as a silica source. The synthesized samples were characterized by several chemical and physical methods. It has been found that incorporation of silica into the aluminophosphate structure leads to the formation of composite crystal with hierarchical structure.

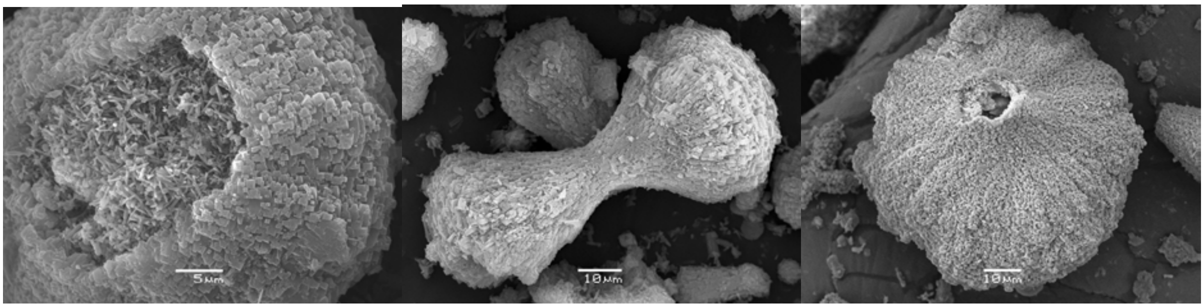


Figure 1 - SEM pictures of hierarchical silicoaluminophosphate SAPO-11 materials synthesized with silica sol.

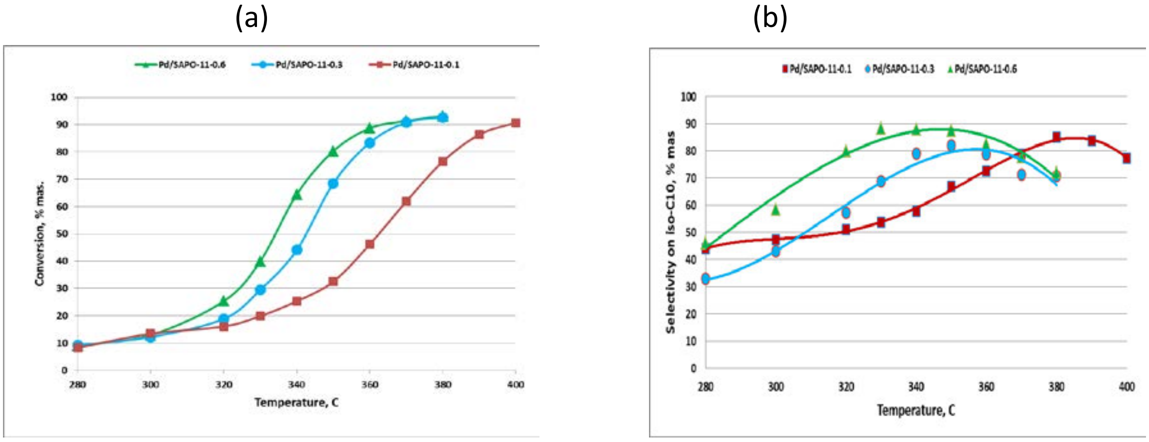
It is evident from the data of Tab. 1 that with the increase of SiO2/Al2O3 molar ratio specific mesopore volume values increase as well, while specific external surface area varies in a minor way. Data of Tab. 2 show the existence of strong acid site in SAPO-11 samples only, not in AlPO-11, concentration of which being practically no influenced with silicon content in the samples.

Table 1. Textural properties of SAPO-11 samples.

Samples	Sp. area, m2/g			Sp. pore volume, cm3/g		
	BET	Micropore	External	Single point	Micropore	Mesopore
ALPO-11	152,0	122,0	30,0	0,08	0,05	0
SAPO-11-P-0,1	213,4	193,0	20,0	0,102	0,074	0,028
SAPO-11-P-0,3	225,0	119,6	25,0	0,122	0,058	0,064
SAPO-11-P-0,6	213,0	195	18,0	0,136	0,074	0,062

Table 2. Broensted acid center concentration in SAPO-11 determined by NH3 TPD method.

Samples	Broensted acid center concentration, mkmol/g		
	Total	weak	strong
ALPO-11	48	48	0
SAPO-11-P-0,1	217	25	246
SAPO-11-P-0,3	311	40	271
SAPO-11-P-0,6	271	30	241



(a)

(b)

Figure 2 - Dependence of n-decane conversion (a) and selectivity of C10 isomers formation (b) on the reaction temperature for Pd/SAPO-11 catalysts.

Our experimental results, showing strong correlation of n-decane conversion and reaction selectivity to decane isomers with specific mesopore volume of the catalysts, support the view on the external surface of SAPO-11 crystals as a right place where the catalytic reaction occurs. The observed growing of mesopore volumes in the synthesized SAPO-11 materials with the increase of Si concentration in them finds its rational explanation in, from one hand, no hindrance effect of silica sol on SAPO-11 crystallization kinetics, and, from the other hand, existence of the limited concentration of Si which can be inserted into AEL type framework.

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PP-I-6

Selective Crystallization of Silicoaluminophosphate SAPO-11

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Silicoaluminophosphate zeolite SAPO-11 is one of the most promising acid components for catalysts for hydroisomerization of n-paraffins, isomerization of n-butenes to isobutylene, methylation of toluene to p-xylene due to the presence of acid sites of "moderate" strength and one-dimensional channel structure [1,2,3]. Despite a large number of publications on the synthesis and use of the aforementioned zeolite in the catalysis, the problem of developing a promising method for its practical synthesis is still urgent [4].

In this paper, we investigated the influence of the chemical and phase composition of the intermediate phases formed upon aging of the initial gel $1.0Al_2O_3 * 1.0P_2O_5 * 0.3SiO_2 * 1.0DPA * 50H_2O$ in the temperature range from 25 to 90°C on the physicochemical properties of silicoaluminophosphates formed upon further crystallization.

Intermediate phases and final materials were characterized by XRD, SEM, N_2 adsorption-desorption (BET analysis), TPD-NH_3, ^{27}Al MAS-NMR, ^{31}P MAS-NMR and ^{29}Si MAS-NMR.

The results showed that only the intermediate phase formed at 90°C allows selective crystallize SAPO-11 of high phase purity and a degree of crystallinity close to 100%.

The silicoaluminophosphate SAPO-11 of high phase purity and degree of crystallinity exhibited a high activity and selectivity in methylation of toluene with methanol.

Acknowledgement. This work was supported by the Russian Science Foundation, grant RSF-DST № 16-43-02010.

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PP-I-7

Synthesis and Functionalization of Merrifield Polymer Divinylbenzene-Chloromethylstyrene Resins for Catalytic Silane Production

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Catalitic disproportionation of trichlorosilane over various catalysts has been studied for years [1, 2, 3]. One of the most promising green catalysts for this process is polymer supported ionic liquids (PSIL) [4]. Merrifield resins are widely used to synthesise catalysts for various processes due to their low cost, the ease of separation from products and versatility in terms of morphology and functionalization [5].

In order to produce PSIL catalysts for gas phase chlorosilane dismutation copolymer divinylbenzene-chloromethylstyrene resin were synthesized (Cl_beads) and then functionalized with imidazole (Imd_beads), 1-Me-imidazole (1-MeImd_beads) and 2-Me-imidazole (2-MeImd_beads).

The following results and data were obtained:

1. SEM and AFM images of the copolymer resin were obtained. The resin is obtained as white microspheres (beads) around 200 µm in diameter (Fig. 1). The AFM topography map shows the microsphere surface has a loose structure with pronounced large-scale relief (Fig. 2). The deflection map shows numerous dark areas, i.e., those with the lowest heights (pores). The pores had the shapes of conical capillaries. The pore size was varied from 40 to 70 nm.

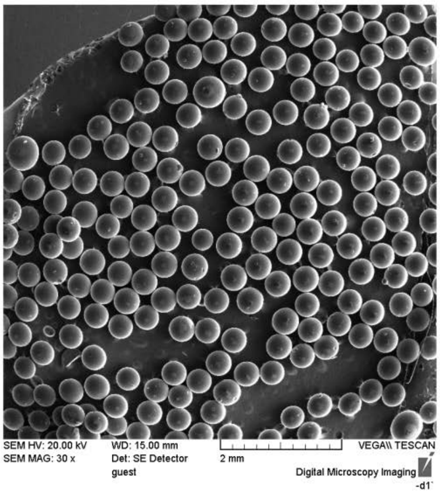

Fig. 1. SEM image of Cl_beads

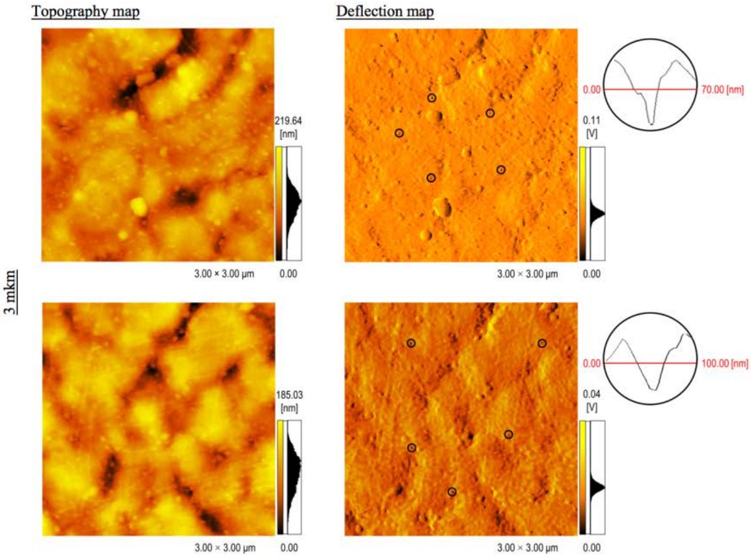

Fig. 2. Topography and deflection maps of Cl_beads obtained with AFM

2. The successful functionalization was confirmed by FT-IR spectroscopy. Bands at 672 cm^{-1} and 1265 cm^{-1} related to vibration of Alk-Cl and $ClCH_2$-Ar bonds respectively disappeared in products' FT-IR spectra.
3. The TPD analysis of initial and functionalized beads was carried out. Thermal stability of polymer resins is rising in an Imd_beads–1-MeImd_beads–2-MeImd_beads–Cl_beads sequence with the lowest starting decomposition temperature of 413 K for imidazole-functionalized resin and the highest one of 473 K for initial non-functionalized chloromethylated polymer beads.
4. In order to establish specific surface area and pore diameter distribution the pore-metric analysis of resins was carried out via BET, STSA and BJV methods (Table 1). Obtained in this work polymer beads have specific surface area around 70 m^2/g and a maximum on pore size distribution curve at 10-40 nm.

Table 1. Specific surface area and pore size distribution maximums of the resins.

Sample	Specific surface area (BET), m^2/g	Specific surface area (STSA), m^2/g	Maximum on a pore size curve, nm
Cl-Beads	70 ± 0.4	85.4 ± 0.4	10 -40
Imd_beads	70.1± 0.4	84.7 ± 1.5	
1-MeImd_beads	40.8± 0.0	34.9 ± 1.0	
2-MeImd_beads	82.1± 0.4	93.2 ± 1.3	

Acknowledgement. This work was supported by the Russian Science Foundation (grant no. 17-73-20275).

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PP-I-8

Synthesis, Properties and Mechanism of the Ion Exchange Resins Based on 2-Methyl-5-Vinylpyridine and Divinylbenzene in the Catalytic Disproportionation of Trichlorosilane

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At present, the main process used to obtain polycrystalline silicon is the Siemens-process. This process has several disadvantages, such as high capital investment, high energy consumption costs, and difficulties in the preparation of electronic-grade polysilicon products. Production of electronic-grade polysilicon by thermal decomposition of silane (SiH4) is attracting greater interest, as it has lower investment and low energy consumption costs, with minimal environmental pollution in production [1, 2, 3]. Currently, silane is mainly produced by the catalytic disproportionation of trichlorosilane (TCS) [4, 5, 6], decomposition of magnesium silicide [7] and variations thereof [8, 9], and plasma treatment [10]. The method of the TCS disproportionation involves a simple process with a lower cost and high industrial safety, compared with the method based on the decomposition of magnesium silicide. The present work is dedicated to synthesise more thermally stable, active catalyst for TCS disproportionation process, study there activity in comparison to industry produced ones, investigate the reaction mechanism, its activation energy and rate determining step.

The following results were obtained:

1. The series of samples of 2-Me-5-vinylpyridin/divinylbenzene copolymer resin with different specific surface area and pore size distribution were synthesized.
2. The obtained samples of copolymer resin were investigated with FTIR spectroscopy, SEM, and TPD analysis. Specific surface area and porosity were determined by low-temperature nitrogen adsorption method (BET). The ion-exchange capacity was determined using titration of chloride-form of the resin with standard $AgNO_3$ solution.
3. The TPD analysis showed that synthesized resin more thermally stable than industry produced one.
4. The catalytic activity of the resin under near equilibrium conditions was examined. The results indicate that the resin with the highest specific surface area has the greatest catalytic activity (conversion value at equilibrium was high up to 99.8%). To further study the kinetics of the disproportionation of TCS, this resin was further studied. It was found that the reaction proceeds in the kinetic region and diffusion is

not a rate-limiting step, the order of reaction was found to be first order, indicating that the reaction order depends on the concentration of TCS, the apparent activation energy of the process was determined to be: Ea = 24,06 ± 0.72 kJ mol−1 (Ea = 34.30 ± 1.03 kJ mol−1 for Amberlyst A-21 resin).

5. The limiting stage of the reaction was found to be the desorption of silane tetrachloride (STC) from the active sites of the resin. In the resin prepared in this study, the desorption process of STC proceeds more easily than in Amberlyst A-21, thus explaining the higher observed catalytic activity.
6. The mechanism including step of $SiCl_3^-$ anion attack on pyridinium-TCS complex has been proposed.

Acknowledgement. The reported study was financially supported by Russian Foundation of Basic Research project No. 16-38-60192 mol_a_dk.

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PP-I-9

Modification Methods for Activation of Al-Zr-Ce Mixed Oxides Catalysts Dopped with Cu for H_2 Production

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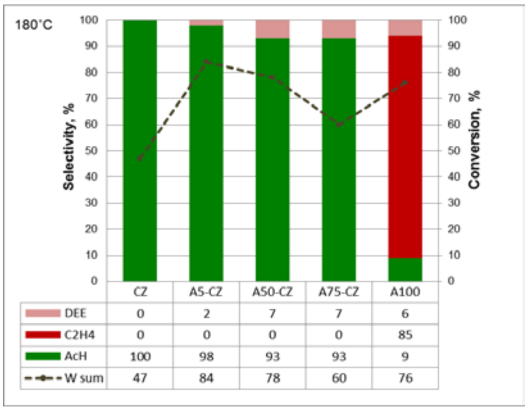
The development of catalysts for ethanol reforming is a very promising direction in the field of searching environmentally friendly alternative fuels in view of the exacerbated environmental problems and global energy crisis.

Mixed oxides of Zr-Ce-Al are actively studied as catalysts in variable catalytic processes including alcohols conversion for obtaining chemically value products [1] as well as a supporting medium for catalyst in oxidation of methanol fuel [2].

In this study we researched the influence of the composition of catalysts supporter and their final synthesis temperature on catalytic activity and selectivity in the processes of ethanol conversion and hydrogen production. Thus, we tested catalysts that consist of ZrO_2-CeO_2-Al_2O_3 mixed oxides, modified by doping with Cu and reduced by H_2. Samples have different composition of Zr-Ce-Al oxide supporters (0%Al_2O_3, 5%Al_2O_3, 50%Al_2O_3, 75%Al_2O_3, and 100% Al_2O_3) and different final synthesis temperature.

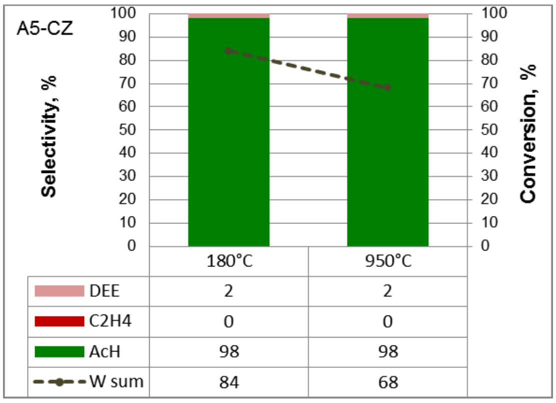
Samples of complex oxide supporting are syntesized by sol-gel method at 180°C and 950°C. Surface modifications with 5%Cu are carried out by impregnation from an aqueous solution of $CuCl_2$. Modified catalysts are undergone hydrogen reduction. The catalytic activity and selectivity of samples is studied in the ethanol conversion reaction in flowing unit the 220-400°C temperature range with gas chromatographic analysis of products. The total surface acidity, Lewis and Brønsted acidity is characterized by pyridine adsorption from solution and CO_2 adsorption. Then, samples are investigated by various physicochemical methods: XRD, REM, N_2-adsorption, EXAFS.

The main process on the samples is the dehydrogenation of ethanol with obtaining acetaldehyde and hydrogen. However, the variation in the supports composition has an effect on the ethanol conversion, as well as on the selectivity of the conversion processes. On the one hand, the increase of Al_2O_3 content in the catalyst lead to cutting down selectivity of dehydrogenation reaction, but the total reaction conversion rise with the addition of aluminum oxide(Fig. 1.). Different final synthesis temperature leads to changing in phase composition of catalysts. This modification does not affect on the process selectivity significantly but inhibits reaction process (Fig. 2.).



	CZ	A5-CZ	A50-CZ	A75-CZ	A100
DEE	0	2	7	7	6
C2H4	0	0	0	0	85
AcH	100	98	93	93	9
W sum	47	84	78	60	76

Figure 1. Selectivity and total conversion of reaction depending on support medium composition on samples with 180°C synthesis temperature.



	180°C	950°C
DEE	2	2
C2H4	0	0
AcH	98	98
W sum	84	68

Figure 2. Selectivity and total conversion of reaction depending on final synthesis temperature on the sample with 5% Al_2O_3.

So this work lets establish patterns between temperature and supporters composition modifications of catalysts and trends in reaction type of ethanol conversion and give a great opportunity to control reaction direction through changing types of catalytic sites.

Acknowledgement. This paper was financially supported by the Ministry of Education and Science of the Russian Federation on the program to improve the competitiveness of Peoples` Friendship University of Russia (RUDN University) among the world`s leading research and education centers in 2016-2020.

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PP-I-10

Control of Active Cr-Sites on the Surface of Chromia–Alumina Catalysts for Dehydrogenation of Isobutane to Isobutylene by Addition of Cu Modifier

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During the last years, production of olefin monomers has increased significantly because of their wide applications in rapid-growing polymer industry. The catalytic dehydrogenation of saturated hydrocarbons (paraffins) is an important refining process and one of the main methods to produce olefin monomers. Chromia-alumina catalysts are widely used for dehydrogenation of paraffins both in processes with fixed-bed (Catofin, Catadiene) and fluidized bed of the catalyst [1]. Chromia–alumina catalysts are studied in oxidative dehydrogenation of light paraffins [2].

Deactivation of chromia–alumina catalysts is associated mainly with aggregation of active component into α-Cr_2O_3 phase, formation of mixed oxides of aluminum and chromium [3]. The isomerization, cracking and coke formation are by-reactions in this process, and occur mainly on acid sites of alumina support. Thus, the new methods of catalyst modification are required to improve the catalytic properties, increase stability and selectivity of chromia–alumina catalysts.

Modification of alumina-chromia catalysts by alkali metals, Si, Zr, etc., to control the functional properties (both acid-base and redox) of the catalyst surface is the main trend to prolong the stability and selectivity of the catalysts. In earlier work [4] the addition of copper into alumina-chromia catalyst was shown to lead to increased activity in isobutane dehydrogenation. The present work is devoted to study of the influence of copper loading in the catalyst on the formation of active chromia sites, acid-base and redox properties of the catalysts and stability in isobutane dehydrogenation.

The series of model catalysts were prepared by impregnation technique. The pseudoboehmite was used as a support precursor. Modification of the support by copper (from 0.5 to 10 % wt. of Cu) was carried out by impregnation of pseudoboehmite with aqueous solution of $Cu(NO_3)_2{*}3H_2O$ followed by drying at 120 ^oC for 12 h and calcination at 750 ^oC for 3 h. To prepare the catalysts, CrO_3 and KNO_3 were used as precursors of active component and alkaline promoter, respectively. Cu-modified alumina supports were impregnated with aqueous solution of CrO_3 and KNO_3 and then dried and calcined at 750 ^oC. The nominal loading of Cr_2O_3 and K_2O in the catalysts was 4.5 and 0.85 % wt., respectively.

To study the synthesized supports and catalysts the methods of the low-temperature N_2 sorption, XRD, H_2-TPR, UV-vis and Raman spectroscopy were used. The catalytic properties of chromia–alumina catalysts were studied in dehydrogenation of isobutane to isobutylene in a fixed-bed reactor in a kinetic mode at 540°C.

Copper was shown to be distributed on the surface of alumina support with formation of a layer of copper aluminate. The CuO was observed by XRD, TPR and UV-vis spectroscopy only in the sample with 10 % wt. content of copper. Using H_2-TPR it was shown that the addition of copper to chromia–alumina catalysts led to increased amount of redox chromium Cr(VI)↔Cr(III) (Fig. 1a) and a shift of peak maximum of Cr(VI) reduction to low-temperature region. The increased amount of Cr(VI) in presence of copper was also confirmed by Raman spectroscopy. The increased activity and selectivity were observed for all copper-modified catalysts in comparison with those for unmodified CrO_x/Al_2O_3 catalyst (Fig. 1b). Thus, the addition of copper provides an increased content of redox chromia in the catalysts, which positively influences on the catalytic properties. The maximum of activity was observed for the catalysts with copper loading of 2 % wt. The subsequent increasing of Cu loading in the catalysts did not provide the growth of activity that may be associated with stabilization of copper as oxide or chromates.

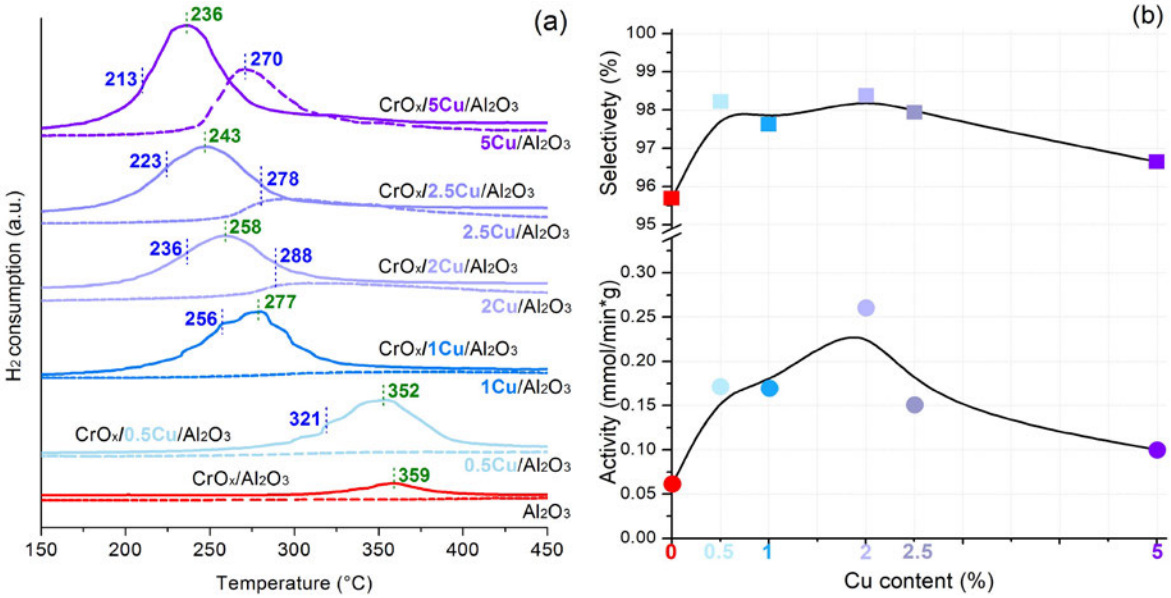

Fig.1 TPR spectra for Cu/Al_2O_3 supports and chromia–alumina catalysts (a) and influence of Cu loading on activity and selectivity of chromia–alumina catalysts (b)

Thus, the influence of copper on formation and stabilization of Cr sites on the surface of CrO_x/Al_2O_3 catalysts was shown. Copper provides activity growth due to an increased amount of redox chromium. The optimal Cu loading in the catalyst is 2 % wt.

Acknowledgement. This scientific research was carried out with the support of the Program for Enhancing the Competitiveness of TSU.

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PP-I-11

Synthesis of Tetrametallic Layered Double Hydroxides

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Layered double hydroxides (LDH) or hydrotalcite-like compounds are materials with layered structure. The general formula for this class of compounds is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[(A^{n-})_{x/n}\cdot mH_2O]$. LDH have a number of unique properties, which depend on their chemical composition and structure [1,2]. The insertion of cations of transition metals into the structure of LDH allows to generate some specific catalytic, magnetic, redox and electrical properties. LDH are known as basic catalysts and especially as catalyst precursors giving rise to fine mixtures of oxides.

The goal of the present work is to synthesize layered double hydroxides containing four types of cations: magnesium and cobalt cations located in the positions of bivalent metal cations in the structure of brucite-like layers and cations of aluminum and iron situated in the positions of triply charged cations. These compounds were expected to have specific catalytic and electrical properties.

MgCo/AlFe-LDHs samples with the following atomic ratio of Mg: Co / Al: Fe = 12: 3: 4: 1 were synthesized by using three different approaches. The first and best known method was co-precipitation. The samples were prepared by co-precipitation of the components from the solutions of the corresponding salts with the solution of precipitant (molar ratio Na_2CO_3: NaOH = 1:8). During the synthesis pH was adjusted to 9-10. Then the precipitate was aged under the mother liquor during the day at room temperature and after that for two days at 98°C. The next method was based on co-precipitation under hydrothermal conditions in the presence of urea. The synthesis was carried out in Autoclave Engineers Parker autoclave for two days at 140°C. pH of the suspension was 10 after the end of the synthesis. The approach makes possible to obtain powders with a well crystallized layered structure. The advantage of hydrothermal synthesis is one-stage and simplicity. The third method consisted of precipitation by urea under the action of microwave radiation. Microwave synthesis was conducted in the reactor system MARS-6. The exposure time of synthesis was 2 minutes under the power 700 Watts. The phase composition of samples was studied by X-ray diffraction (XRD) using Rigaku diffractometer. The XRD patterns of the synthesized samples are shown in Fig. 1.

XRD patterns of the samples look typical for this class of compounds; they have a set of five reflections, which correspond to basal reflections (003), (006), (009), (015), and (018) in the increasing order of diffraction angles 2θ. At high angles (over 56º), the diffraction patterns from LDH samples feature a doublet of the sixth and seventh reflections, which corresponds to basal reflections (110) and (113) [1,2]. Based on the patterns we can conclude that the samples have sufficient degree of crystallinity, which is indicated by rather narrow peaks and high intensity values. The doublet of reflexes is not always well resolved, but its presence also indicates a good crystallinity of the synthesized LDH. Comparing the obtained diffractograms it can be noted that the most intense and narrow peaks are observed for a sample obtained under hydrothermal conditions (MgCo / AlFe-LDH-term). It can be due to an increase in the degree of crystallinity and / or an increase in the crystallite size. However, this sample is not a single-phase product. There are reflexes of impurity phases in the diffractogram. In turn, the peaks are much wider for samples obtained by co-precipitation (MgCo / AlFe-LDH-c) and microwave method (MgCo / AlFe-LDH-mw) but there are practically no extraneous phases.

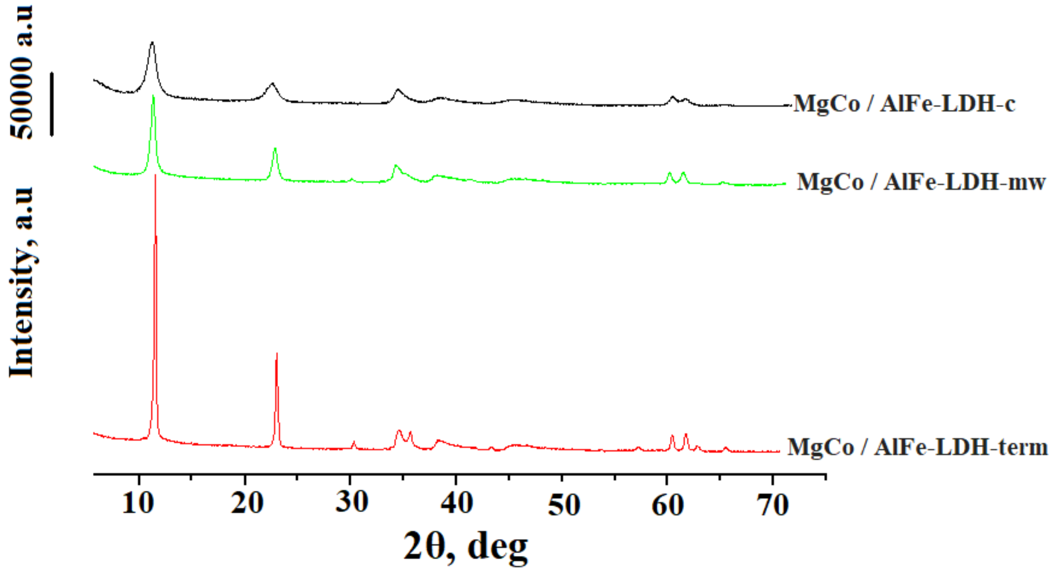

Fig.1. XRD patterns of MgCo/AlFe-LDHs samples synthesized by:
co-precipitation- MgCo / AlFe-LDH-c; microwave method - MgCo / AlFe-LDH-mw;
hydrothermal method- MgCo / AlFe-LDH-term

Based on the obtained data, it can be concluded that the optimal method for obtaining MgCo / AlFe-LDH is the synthesis with microwave treatment. This method is less time- and energy-consuming. It allows to obtain single-phase samples with good crystallinity.

Acknowledgement. This work was worked out at facilities of Joint Research Centre, «Technology and Materials», Belgorod State National Research University.

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PP-I-12

Mono- and Bimetallic $Mo(W)S_2$ /Al_2O_3 and $Mo(W)S_2$/SBA-15 Hydrotreating Catalysts Based on $SiMo_{12}$- and SiW_{12}- Heteropolyacids

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Growing demand for ultrapure motor fuels in combination with strengthening of environmental requirements to these fuels makes it necessary to improve the existing hydrotreating (HDT) catalysts. In this investigation, we report the synthesis and characterization of mono- and bimetallic Mo(W) catalysts prepared by using HPAs of Keggin structure. A comparison of Al_2O_3 and SBA-15 supported Mo(W) catalysts are also made.

Mono- and bimetallic $Mo(W)S_2$ catalysts supported on γ-Al_2O_3 and SBA-15 were synthesized using $H_4SiMo_{12}O_{40}$ и $H_4SiW_{12}O_{40}$ HPAs. All Mo(W)/Al_2O_3 and Mo(W)/SBA-15 catalysts with the equal surface loading of metals (Mo + W)~4 at. nm^{-2}, were prepared by pore volume impregnation of supports. The samples were characterized by N_2 physisorption, temperature-programmed reduction (TPR-H_2), high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS). The catalytic activity in HDT of model feed (1500 ppm of sulfur from dibenzothiophene and 3 wt.% of naphthalene in toluene) was evaluated using a high-pressure bench-scale flow reactor at 320 °C and 3 MPa. Table 1 shows the hydrotreating results for the mixture of DBT and naphthalene over the prepared samples.

Table 1. Catalytic properties of prepared Mo(W)/Al_2O_3 and Mo(W)/SBA-15 catalysts in HDT of a mixture of DBT and naphthalene.

Catalyst	Conversion, %		Rate constants, × 10^5 моль $г^{-1}$ $ч^{-1}$		TOF values, × 10^4 $с^{-1}$	
	DBT	Naphthalene	k_{HDS}	k_{HYD}	TOF_{HDS}	TOF_{HYD}
Mo/Al_2O_3	30.5	24.0	22.4	83.2	3.6	13.9
W/Al_2O_3	2.9	3.9	1.8	12.0	0.5	3.0
MoW/Al_2O_3	12.2	11.9	8.0	38.5	1.8	8.5
Mo/SBA-15	46.1	30.4	62.5	182	13.1	42.7
W/SBA-15	3.9	4.0	4.0	21	1.5	7.7
MoW/SBA-15	11.3	9.8	12.2	52	5.3	22.6

It was found that using of SBA-15 as support led to decrease the average length of the particles of the active phase and increase of the number of slabs per stack and the dispersion of the particles relative to Mo(W)/Al_2O_3 catalysts. The activity results showed that Mo(W)/SBA-15 catalysts had the highest activity in both hydrodesulfurization (HDS) and hydrogenation (HYD) reactions. Moreover, the turnover frequencies numbers (TOF) were calculated. TOF values of the SBA-15 supported catalysts were ~ 3 times higher compared to their analogies on alumina.

It should be marked that when Mo was incorporated to the catalysts with W a large enhancement in catalytic performance was observed compared to pure W samples. This resulted in a better metals sulfidation and consequently, HDS activity increased more than 3 times HYD more than 2.5 irrespective of the support.

Acknowledgement. The research was financial supported by the Russian Science Foundation, project No. 17-73-20386. M. Nikulshina thanks French Ambassy in Russia for the Vernadsky fellowship and Haldor Topsøe Company for the grant to perform her PhD thesis.

PP-I-13

Carbon-Encapsulated Cobalt Particles Fixed in a Rigid CNT Framework: Synthesis by Spark Plasma Sintering and Catalytic Properties in CO Hydrogenation

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Carbon encapsulated metal nanoparticles are known to be active in different catalytic reactions. For example, Pt@C was used for acetylene hydrogenation, N-doped carbon nanosheets embedded with Co nanoparticles were reported to be appropriate catalysts for oxygen reduction reactions, Fe and Ni can activate H_2 in phenylacetylene hydrogenation, Co@C core-shell nanoparticles showed a high catalytic performance in Fischer-Tropsch synthesis [1]. There are several methods to prepare such systems: arc discharge, chemical vapor deposition, metal-template graphitization, spark plasma sintering (SPS) etc. Spark Plasma Sintering (SPS) is a technique utilizing uniaxial force and a pulsed direct electrical current under low atmospheric pressure to perform high speed consolidation of the powder. It is widely used for the synthesis of different materials, mainly ceramics and metal alloys, with carbon additives. Among many other approaches, it stands out for its rapidity, wide range of sintering pressure/temperature, and combination of compaction and sintering stages in one operation [2].

At the same time, important issue for catalysts preparation is the choosing of appropriate support which must have the following properties: thermal and chemical resistance, high thermal conductivity, facilitate uniform surface distribution of catalyst`s particles. Carbon nanotubes (CNTs) meet all these requirements and, besides, show lower degree of metal-support interaction, large surface area, ability to tune the surface properties in a wide range in comparison with oxide supports. SPS treatment of Co/CNT system should provide a simple one-stage technique to obtain novel type of material for catalysis in which Co nanoparticles are already reduced, stabile to oxidation, and rigidly fixed in the support framework. Moreover, such a way results in compaction and densification of CNT-based catalyst which is also important due to low density of carbon nanomaterials.

In the present work a new type of 3D-material contained carbon-encapsulated cobalt nanoparticles in the framework of CNTs was synthesized by SPS to be tested in CO hydrogenation. Co/CNTs composite material was prepared by the impregnation of the multi-walled CNTs by $Co(NO_3)_2{\cdot}6H_2O$ ethanol solution. Samples where annealed at 350 °C for 2 h in N_2 flow in quartz tubular reactor with the inner diameter of 10 mm. It was proved by XRD, TEM, and XPS that Co_3O_4 particles were reduced during the sintering process. Cobalt loading relative to Co^0 was of 10 wt. % and samples were sintered at 800, 900, 1000, and 1200 °C and 30 MPa. Sintered Co/CNT samples were named as “CoTs” where T_S is the sintering temperature. The influence of T_S on the morphology, structure and catalytic properties of this material was investigated by Raman spectroscopy, electron microscopy, XPS, XRD. TEM and SEM images of Co800 sample are shown in Fig. 1. It was established that average diameter of the nanoparticles varied from ~7-8 in case of Co800 to few tens of nm in Co1200. Thickness of graphitic shells around Co increased and their defectiveness decreased with T_S growth. According to the previously obtained data, particle size of 8-10 nm is the most effective for the achieving of optimal balance between activity and selectivity to C_{5+} fraction in CO hydrogenation to hydrocarbons [3]. Thus, samples sintered on 800, 900, 1000, 1200 °C have different carbon shells thickness, density and cobalt particles size increases with the sintering temperature. Most of Co particles in these samples are in metallic state and their nanoscale size make them promising for CO hydrogenation.

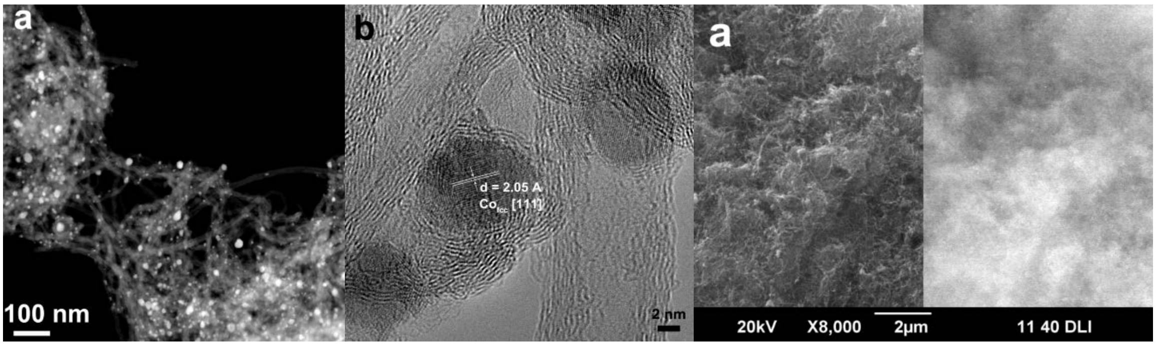

Figure 1. TEM images of Co800 sample; secondary (left) and back-scattered (right) SEM images of 10Co800 (c).

Acknowledgement. The reported study was funded by RFBR according to the research project № 18- 33-00390 in part of catalytic experiments and by RAS Program of Basic Research № 35 in part of material preparation.

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PP-I-14

Influence of Si Source Origin on Physico-Chemical Properties of SAPO-31 Catalysts and Their Performance in Hydroisomerization of n-Decane

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Silicoaluminophosphates with the ATO structure have been synthesized using three types of silicon source (silica sol, metakaolin and tetraethoxysilane). The different sources of silicon were used in order to create intra-crystalline porosity while the later stimulates the growth of nanoparticles aggregates that selfassemble into a mesoporous network (inter-crystalline porosity) [1, 2]. To determine the composition, morphology, and acid properties, SAPO-31 samples have been characterized by various methods. It has been found that the samples synthesized using different silica sources have very different properties. Samples of SAPO-31 synthesized with tetraethoxysilane (TEOS) have a higher acidity and are more active in the catalytic hydroisomerization of *n*-decane as compared with their counterparts prepared with metakaolin (MK) and silica sol (sol). The difference in the effect of the type of silicon source has been explained by morphological features of silica particles formed during the dissolution of silicon source (spherical particles of a ~10 nm size in the case of silica sol, nanoplates of a ~1 nm size in the case of metakaolin and practically molecular size in case tetraethoxysilane). Increase of silica concentration leads to the increase in acid sites concentration in the resulted SAPO-31 samples. Specific external surface area of crystalline samples increases in the following order: sol < MK < TEOS. The obtained results allowed making a conclusion that only acid centers on the external surface of crystals are active in the hydroisomerization of *n*-decane reaction. Dependence of degree of transformation of *n*-decane on the temperature of reaction for different catalysts (0.5Pd/SAPO-31) is brought around to a Fig. 1.

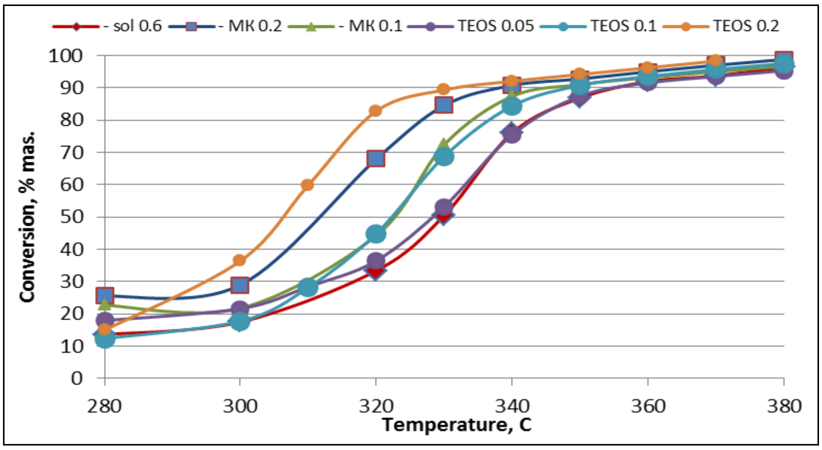

Figure 1 - Dependence of degree of transformation of *n*-decane on the temperature of reaction for different catalysts

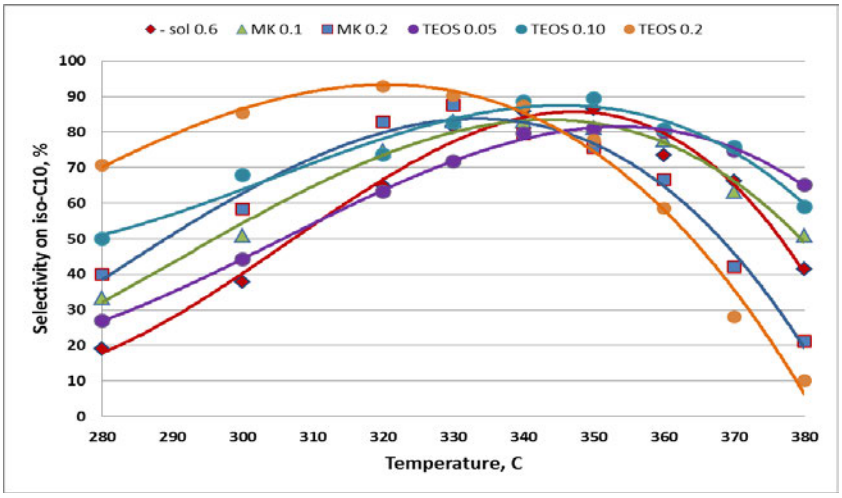

Figure 2 - Dependence of selectivity of isodecane formation on the temperature of reaction for different catalysts

In accordance with Fig. 2 selectivity’s to C10 isomers formation at 340 ºC are very close, 80 – 88%, on all Pd/SAPO-31 catalysts synthesized with different silica sources. Detailed examination shows that isomerization selectivity for different catalysts get its maximal value at different temperatures. Thus, TEOS 0.05 reaches the maximal selectivity of 80% at 360 °C, and TEOS 0.2 reaches 92.9% at 320 °C. At low reaction temperature (280 °C) the ranking of the catalysts in their isomerization selectivity’s coincides with that how they are arranged in increase of their external surface area. At the same time, the actual value of *n*-decane isomerization selectivity is affected from the hydrogenolysis reaction on metallic palladium particles. With the increase of the reaction temperature up to 320 – 350 °C isomerization selectivity of all catalysts increase as well, but further it starts to decrease due to enhanced action of the catalyst’s acid centers. At high reaction temperatures (370 – 380 °C) isomerization selectivity substantially decreases due to preferential formation of the cracking products on acid centers.

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PP-I-15

The Cellulose Hydrogenolysis to Low Alcohols Catalyzed by Ru-Containing Magnetically Recoverable Catalysts

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Biomass processing to value-added chemicals and biofuels received considerable attention due to the renewable nature of the precursors. In particular, ethylene glycol (EG) and propylene glycol (PG), are important precursors for pharmaceuticals, liquid fuels, emulsifiers, and surfactants. The natural resource for the industrial production of these glycols, however, is a fossil fuel, oil. An alternative, “green”, pathway to EG and PG is cellulose catalytic hydrogenolysis in water.

The transformation of cellulose to EG and PG can be carried out as a *one-pot* process in subcritical water with various heterogeneous catalysts [1]. When catalysts are magnetically retrievable, an additional advantage from the environmental point of view is realized [2]. Here, we describe successful one-pot syntheses of EG and PG from cellulose in a sustainable environment of subcritical water using Ru-containing magnetically recoverable catalysts based on magnetic silica.

The synthesis of the catalysts includes three stages: the synthesis of Fe_3O_4-SiO_2, the synthesis of Ru- Fe_3O_4-SiO_2 and the reduction by hydrogen. The samples were characterized by TEM, scanning TEM EDS, XRD, XPS, XRF, magnetic measurements, Nitrogen adsorption measurements etc. The experiments were performed in a steel reactor (50 mL, Parr Instruments, USA) equipped with a controller PARR4843 and a propeller stirrer. Hydrogenolysis was carried out varying the reaction temperature (205-260 °C), reaction time (0 - 60 min), and the catalyst loading. The content of the main products was determined by liquid chromatography using UltiMate 3000 (Dionex, USA).

The dependence of the cellulose conversion on temperature was studyed. At 240 °C it reaches 100 % in 60 min (figure 1). The highest selectivities to EG and PG are observed at 255 °C (12% and 22%, respectively).

We also studied the influence of time on the cellulose conversion and selectivities to EG and PG. Zero time was chosen at the moment when the reaction setup reached the desired temperature (255 °C). At this moment the cellulose conversion was about 80 %. The highest selectivities were observed at 30 min reaction time however, the C_6–C_3 polyols amounts were still significant. By 50 min these polyols were practically absent in the reaction mixture. 100% cellulose conversion was observed at 20 min reaction time.

Our catalysts containing 2 nm Ru NPs in mesoporous Fe_3O_4-SiO_2 with the Ru nominal loading of 1, 3, and 5 wt.% exhibited excellent activities in cellulose hydrogenolysis to EG and PG. The EG and PG selectivities were shown to depend on temperature, reaction time, and

Ru and $Ca(OH)_2$ loadings. The highest selectivities to EG (19%) and PG (20%) were obtained for 50 min at 255 °C, 60 bar hydrogen pressure, 0.1167 mmol of Ru per 1 g of cellulose and 0.195 mole of $Ca(OH)_2$ per 1 mole of cellulose. In these conditions the cellulose conversion was 100%. These factors and the excellent stability of the Ru-Fe_3O_4-SiO_2-3 catalyst in the repeated use after magnetic recovery make this catalyst promising for industrial applications in biomass processing to value-added chemicals and biofuels.

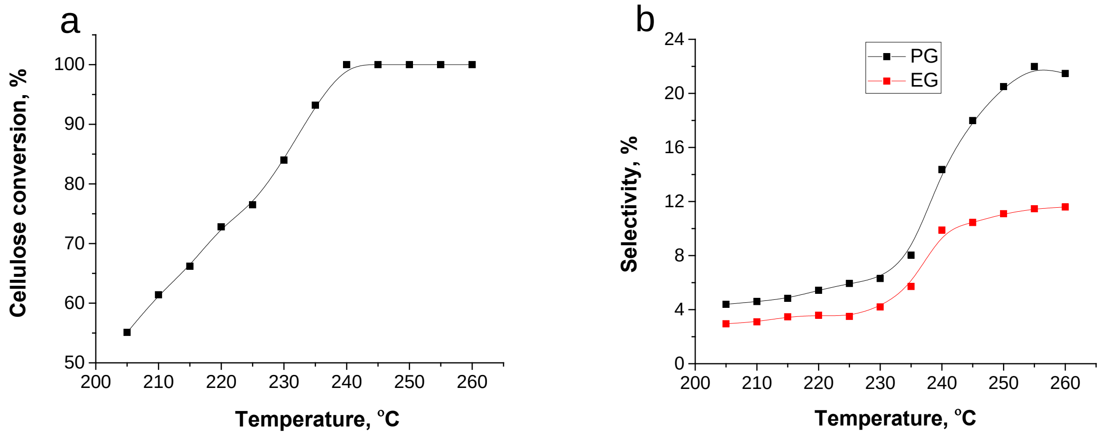

Fig. 1. Cellulose conversion (a) and selectivity to EG and PG (b) over temperature for Ru-Fe_3O_4-SiO_2-3 (0.1167 mmol Ru per 1 g of cellulose; 0.3 g of cellulose; 0.07 g of catalyst; 30 mL of H_2O; P(H_2) 60 bar, 50 min).

The activity and selectivity of the reaction for different catalysts are shown in Table 1.

Table 1. Catalytic activities for EG and PG with the catalysts tested.[a)]

Catalyst	Catalytic activity calculated as a gram of EG or PG per gram of the catalyst per hour, h^{-1}		Specific catalytic activity calculated as a gram of EG or PG per gram of Ru per hour, h^{-1}	
	EG	PG	EG	PG
Ru-Fe_3O_4-SiO_2-1	0.12	0.23	13.39	25.66
Ru-Fe_3O_4-SiO_2-2	0.36	0.68	13.72	25.69
Ru-Fe_3O_4-SiO_2-3	0.62	1.18	13.84	27.02
Ru-Fe_3O_4-SiO_2-3[b)]	0.99	1.08	25.29	27.72

[a)] 0.1167 mmol Ru per 1 g of cellulose; 0.3 g of cellulose; 30 mL of H_2O; 255 °C; P(H_2) 60 bar, 50 min;
[b)] Addition of 0.195 mol of $Ca(OH)_2$ per 1 mol of cellulose.

Acknowledgement. The research leading to these results has received funding from the European Community's Seventh Framework Programme [FP7/2007-2013] under grant agreement no. 604296. O.M., O.K., V.M., and E.S. thank the Russian Foundation for Basic Research (15-08-00455_A and 16-08-00401) and Russian Science Foundation (project 15-13-20015).

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PP-I-16

Selective Oxidation of 2,3,6-Trimethylphenol in the Presence of Magnetically Separated Catalysts

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One of the most significant catalytic processes of fine organic synthesis, serving for the production of synthetic biologically active compounds, is the selective oxidation reaction.

It is planned to refine the parameters of the synthesis of 2,3,5-trimethylhydroquinone (a half-product of vitamin E) (Fig.1) with optimal biocatalysts in a batch reactor. The obtained fundamental and applied data on the kinetics and mechanisms of the 2,3,6-trimethylphenol oxidation process will allow to create in the future innovative technologies for producing biologically active compounds, in demand by the modern pharmaceutical industry. This project proposes the development of a directed synthesis of highly effective catalytic systems of a new generation by immobilizing of enzymes of the class of oxidoreductases to functionalized inorganic carriers, including magnetic separated catalysts. Catalytically active centers formed on the surface of carriers combine the advantages of enzymes (selectivity, activity) and heterogeneous (ease of separation, especially in the case of magnetic separation, and the possibility of modification) catalysts. Depending on the characteristics of the enzyme, carrier, modifier, cross-linking agent and synthesis conditions, the catalytic properties of such systems can be varied.

Increasing requirements for the production of the chemical, pharmaceutical and food industries require the creation of new ways of obtaining of biologically active compounds. A number of currently existing syntheses are based on the selective oxidation of organic compounds [1-3]. The selectivity of the oxidation processes of such as 2,3,6-trimethylphenol compounds to 2,3,5-trimethylhydroquinone (production of vitamin E) is generally not high, and additional stages of separation and removal of by-products occur.

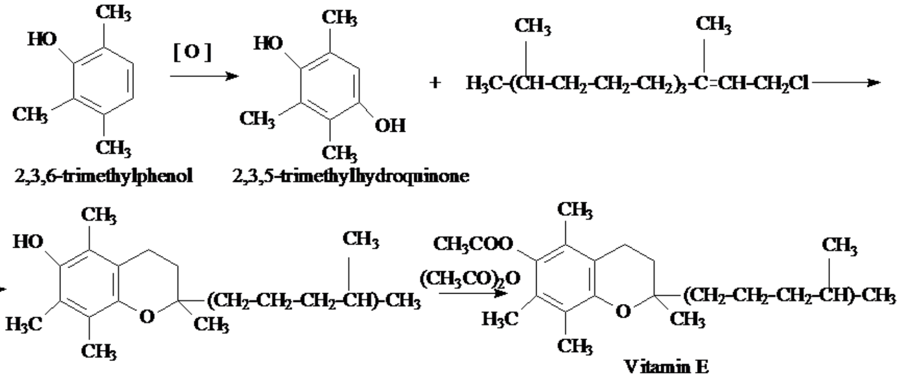

Fig.1. The oxidation of 2,3,6-trimethylphenol compounds to 2,3,5-trimethylhydroquinone (production of vitamin E)

In addition, in these industries there is a problem of using of expensive and toxic oxidants, which inevitably leads to the need to recycle a large amount of waste [4, 5]. Thus, existing production of biologically active compounds requires new catalytic systems. Despite the existing modern developments [6-9] aimed at creating an alternative to existing industrial methods, the problem of increasing of the selectivity of oxidation of the above compounds still remains relevant. The question of the reasons for the selective or nonselective behavior of the catalysts being developed is also open to the public, the answer to which can be given by the study of the kinetic features of the behavior of the catalysts and the mechanism of catalytic selective oxidation of the aforementioned compounds. It is important to note that in the process of developing of new efficient catalytic systems, the creation of biocatalysts, including magnetic separators, is of increasing interest [10 - 13].

Within the framework of the project, biocatalysts will be synthesized for the first time by immobilizing of enzymes of the class of oxidoreductase (peroxidase KF 1.11) on inorganic carriers, including magnetic separators. Effective action of amine-containing modifiers and crosslinking agents on the enzyme immobilization process will be studied. By varying the carrier / modifier / crosslinking agent / enzyme ratio, the catalytic properties of the biocatalysts can be varied.

For the first time, a study of the kinetic features, equilibrium, and mechanisms of selective oxidation reactions of 2,3,6-trimethylphenol using biocatalysts, including magnetic separators will be made. The fundamental principles of selective behavior of the systems obtained during the project will allow to develop new approaches to the synthesis of effective catalysts based on the understanding of equilibrium processes during the catalytic cycle. This will avoid the disadvantages of traditional industrial catalysts, including: (i) increasing the selectivity; (ii) extending the life of the catalyst system; (iii) eliminating undesirable by-products; (iv) facilitating the separation of catalysts in a magnetic field.

Thus, the developed biocatalysts can be characterized as promising research objects that can later be used to implement new technical solutions in the field of catalysis.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 17-19-01408 and Russian Foundation for Basic Researches

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PP-I-17

Structural and Catalytic Characteristics of V_2O_5-MoO_3/Al_2O_3 Catalysts for Oxidative Dehydrogenation of Propane

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Vanadium catalysts are the most studied systems for oxidative dehydrogenation (ODH) of light alkanes [1]. The sample modification with various metal oxides (Mg, Mo, etc.) was shown to improve the catalyst selectivity to the target product [1-3]. However, the surface phase structure and composition of such multicomponent catalysts and their relationship with catalytic properties remain poorly understood.

The present work is focused on the study of formation of the active surface of V_2O_5-MoO_3/Al_2O_3 catalysts for oxidative dehydrogenation of propane.

A set of five catalysts was prepared. NH_4VO_3 and $(NH_4)_6Mo_7O_{24}$ were used as parent compounds of the components deposited. In all cases, to increase the solubility of NH_4VO_3 and $(NH_4)_6Mo_7O_{24}$, oxalic and citric acids were used, respectively. The V_2O_5/Al_2O_3 and MoO_3/Al_2O_3 samples were obtained by incipient wetness impregnation of the alumina support with aqueous solutions of NH_4VO_3 and $(NH_4)_6Mo_7O_{24}$, respectively, followed by calcination at 500 °C. The V_2O_5-MoO_3/Al_2O_3 samples were obtained by subsequent impregnation of V_2O_5/Al_2O_3 and MoO_3/Al_2O_3 samples, respectively, with $(NH_4)_6Mo_7O_{24}$ and NH_4VO_3 solutions, or by combined impregnation of the alumina support with a mixed solution of NH_4VO_3 and $(NH_4)_6Mo_7O_{24}$. The prepared V_2O_5-MoO_3/Al_2O_3 samples were also calcined in air at 500 °C. Textural characteristics, phase composition and structure of the samples obtained were investigated by low-temperature nitrogen adsorption, XRD, UV-vis and Raman spectroscopy. Sample reactivity was investigated by TPR-H_2. The catalytic properties of the samples were studied in oxidative dehydrogenation of propane.

According to the data obtained, the prepared samples do not contain crystalline phases of vanadium and molybdenum oxides. The analysis of nitrogen adsorption data indicates that the supported components are uniformly distributed in the alumina support for all samples. According to the UV-vis spectroscopy data, the supported components are present in the form of surface polymeric vanadium and molybdenum oxide species in V_2O_5/Al_2O_3 and MoO_3/Al_2O_3, respectively. The spectra of all V_2O_5-MoO_3/Al_2O_3 catalysts are identical and primarily caused by the presence of surface polymeric vanadium oxide species. However, the presence of the second component leads to an increase in the intensity of absorption at molybdenum on the structure and electronic configuration of the surface vanadium oxide phases.

The composition and structural characteristics of the formed surface phases in the V_2O_5-MoO_3/Al_2O_3 catalysts, and their interconnection with the reactivity and catalytic properties is discussed in details.

Acknowledgement. This work was supported by "The Tomsk State University Academic D.I. Mendeleev Fund Program" grant.

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PP-I-18

Effect of Preparation Method on the Morphology of MoS_2 Phase and Catalytic Performance of MoS_2/Al_2O_3 Catalysts in HDO of Rapeseed Oil

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The growing demand for transportation fuels along with the vital tendency to reduce the greenhouse gas emissions have stimulated the development of new catalysts for the production of liquid transportation fuels from the renewable resources. The hydroprocessing of triglyceride-based feedstock gives the mixture of alkanes, which are the valuable components for the improvement of the petroleum-based motor fuels properties. The HDO of triglycerides over sulfide $Co(Ni)Mo/Al_2O_3$ catalysts proceeds through the deoxygenation (with the water formation) or via decarbonylation/decarboxylation (with CO_x production) pathways, the latter route is undesirable because of ecological and technological reasons. The non-promoted sulfide MoS_2/Al_2O_3 catalyst was shown to provide RSO conversion without considerable COx formation [1], becoming the promising candidates for the HDO of triglycerides. In our work the effect of preparation method on the state of the active phase and the performance of MoS_2/Al_2O_3 catalysts in HDO of rapeseed oil (RSO) was investigated.

MoS_2/Al_2O_3 catalysts (~13 wt.% of Mo) were prepared by the impregnation of full-sized γ-Al_2O_3 granules (d~1,2 mm, l - 4-6 mm) with the solution differing in composition: first one was prepared using MoO_3 and citric acid (MoS_2/Al_2O_3); second solution except MoO_3 and citric acid (CA) contained H_3PO_4 (P-MoS_2/Al_2O_3). The samples were dried in flowing nitrogen at room temperature and then at 110 °C for 4 hours; the obtained catalysts were heated in 5%H_2S/H_2 flow to transform precursors into the sulfide MoS_2 phase. The catalytic experiments were performed in a trickle-bed down-flow reactor at H_2 pressure 4.0 MPa, H/C – 300 Nm^3/m^3; LHSV – 1.5 h^{-1}, temperature – 260, 280, 300, 320 and 340°C; using mixture of 20 wt.% of RSO diluted with straight run gas oil (SRGO). HRTEM studies were carried out using a JEOL JEM-2010 electron microscope with 1.4 Å lattice resolution at a 200 kV accelerating potential. XRD investigations were carried out at an ARL X'TRA diffractometer (Thermo, Switzerland) with a Si(Li) solid-state detector and Cu K_α radiation. The measurements were carried out in the 2θ range of 10°-80° with a step of 0.1°. Phase analysis was performed using the ICDD PDF-2 database.

The results of catalytic testing of the MoS_2/Al_2O_3 and P-MoS_2/Al_2O_3 led us to several conclusion. First of all, the result of CO_x analysis in the exit gas flow confirmed the high selectivity of RSO hydrodeoxygenation though the "direct" HDO route over both catalysts. Although the CO_x content was slightly increased with the temperature raising the selectivity of $DeCO_x$ pathway did not exceed 3.0% even at 340°C. Degree of RSO hydrodeoxygenation (monitored as oxygen content in the liquid products by means of Vario EL Cube analyzer) achieved 100% at 320-340°C over both catalysts; but P-MoS_2/Al_2O_3 catalyst demonstrated higher HDO activity at

260, 280 and 300°C. P-MoS_2/Al_2O_3 catalyst as well displayed higher activity in HDS of SRGO in comparison with MoS_2/Al_2O_3 catalyst in the whole temperature range.

Powder X-ray diffraction (XRD) analysis and high-resolution transmission electron microscopy (HRTEM) were used to study the structure and dispersion of the supported MoS_2 particles in the sulfide catalysts, the results are presented in the table 1. The Debye Function Analysis (DFA) was used to extract information on the structure of MoS_2 nanoparticles from the XRD data. The Debye Scattering Equation (DSE) allows calculating XRD pattern of model nanoparticle with taking into account the particle shape, size, chemical composition, and atomic structure [2-4]. Calculating and fitting XRD patterns were performed using the DIANNA software [5].The agreement between the calculated and experimental XRD profiles was evaluated using a profile discrepancy factor (R_p).

The obtained data show that MoS_2 particles in the P-MoS_2/Al_2O_3 catalyst are characterized by a lower average size of coherently scattering domain d_{XRD}. The best fitting results were obtained at the slab sizes of 2.5 and 3.2-3.5 nm for P-MoS_2/Al_2O_3 and MoS_2/Al_2O_3catalysts, respectively. A comparison of the particle sizes evaluated from XRD and HRTEM data shows a pronounced discrepancy. The dimensions of the coherent scattering domains determined from XRD data are significantly smaller than slab length of MoS_2 determined from HRTEM data. The discrepancy is explained by deformation of MoS_2 particles, which leads to breaking coherence. Indeed, the MoS_2 sheets observed in the HRTEM images are curved or folded. A lower value of d_{XRD} in the case of P-MoS_2/Al_2O_3 catalyst seems to result from a higher degree of deformation of the supported MoS_2 particles. Higher degree of deformation in turn could be a reason of higher activity of P-MoS_2/Al_2O_3 catalyst in HDO and HDS reactions.

Table 1. Dispersion of MoS_2 particles in the sulfide catalysts from the XRD and HRTEM data

P-MoS_2/Al_2O_3		MoS_2/Al_2O_3	
average slab length of MoS_2 crystallites according to the XRD data modeling			
d_{XRD} (nm)	R_p (%)	d_{XRD} (nm)	R_p(%)
2.2x2.2	8.3	2.5x2.5	9.0
2.5x2.5	**7.7**	2.8x2.8	8.5
2.8x2.8	8.2	3.2x3.2	7.9
		3.5x3.5	**7.8**
		3.8x3.8	8.6
average slab length of MoS_2 particles according to the HRTEM data			
4.6		4.9	
average stacking number according to the HRTEM data			
1.6		1.6	

Aknowledgement. This work was supported by the Ministry of Education and Science of the Russian Federation, project № 14.575.21.0128, unique identificator RFMEFI57517X0128.

PP-I-18

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PP-I-19

Synthesis, Structure and the Photocatalytic Properties of $B_2O_3/TiO_2/Ag$ Material

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Currently, most investigations in the field of heterogeneous photocatalysis are focused on researching of new materials based on titanium dioxide. Primarily, this is due to its high oxidizing and reducing powers in photoinduced state, low cost, high chemical stability in different media and non-toxicity. However, these materials have a number of drawbacks: high recombination rate of photoinduced electron-hole pairs, exciton production only under UV light, low mechanical strength of materials with a high specific surface area and a reduced photocatalytic activity in alkaline and neutral media. The solution of the last two problems may be found in the deposition of the photocatalyst on a stable porous framework [1], which, on the one hand, does not allow photocatalyst to crumble, and, on the other, does not reduce its specific surface area. Furthermore, the use of an acidic oxide to make a skeleton allows creating local centres of acid catalysis in aqueous medium. In this article, the synthesis of the new $B_2O_3/TiO_2/Ag$ materials with a developed surface is discussed. Attention is also paid to their structure and photocatalytic properties.

The authors of this study propose several synthesis protocols. According to them, organic fibrous template was first soaked in aqueous H_3BO_3 solution, and then immerges in titanium (IV) alkoxide solution in propanol-2, dried, and calcinated in the air at 650-950 °C. Modification of composite by the silver nanoparticles was carried out by thermal or photochemical decomposition silver nitrate, whose concentration in the impregnating composition is 1×10^{-3} mol/l. Pure mesoporous TiO_2 prepared according to the procedure described in [2] was used as reference samples in the analysis of structure and properties of frame photocatalysts. The catalytic properties of the synthesized samples were investigated in the reaction of the photochemical degradation of methyl orange.

The IR spectroscopic data confirmed the absence of traces of organic template in both B_2O_3 and B_2O_3/TiO_2 samples. XRD patterns show a set of well-defined reflections typical of materials containing anatase and B_2O_3. Diffraction peaks at 2ϑ equal to 25.4 (101), 38.3 (004), 48.2° (200) is indexed as anatase phase of TiO_2 (PDF# 00-001-0562) whereas diffraction peaks at 2ϑ equal 14.95 (111), 27.90° (310) is related to cubic crystalline phases of B_2O_3 (PDF# 00-006-0297). The average crystallite size of anatase phase calculated by using Scherer equation is about 22 nm. The peaks observed at 38.1 (111) and 44.5° (200) belong to cubic crystalline phase of silver (PDF# 00-004-0783) in $B_2O_3/TiO_2/Ag$.

TEM image (Fig. 1a) shows that the sample consists of individual crystallites apparently embedded in a matrix of amorphous-like phase, rather than separated by grain boundaries. A typical example of anatase crystallite is presented in Fig. 1b. Crystallites identification was carried out at a careful examination of *d*-spacing of the high resolution TEM patterns. According TEM images average size of the silver crystallites is 22 nm (Fig. 1c).

The results of photodecomposition of methyl orange under UV-irradiation (λ_{exit} 254 nm) in the presence of the synthesized photocatalysts are presented in Table. Thermal and photochemical modification of B_2O_3/TiO_2 with silver nanoparticles allows maintaining a relatively constant degradation rate over a wide concentration range that makes possible the fullest decomposition. Also, the advantage of Ag-containing samples is the maintenance of their structure during photodecomposition that eliminates the need for subsequent separation of the catalyst and used irradiated solution.

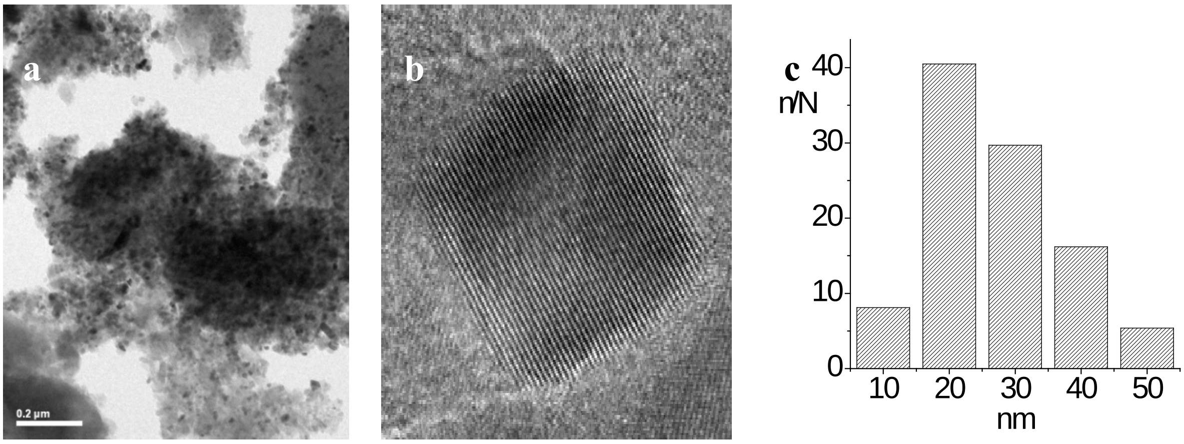

Figure 1. (a) TEM image of *$H_3BO_3/TiO_2/Ag$ sample;* (b) HR TEM image of *$H_3BO_3/TiO_2/Ag$ sample;* (c) Size distribution of silver *crystallites*.

Table. Dependence of the relative rate of photodecomposition of methyl orange on the composition of the catalyst

Sample	Relative rate of decomposition
TiO_2	1
B_2O_3/TiO_2	1,96
B_2O_3/TiO_2/Ag(therm.)	2,58
B_2O_3/TiO_2/Ag (photochem.)	3,02

Acknowledgement. Authors would like to thank Prof. T.B. Boitsova for help in discussing the results.

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PP-I-20

The Study of the Properties of Enzymes Immobilized on Modified Titanium Dioxide

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The aim of this work is co-immobilization of enzymes of oxidoreductases class (horseradish peroxidase and glucose oxidase) on a modified titanium dioxide and testing of activity of the obtained heterogeneous biocatalyst.

Organic substances of phenolic series constitute a large group of particularly hazardous organic contaminants of the aquatic media, therefore, the detection of these compounds and purification of water from them is one of the important environmental problems [1, 2]. The use of enzymes allows overcoming the shortcomings of existing methods of water treatment, and much attention is paid to methods of their immobilization [3].

Horseradish peroxidase (HRP) was obtained from the core of the root of horseradish (Armoracia rusticana) by standard methods [4]. The source of glucose oxidase (GOX) – medication Multifect® GO 1500L (Genencor, A Danisco Division). Modification of titanium dioxide was carried out as follows: the sample of TiO2 (0.5 g) successively aged in 25 ml of 0.1 n hydrochloric acid solution (1 hour), 50 ml of 0.2% solution of chitosan (1 hour), 4 ml of 5% solution of 3-aminopropyltriethoxysilane (1 hour), 50 ml of 2% solution of the dialdehyde glutaraldehyde (24 hours). The obtained modified carrier was hold in the enzymatic solution (1 hour).

All stages of preparation of the biocatalyst was carried out with an intermediate washing with distilled water and filtering. Determination of the activity of the synthesized biocatalyst was carried out in the course of oxidation of 4-chlorophenol in presence of hydrogen peroxide (derived from the oxidation of glucose by glucose oxidase) and 4-aminoantipyrine to change the optical density of the reaction mixture at a wavelength of 506 nm [5]:

$$\beta\text{-D-glucose} + O_2 + H_2O \xrightarrow{GOX} \text{Gluconicacid} + H_2O_2 \qquad (1)$$

$$H_2O_2 + \text{4-chlorophenol} + \text{4-ААП} \xrightarrow{HRP} \text{Quioneimine} + 2H_2O + HCl \qquad (2)$$

The family of curves presented in the figure 1. Kinetic parameters of native enzymes and immobilized system are given in the table 1.

The decrease in values of kinetic parameters of immobilized systems is related to system heterogenization and limited access of molecules of substrates to the active sites of enzymes [6].Thus the possibility of enzymes immobilizing on a modified titanium dioxide was demonstrated, the resulting catalyst is active and can be used for detection and removal of chlorophenolic contaminants from aqueous media.

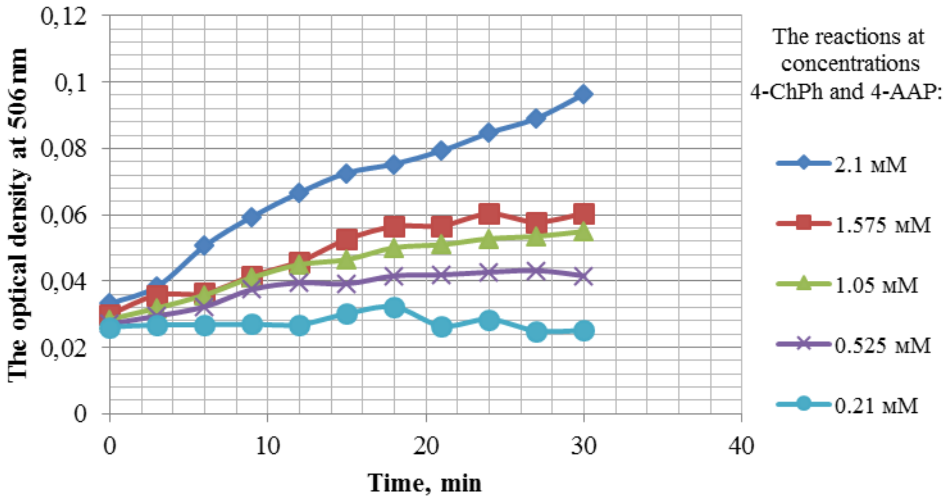

Figure 1 - Oxidation of 4-chlorophenol with heterogeneous biocatalyst

Table 1 - Kinetic parameters of catalytic systems

Catalytic systems	Kinetic parameter	
	Vm× 10^3, mmol/l·s	*Км*, mmol/l
Enzymatic solution	3.327	0.034868
Biocatalyst	1.074	0.152758

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 15- 08-00534.

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PP-I-21

Effect of High-Temperature Treatment on Acidic and Catalytic Properties of a Zn-Containing ZSM-5 Zeolite

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During the extraction of oil and natural gas, a significant amount of light hydrocarbons, mainly C_2-C_4 alkanes are extracted, which do not find adequate use in the oil producing areas. Their transportation in a gaseous state through the main pipeline is difficult. A possible way to put them to good use is their processing into liquid products (aromatic compounds), whose transportation is easy. The efficiency of the process of aromatization of light alkanes is mainly influenced by the zeolite-containing catalyst used and the reaction conditions. To increase the formation of desired product, chemical and thermal modifications of the zeolite are used. One of the methods of thermal modification of a zeolite is its high-temperature treatment in an air atmosphere, which allows to regulate the ratio of active sites of different types of catalyst and, as a consequence, the route of conversion of lower alkanes. The purpose of this work is to study the effect of preliminary high-temperature treatment of a zinc-containing zeolite on its acid and catalytic properties during the process of propane conversion into aromatic hydrocarbons.

For investigation purposes a high-silica zeolite of the pentasil family with a SiO_2/Al_2O_3 = 40 molar ratio was synthesized. Zinc was introduced by impregnating zeolite with an aqueous solution of zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$). The concentration of zinc in the catalyst expressed in terms of the metal was 3.0% by weight. To study the effect of calcination temperature on the properties of catalyst, it was treated in an air atmosphere at 400-800 °C for 6 hours at each temperature.

The acidic properties of Ga-containing catalysts were tested by the method of temperature-programmed desorption of ammonia, which allows determining not only strong, but also weak acid sites (TPD).

The catalysts under study were tested in the course of a propane conversion in a flow-type reactor at an atmospheric pressure, 400-600 ° C, and the feed space velocity 500 h^{-1}. The reaction products were analyzed by GLC using a Chromatek-Kristall 5000.2 chromatograph. In order to estimate the catalytic activity of the samples, the degree of propane conversion was estimated. The yield and formation selectivity of the gaseous and liquid products were also calculated.

The conducted investigation showed that an appreciable transformation of propane over an uncalcined zinc-containing zeolite begins at a reaction temperature of 450 °C, while the desired products i.e. aromatic hydrocarbons are formed at 500 °C or higher. By-products are represented by gaseous hydrocarbons – methane and ethane and trace amounts of hydrogen, C_2-C_4 olefins, and unconverted propane are also observed. The degree of propane conversion and selectivity towards the formation of aromatic hydrocarbons increases with increasing process temperature. At a reaction temperature of 600 °C, the selectivity towards the formation of aromatic hydrocarbons over the initial sample reaches 39%, while the degree of propane conversion is 100%. Preliminary calcination of the Zn-containing zeolite at 400 °C results in an increase in its total and aromatization activities. At a reaction temperature of 550 ° C, the amount of aromatic hydrocarbons formed over this sample increases by 5.7% compared to the uncalcined catalyst. For the Zn/ZSM-5 sample calcined at 500 °C, a further increase in the aromatization activity is observed. Hence the yield of aromatic hydrocarbons reaches a maximum value (44%) with a 100% conversion of propane at a reaction temperature of 600 °C. An increase in the temperature of catalyst treatment to 600 °C and higher results in a decrease in the degree of propane conversion and the yield of aromatic hydrocarbons. For the Zn/ZSM-5 sample calcined at 800 °C, the selectivity towards the formation of aromatic hydrocarbons at 550 °C is only 16.6%, while the degree of propane conversion is 42%. The products formed over this catalyst contain a large amount of C_2-C_4 olefins, whose selectivity towards their formation varies from 13.1 to 36.4% vs the process temperature, which indicates a decrease in the activity of the catalyst in the oligomerization reaction involving protonic acid sites.

The fraction of monoaromatic hydrocarbons (benzene, toluene, and xylenes) in formed liquid products increases with increasing temperature of calcination of the Zn-containing zeolite, while the formation of naphthalene hydrocarbons decreases substantially.

The pattern of changes in the degree of propane conversion and selectivity towards the product formation are due to changes in acidic properties of the Zn-containing zeolite catalyst during its calcination at various temperatures. An increase in the temperature of catalyst treatment results in a significant decrease in the concentration of its strong acid sites and a slight decrease in the concentration of weak acid sites characterized by higher thermal stability. In addition, when the catalyst is treated at high temperatures, the maximum of low temperature-programmed desorption of ammonia shifts to lower temperatures, which indicates a decrease in the strength of acid sites.

Thus, upon calcination of the Zn-containing zeolite catalyst its acid sites are redistributed by strength and concentration. As a result, weak Lewis acid sites predominate in the catalyst, which leads to a change in its catalytic properties in the course of propane conversion into aromatic hydrocarbons. To prepare the most effective catalyst for the aromatization of propane, it should be pretreated at a temperature of 500 °C.

Acknowledgment. The work was carried out within the framework of the project No. V.46.2.1 of the Program of Fundamental Scientific Research of the State Academies of Sciences.

PP-I-22

The Problem of Removal of the Active Metal in the Process of SC-CO_2 Regeneration of Nickel-Molybdenum Hydrotreating Catalyst DN-3531

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The results of research of supercritical fluid CO2-extraction process within the task of regeneration of industrial Nickel-molybdenum Hydrotreating catalyst DN-3531, implemented in the temperature range 323.15 – 383.15 K at pressures up to 30 MPa, and involving a modification of the basic extractant with polar compounds, such as chloroform, methanol, ethanol, acetone and dimethyl sulfoxide (DMSO) are presented. Studies have revealed that in the case of the most effective co-solvent – DMSO not only destruction of decontamination compounds is observed, but also the removal of Nickel and molybdenum, which significantly reduces the total activity of the thus recovered sample. Further studies on the solubility of Nickel oxide separately in SC CO_2 and in DMSO showed that the Nickel oxide in these solvents is virtually insoluble. However, in the case of a mixture of SC CO_2+DMSO (5% wt) in the indicated conditions according to the authors is the formation of complex $Ni[DMSO]_xOH_y$, soluble in the supercritical fluid solvent. The paper also presents the results of research of supercritical fluid CO_2 - impregnation process (the static mode) applied to the problem of synthesis of palladium and palladium - silver catalysts. The results of the evaluation of the surface metal content and activity the synthesized and regenerated catalyst samples give reason to the conclusion about the prospects of SC impregnating process in relation to the task.

PP-I-23

Synthesis and Limitations of Cu-Fe Based Novel Layered Double Hydroxides (LDH) Precursors of Catalysts and Their Application for Depolymerization of Lignin and Its Model Molecules

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The depletion of fossil fuel resources and the perceived dangers of global warming have fostered the role of lignocellulosic biomass as sustainable potential source of both chemicals and fuel. However, the valorisation of lignin has been given much less attention than the valorisation of cellulose, despite the interest of its aromatic components. The complex and recalcitrance nature of lignin makes especially challenging its conversion into valuable products at reasonable cost. For this task, the development of effective and robust catalytic system specifically designed for depolymerisation of lignin is crucial. Dealing with the complexity of the structure and choosing the proper upgrading approach requires preliminary knowledge acquired by testing simpler model molecules which mimic linkages present in real lignin. Therefore, we synthesized three model molecules representative of β-O-4 linkages in different environments and characterized them by GCMS, NMR, MALDI-TOF, HPLC and elemental analysis techniques. Study of the reactivity of these model molecules will allow the development of the heterogeneous catalysts able to exploit the potential market of biomass-derived products.

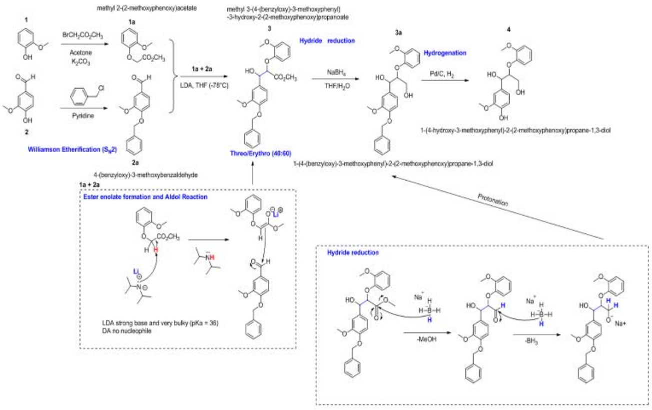

Figure 1: Schematic representation of synthesis of model molecules of lignin

Layered double hydroxides (LDH) are especially effective precursors of finely dispersed mixed metal oxides which have not been studied in depth for the depolymerisation of lignin. Taking into account their high surface area and redox properties, mixed hydroxides of the Ni-Cu-Fe system were synthesized and characterized. The LDH precursors were calcined at 400, 500 and 600°C to form mixed oxides with different crystallographic phases. In the Ni-Cu-Fe system, NiO, CuO, and spinel phases were identified. The calcination of Ni-Cu-Fe system catalyst at 400°C do not exhibit any Fe-bearing crystalline phase and the presence of amorphous iron oxide is an important feature of the system. [1]

Cu-LDHs arose a special interest as they are not easily synthesized despite the ionic radius of Cu^{2+} (0.73Å) being very close to Mg^{+2} (0.72Å), the commonest divalent in LDH.[2] Early reports have suggested that copper does not form an LDH with only iron due to geometrical distortion by Jahn-Teller's effect. [2] In the attempt to understand the threshold value of Cu needed for formation of the LDH phase, the Ni/Cu ratio was altered, keeping a fixed amount of Fe^{+3} (Figure 2) and it can be seen that the syntheses having low amount of Ni^{+2} are unable to form a LDH phase. Moreover the results were finally compared with Cu-Al LDH. Various attempts to synthesize Cu-Fe LDH were made as this materials, predicted as thermodynamically stable, remains an elusive target.[3]

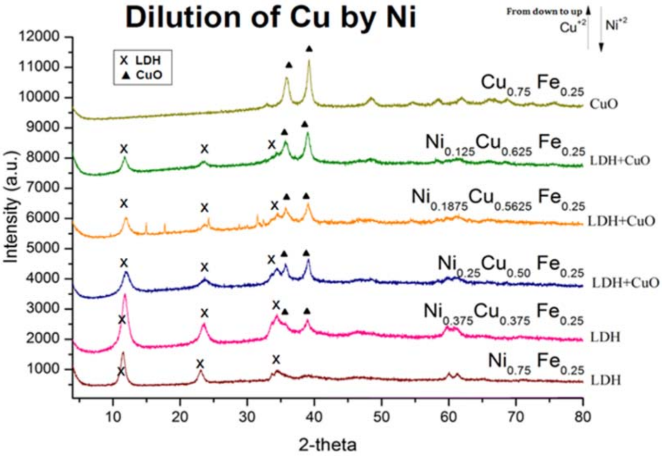

Figure 2: Phase transformation of LDH as a function of amount of Nickel in the presence of Cu

The catalysts are being studied for the hydrolysis and oxidation of β-O-4 linkages in lignin and its model molecules. The formation of finely intermixed oxide phases from LDH can provide promising catalysts allowing selective bond cleavage of β-O-4 linkages or carbon-carbon bonds. The significance of copper in the redox behaviour of iron cations could not only provide useful explanation for the oxidation pathways in lignin model molecules but also for the reactivity trend in different conditions. [4]

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PP-II-1

In situ XRD Study of Metal and Oxide Catalyst for Oxidation of Hydrocarbons

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In situ investigations of catalytic processes open new opportunities to study the mechanisms for catalytic reactions. Many heterogeneous catalytic reactions show an unusual behaviour including rate oscillations, spatiotemporal patterns and deterministic chaos [1]. Among the various phenomena the self-sustained rate oscillations in the oxidation of light alkanes over transition metals (Ni, Pd, Co) have become a focus of research over the last two decades. Mn-Co oxides show high catalytic oxidation performance and its correlate well with redox properties. X-ray diffraction technique and mass spectrometry were used to characterize the self-sustained rate oscillations in the oxidation of methane over polycrystalline supported, single crystal Pd catalysts at atmospheric pressure and mechanism of reduction of Mn-Co oxide catalyst by hydrogen.

In situ XRD/MS experiments were carried out at the “High Precision Diffractometry II” station at Siberian Synchrotron and Terahertz Radiation Center. The diffractometer was equipped with high temperature reaction chamber XRK-900 (Anton Paar GmbH), that allows measuring the diffraction patterns within temperature range from RT to 900°C in different environments, and quadruple-type gas analyser UGA-100 (Stanford Research Systems Inc.) to analyse the products and reactants. In situ XRD experiments were performed using position sensitive parallax-free linear OD-3M detector. X-ray wavelength of 1.642 Å was set by a sngle reflection from flat crystal monochromator Si(111). Mass flow controllers SEC-Z500 (Horiba Ltd.) were used to supply the feed gas composition at selected position.

According to the results the periodic changes of XRD reflections intensities corresponding to Pd, PdO, and PdCx phases were accompanied by synchronous variations of the catalyst temperature. In the low active state the catalyst surface was oxidized, and transition to the high active state occurred simultaneously with the formation of metallic phase. In addition to the latter we also observed formation of PdCx phase with larger lattice parameter on the catalyst surface. In situ XRD study of Mn-Co oxide reduction shows that addition of Mn cations to Co oxide leads to decrease the rate of phase transformations and stabilization of the intermediate compound.

Acknowledgement. This work was supported by the RFBR, grant 18-33-00542. XRD experiments were carried out using the equipment of the shared research centre (BINP, Novosibirsk, Russia).

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PP-II-2

Molecular Structures of Supported Oxide Catalysts Investigated by Raman Spectroscopy

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Nowadays, the catalysts are extensively used in numerous chemical processes, especially supported metal oxides. Knowledge of the structure, composition and character of the active sites on the material surface and the identification of a mechanism that controls a catalytic cycle is crucial to understanding and improving the catalysts properties. The discovery of the adsorbate-induced restructuring of surfaces brought new light on the chemistry of catalysts materials at an atomic level [1,2]. The catalysts structure, which can only be defined and optimized at the molecular level, is responsible for the overall catalyst performance. The surface structure changes in a dynamic way during adsorption/desorption process of reactants or reaction intermediates. Raman spectroscopy has proved to be a very powerful technique to describe the surface properties of catalysts in details.

In presented study the structural properties of the cobalt and palladium-based catalysts deposited onto γ-Al_2O_3 were investigated by *in situ* Raman spectroscopy. The catalysts has been prepared with classical wetness impregnation method and with application of ultrasound irrigation as a method that results in reducing of particle size. The molecular form of the oxides has been determined and the band present in the Raman spectra has been compared with literature data. The Raman spectra disclosed that the active cobalt form of the catalysts in catalytic combustion is Co_3O_4 spinel structure, and for the palladium-based catalysts, the PdO oxide is dominant phase. The differences in Raman spectrum (shifts and broadening of the bands) has been correlated with the preparation route used. The activity test for methane abatement under oxidative conditions has been tested with usage of fixed-bed reactor and the low concertation of methane in the reactant flow. The results obtained proved higher activity of palladium and mixed palladium–cobalt catalyst prepared by sonication than the standard wetness impregnation method.

Acknowledgement. This work was supported by National Science Centre, Poland research grant No. 2015/19/N/ST8/00181.

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PP-II-3

Investigation on Active Centres of Cerium-Based Structured Catalysts by *in situ* FTIR Spectroscopy

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Methane in an active greenhouse gas whose effect is estimated to be substantially higher than that of carbon dioxide. Both create serious environmental problems. For this reason, EU implemented new regulation – Waste Incineration Directive (2000/76/EC) – concerning the considerable reduction of methane emissions by 2021. The catalytic combustion on stabilised catalysts is one of the most attractive ways for its elimination from air. The main obstacle comes from a huge energetic barrier of the C-H bond breakage which follows according to radical mechanism. Because of analytical limitations each steps that antecede this slowest step has not been understood, yet.

Most of the catalysts, designed for methane combustion, are based on palladium – separately or in combination with different metals or metal oxides, supported on alumina. The main problem in practice is the deactivation of the Pd-based catalysts. The efforts of the researchers are focused on the development of new types of catalysts and their optimisation. It is referred that ceria offers, however better properties as a heterogeneous catalyst support or active component with its redox properties, improvement of active phase stabilisation as well as high methane oxidation activity [1-5]. However, previous *in situ* FTIR studies of the stable surface intermediate products of methane oxidation on Pd-based catalysts have not realised unambiguous band assignment [6-9]. Finally, it is not elucidated the mechanism of methane oxidation, whether it proceeds via adsorption step by forming methoxy groups according to Langmuir-Hinschelwood mechanism or without adsorption by Eley-Rideal mechanism.

In presented study, metal oxide catalysts (Fe, Co, Ni, Pd) on cerium oxide as a support were tested for their activity in the methane combustion reaction. The evaluation of active centres was done by *in situ* FTIR method coupled with the application of different probe molecules. The obtained IR vibrations of the surface intermediates have been assigned to different products: formates and carbonates on different active centres. The presence of methoxy groups on the surface of the working catalyst during the experiments performed *in situ* with FTIR detection proved the Langmuir-Hinschelwood and partially Mars-van Krevelen mechanism for methane catalytic combustion.

Acknowledgement. This work was supported by the National Science Centre Poland based on the decision no. 2017/25/N/ST8/01029.

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PP-II-4

Catalytic Etching of Polycrystalline Platinum Foil during NH_3 Oxidation

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SEM study of the polycrystalline platinum surface microstructure after treatment in O_2 and in the reaction mixture NH_3 + air shows different microstructural rearrangement of the surface. In the O_2 atmosphere the surface graphite-like film is destroyed during the oxygen reaction with carbon resulting in the growth of grains to 10–200 μm. During these processes the grain surface morphology does not significantly change and remains practically smooth. In the reaction mixture NH_3 + air the surface graphite-like film is quickly destroyed, and oxygen is penetrated at the grain boundaries, dislocations and other defects. The NH_3 reaction with the penetrated oxygen results in local overheating in the defect area leading to intense release of Pt atoms to the surface. Pt atoms migrate on the surface and gradually form new crystalline faces and facets. As a result, a continuous corrosion layer covering the entire surface of polycrystalline platinum is formed.

1. Scope

Ammonia oxidation with air on platinum catalyst gauzes is widely used in chemical industry for synthesis of nitric acid [1]. It is well known that during this process the gauzes undergo deep structural rearrangement of surface layers (catalytic etching) leading to the loss of platinum and decrease of catalytic activity [2-4]. The possible mechanisms of the catalytic etching are related to increased surface mobility of metal atoms due to the influence of adsorbates [2-3] and to the formation of volatile platinum oxides (PtO_2, etc.) [4]. To reveal the mechanism of the catalytic etching of platinum catalyst gauzes during the NH_3 oxidation, we carried out detailed investigation of the surface microstructure of platinum catalysts treated in oxygen, and in the reaction medium (NH_3-air). Polycrystalline Pt foil with the size of 10 × 5 × 0.04 mm was used as the catalyst. The sample was assembled into a package with four platinum gauzes required to maintain standard conditions of the NH_3 oxidation process. The platinum catalyst gauzes were made from a polycrystalline wire ($d \approx 82$ μm) with composition (in wt.%) 81%Pt, 15%Pd, 3.5%Rh and 0.5%Ru. A quartz laboratory flow reactor was used at the feed (ca. 10%NH_3 in air) flow rate 880–890 l/h, the gauze temperature 1133 K and total pressure about 3.6 bar. The surface microstructure was studied using a scanning electron microscope (SEM) JSM-6460 LV (Jeol). It was determined that the surface of the initial platinum foil was covered with a continuous graphite-like carbon film with the thickness ~5-10 nm.

2. Results and discussion

Different microstructure of polycrystalline Pt foil was observed by SEM after the treatment of the platinum sample at T ~ 1400 K for 3 h in oxygen (21.5%O_2 in He), and at

T ~ 1133 K for 5 h in reaction medium (~10% NH_3 in air). A micrograin structure with 10-200 μm grains was formed on the surface of the sample during the reaction of O_2 with the platinum foil. The grain structure is formed during decomposition of the surface film including the graphite-like layer covering the surface of the grains and grain boundaries in the bulk of the polycrystalline sample. The grain structure was observed on the platinum surface both in the SE and BSE modes. This result indicates that this structure is spread deep into the bulk of the foil because the depths of the analysis are significantly different in these modes, ≤5 and ≤300 nm, correspondingly. After the catalytic reaction of ammonia oxidation the corrosion layer of each grain has definite orientation that differs from that of adjacent grains. Apparently, this orientation of the grain corrosion layer is related to the structure of the grain surface. The catalytic NH3 oxidation on Pt at T~860°C for 5 h results in minor structural reconstruction of the foil surface layer related to the formation of grain boundaries and shallow parallel furrows with the width 1-2 μm covered with crystalline facets. During the NH_3 oxidation over Pt foil the O_2 interaction with platinum results in removal of the surface graphite-like layer followed by dissociative chemisorption of oxygen on the surface. It is well known that oxygen dissolution in the Pt lattice with the formation of oxide phases is substantially slower than on other platinum metals (Pd, Rh). The O_2 interaction with Pt can lead to intense dissolving of oxygen atoms at defects.

3. Conclusions

After the treatment of the platinum sample in O_2 and in reaction medium (~10%NH_3 in air) different microstructure of polycrystalline Pt foil was observed. Large amount of oxygen atoms can be absorbed at the grain boundaries and other defects. During the interaction of the sample with oxygen the surface graphite-like layer is destroyed and the grain structure is gradually formed on the platinum catalyst. The reaction of gaseous NH_3 molecules with absorbed oxygen atoms O_{abs} results in local overheating of the surface initiating the release of metal atoms to the surface. Intense release of metal atoms from the grain boundaries leads to the formation of extended voids between the grains. Adsorbed Pt atoms quickly migrate over the metal surface and get incorporated into energetically the most favorable sites. Due to these processes, pits and crystalline facets grow on the surface. So, structural reconstruction of the Pt foil surface layer with the formation of a rough layer (catalytic etching) takes place during the catalytic NH_3 oxidation.

Acknowledgement. This work was conducted within the framework of budget project
No. 0303-2016-0002 for Boreskov Institute of Catalysis SB RAS

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PP-II-5

Catalytic Etching of Platinum Gauzes Used in NH_3 Oxidation

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SEM study of the platinum catalyst gauzes treated in the NH_3-air mixture at 1133 K for 50 h demonstrates deep structural rearrangement of the surface layers (catalytic etching). The surface of the gauzes is covered by a continuous corrosion layer consisting of crystalline agglomerates with the sizes 5–15 μm separated by deep voids with the width 1–10 μm. The agglomerates have different shapes, crystalline faceting and contain through pores with the diameter 1–5 μm. Catalytic etching is initiated by the reaction of ammonia molecules with oxygen atoms absorbed at the grain boundaries, dislocations and other surface defects. This reaction results in local overheating of the surface initiating the release of metal atoms to the surface. Intense release of metal atoms from grain boundaries forms extended voids between the grains. So, the grains are gradually reconstructed into faceted crystalline agglomerates forming a corrosion layer.

1. Scope

Ammonia oxidation with air on platinum catalyst gauzes is widely used in chemical industry for synthesis of nitric acid. It is well known that during this process the gauzes undergo deep structural rearrangement of surface layers (catalytic etching) leading to the platinum loss and catalytic activity decrease. To determine the mechanism of the catalytic etching of platinum catalyst gauzes during the NH_3 oxidation, we studied in detail the surface microstructure of platinum catalyst gauzes used in ammonia oxidation. The platinum catalyst gauzes used in the study were made from a polycrystalline wire with $d \approx 82$ μm with the chemical composition (in wt.%) 81% Pt, 15% Pd, 3.5% Rh and 0.5% Ru. A laboratory flow reactor made of quartz tube with the inner diameter of 11.2 mm was used at the feed (ca. 10% NH_3 in air) flow rate 880–890 l/h, the gauze temperature 1133 K and total pressure ca. 3.6 bar. A pack of four gauzes was loaded into the reactor to maintain standard conditions of the catalytic process. The surface microstructure was studied using a scanning electron microscope (SEM) JSM-6460 LV (Jeol) in the mode of secondary electrons (SE) at beam energy 25 keV.

2. Results and discussion

A continuous corrosion layer on the front side of the first gauze relative to the gas flow after the treatment at T ≈1133 K for 50 h was observed after the SEM study. We observed that the front side of the wire is significantly etched due to the reaction of NH_3 oxidation. **The surface of the gauze was covered by a continuous corrosion layer consisting of crystalline agglomerates with the sizes 5-15 μm.** The agglomerates have different shapes, crystalline faceting and are separated by deep voids with the width 1–10 μm. As well the crystalline agglomerates have different pores and contain through pores with the diameter 1–5 μm. The obtained data indicate that the size of agglomerates on the front side of the gauze (5–15 μm) is close to that of grains observed on the back side (1–13 μm). This result seems to suggest that the etching develops in the course of gradual growth and transformation of the grains into crystalline agglomerates during the growth and merging of etching pits at the grain boundaries. Through pores with the size of 1–5 μm inside the agglomerates may be formed during merging of growing etching pits on the surface and in the bulk of the grains. **The reaction of gaseous NH_3 molecules with absorbed oxygen atoms with the formation of gaseous NO results in local overheating of the surface initiating the release of metal atoms to the surface.** The emergence and growth of the pits can be related to the reaction of ammonia molecules with oxygen atoms absorbed at the grain boundaries, dislocations and other surface defects. During this reaction the surface of the gauzes is covered by a continuous corrosion layer consisting of crystalline agglomerates with the sizes 5–15 μm separated by deep voids with the width 1–10 μm. These agglomerates contain through pores with the diameter 1–5μm.

3. Conclusions

So, the treatment of the platinum catalyst gauzes in the NH_3-air mixture at 1133 K for 50 h leads to deep structural rearrangement of the surface layers (catalytic etching). The next mechanism of the catalytic etching of platinum catalyst may be suggested. The reaction of gaseous NH_3 molecules with oxygen atoms absorbed at the grain boundaries, dislocations and other surface defects results in local overheating of the surface initiating the release of metal atoms to the surface. Intense release of metal atoms from pits at the grain boundaries forms extended voids between the grains. Metal atoms released from the defects quickly migrate over the grain surface and are gradually incorporated at the energetically most favorable sites. As a result, the grains are gradually reconstructed into faceted crystalline agglomerates with through pores formed due to the growth and merging of pits. A prolonged occurrence of these processes leads to the formation a rough corrosion layer including crystalline agglomerates separated by deep extended void.

Acknowledgement. This work was conducted within the framework of budget project No. 0303-2016-0002 for Boreskov Institute of Catalysis SB RAS.

PP-II-6

Catalytic Etching of Palladium Used in CO Oxidation

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SEM study of the surface of polycrystalline palladium treated in the $CO+O_2$ reaction mixture at T=800–1000 K demonstrates significant microstructural rearrangement of the surface initiated by catalytic CO oxidation (catalytic etching). The O_2 reaction with palladium produces a continuous oxide layer with the thickness 200–300 nm formed from 5–10 nm PdO particles. The CO reaction with O atoms in PdO particles leads to the formation of pyramidal oxide fragments with the height 200–300 nm containing Pd metal particles at the top. The pyramidal fragments are gradually transformed into PdO crystals with the sizes about 200–300 nm. The CO reaction with O atoms on the surface of PdO crystals results in intense release of Pd atoms on the surface of PdO crystals and into the gas phase. Higher concentration of Pd atoms in the border gas layer leads to nucleation and growth of Pd nanocrystals that merge into agglomerates and gradually form a continuous layer on the surface of PdO crystals.

1. Scope

Investigation of the catalytic CO oxidation by oxygen on platinum metals is interesting both for determining mechanisms of heterogeneous catalytic reactions and for protection of the environment from harmful exhausts of automobile engines, which contain a lot of CO that is very dangerous for the environment. Today palladium is widely used for preparing catalysts for converters of automobile exhaust gases because both Pd and PdO are more active than other platinum metals in catalytic oxidation reactions in the O_2 excess. The goal of this investigation was to study the microstructure of the palladium surface during the catalytic CO oxidation by oxygen at T = 800–1000 K when oxidation of the surface layers of Pd metal and CO oxidation by oxygen are very fast. Polycrystalline palladium foil with dimensions 10 × 5× 0.04 mm was used in the study. The sample was treated in the feed containing 2%CO, 10%O_2 and 88%He in a quartz flow reactor at ~1 atm pressure and 1.5 l/h flow rate at 800, 900 and 1000 K for 3 hours. The surface microstructure was studied using a scanning electron microscope SU8240 (Hitachi).

2. Results and discussion

After the sample was treated at T = 800–1000 K, light areas with dimensions 50–500 μm evenly distributed on the dark surface were observed in the microscopic images of the surface. The analysis of the microscopic images showed significant differences in the microstructure of the light, dark and border surface regions. The dark regions were formed by a continuous dense layer of particles with the sizes of 5–10 nm. Agglomeration of pyramidal fragments with the height of 200–300 nm and base ca. 50 nm consisting of

5–10 nm particles was observed at the border between the light and dark areas. The particles – crystals with the size of 10–20 nm were observed at the top of these fragments. The light regions consisted of two layers with the thickness reaching ca. 1 μm. The top layer included particles and crystals with dimensions 10–100 nm, which were connected to each other and formed elongated structures that could be as long as 1 μm. This layer was located on 200–300 nm crystals covered with a continuous layer of particles with the sizes 10–20 nm. In the CO + O_2 reaction medium at T = 800–1000 K oxygen dissociatively chemisorbs on the palladium surface, penetrates into subsurface layers and dissolves in the metal. These processes result in the formation of a surface oxide film on palladium with the thickness ca. 2–3 nm where PdO particles with dimensions 5–10 nm are formed. These particles gradually produce a continuous oxide layer with the thickness 200–300 nm. CO molecules from the gas phase react with O atoms in the surface layer of PdO particles with desorption of gaseous CO_2. This reaction results in the formation of surface oxygen vacancies and adsorbed Pd_{ads} atoms. The Pd_{ads} atoms migrate on the oxide surface and form nuclei of metal particles, which rapidly grow due to fast generation of Pd_{ads} atoms in the CO oxidation reaction. Preferential formation of Pd_{ads} atoms at the grain boundaries of the oxide layer leads to the rupture of this layer along these boundaries with the formation of pyramidal fragments with the height 200–300 nm containing palladium metal particles at the top.

3. Conclusions

Detailed SEM study of the surface of palladium foil demonstrates significant microstructural rearrangement of the surface initiated by catalytic CO oxidation (catalytic etching). The O_2 reaction with palladium produces a continuous oxide layer with the thickness 200–300 nm formed from 5–10 nm PdO particles. The CO reaction with O atoms in PdO particles leads to the formation of pyramidal oxide fragments with the height 200–300 nm containing Pd metal particles at the top. The pyramidal fragments are gradually transformed into PdO crystals with the sizes about 200–300 nm. The CO reaction with oxygen atoms is different on the surface of PdO crystals than on PdO particles due to decelerated filling of surface vacancies by O and Pd atoms diffusing from the bulk of the oxide crystals to the surface. As a result, the concentration of oxygen vacancies and Pd_{ads} atoms on the surface of the oxide crystals increases. In addition, Pd_{ads} atoms are bound to the surface of PdO crystals much weaker than to the surface of PdO particles. Therefore, Pd_{ads} migrate faster on the surface of crystals forming metal particles and are also desorbed into the gas phase. Higher concentration of Pd atoms in the border gas layer initiates growth of particles and nanocrystals of Pd with low defect concentration. Pd nanocrystals merge and gradually form aggregates and elongated structures producing a surface layer.

Acknowledgement. This work was conducted within the framework of budget project
No. 0303-2016-0002 for Boreskov Institute of Catalysis SB RAS.

PP-II-7

PdIn/Al_2O_3 Catalyst for Selective Akyne Hydrogenation: Formation of Intermetallic Nanoparticles with Pd Single-Atom Structure

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Over the past few years a methodology of designing catalyst active sites as isolated metal atoms has received considerable interest. Calling single-atom catalysts (SACs) these systems provides a great potential for significant improvement of a number of chemical reactions [1]. For example, the possibility of effective elimination of alkyne multi-bonded adsorption makes SACs a promising candidate for the semi-hydrogenation of acetylenic compounds giving optimum selectivity to the target alkene. Despite the high activity and selectivity the long-term stability of SACs under reaction conditions can also be improved. Thus the use of intermetallic compounds (IMCs) is an effective method for controlling the selectivity of chemical processes because of the high degree of ordering of these compounds and their unusual structural stability [2]. A combination of these two methodologies might allow us to obtain a catalyst with excellent catalytic selectivity and stability [3].

In this study structural and catalytic characteristics of PdIn nanoparticles were investigated in selective liquid-phase hydrogenation of diphenylacetylene (DPA). The choice of PdIn system was determined by its greater stability in comparison with traditional PdGa and PdZn compositions traditionally used in hydrogenation.

The PdIn/Al_2O_3 catalyst was obtained via incipient wetness impregnation of Al_2O_3 with acetic acid solution of $PdIn(CH_3COO)_5$ (pH 2.8). The final material was dried overnight and step-wised reduced at 200, 300, 400, 500 and 600°C. The formation of the PdIn intermetallic species was monitored by XRD, TEM, FTIR-CO, H_2-TPR, and H_2-TPD techniques.

According to XRD analysis data, formation of supported intermetallic PdIn particles begins after PdIn/Al_2O_3 reduction at 200°C. As the reduction temperature rises, the signal characteristic of PdIn intermetallic compound becomes more symmetric and increases in intensity, indicating the ordering of the catalyst structure and the enlargement of the active component particles, which agrees well with the TEM data. In the XRD spectrum obtained after reduction at 400°C the symmetric peak at 2θ ~39° suggests that the crystal lattice of substitutional solid solution based on Pd (FCC) is finally rearranged into the tetragonal lattice typical for PdIn intermetallics. The following increase in the reduction temperature (up to 500 and 600°C) does not lead to qualitative changes in the diffraction pattern. The intensity of the intermetallic PdIn peak remains practically unchanged, which indicates the complete ordering of its structure. The data obtained are in agreement with the results of the TEM data.

FTIR-CO data also confirmed the formation of intermetallic PdIn nanoparticles. It was observed that the surface of PdIn nanoparticles contains predominantly Pd atoms separated from one another by indium atoms providing SACs structure. This is evidenced for PdIn/Al_2O_3 by the absence of the characteristic band of CO adsorbed in bridged form and by the disappearance of the CO band shift resulting from the lateral dipole–dipole interaction between adsorbed CO molecules. Complete inhibition of PdHx phase in PdIn catalyst provides additional evidence of the formation of PdIn bimetallic particles as it was demonstrated by H_2-TPD analysis.

A significant effect of In on the selectivity of the Pd catalysts was shown in the liquid-phase hydrogenation of DPA. PdIn catalyst exhibits a high selectivity close to the ones of the Lindlar's (commercial catalyst for liquid-phase alkyne hydrogenation). It should be especially mentioned that high selectivity and sufficient activity were obtained at 1 wt % Pd content which is lower than that of the Lindlar catalyst (5 wt % Pd) and in the absence of toxic Pb species. This makes the PdIn system attractive for industrial and laboratory application.

Acknowledgement. This work was financially supported by the Russian Science Foundation (Grant 16-13-10530). Authors also kindly thank Department of Structural Studies of ZIOC RAS for the catalysts characterization by electron microscopy.

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PP-II-8

The Complexation in the $PdBr_2$-LiBr-CH_3CN-H_2O Catalyst System, Used in the Synthesis of Succinic Anhydride

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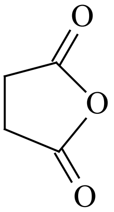
Many reactions catalyzed by complexes of metals are the basis of many chemical industrial processes. The information about the detailed mechanism of a process and about the distribution of metal complexes *in situ* is necessary to design and to improve catalysts and catalytic systems. It is very important for the catalyst design for coupled reactions on the basis of the kinetic coupling principle [1]. The palladium-containing homogeneous catalytic systems are used to obtain valuable products of organic synthesis: carboxylic acids and their derivatives [2].

So, succinic anhydride is selectively produced (1) in the $PdBr_2$-LiBr-CH_3CN-H_2O catalytic system at 40°C and 1 atm [3].

$HC{\equiv}CH + 2CO + H_2O =$



(1)

The kinetic regularities of this process were studied earlier [3], but the lack of information on the state of the catalytic system and the distribution of palladium complexes did not allow us to offer a sufficiently detailed mechanism of the process. The main aim of this work is to provide information on the equilibrium of palladium complexes in this catalytic system. This information was obtained by UV-Vis and infrared spectroscopy. The model and catalytic systems were studied both in the initial state and under the action of the catalytic process reagents. The assignment of absorption bands to various palladium complexes for the model and reaction systems has been carried out.

The electronic spectra of the model system $PdBr_2$-LiBr-CH_3CN were recorded with respect to the solvent (acetonitrile) at a temperature of 23±2°C in quartz cuvettes (0.01 cm and 0.5 cm thick). A mathematical treatment of the obtained data was carried out using hypotheses including the formation of monomeric and dimeric palladium complexes (table 1). The equilibrium constants of the complexation stages, as well as extinction coefficients of palladium complexes, were calculated. The discrimination of hypotheses was carried out by the comparison of the mean-square errors in the description of experimental results for the considered models. It was shown that the model taking into account the formation of $Pd_2Br_2^{2+}$, Pd_2Br_4 and $Pd_2Br_6^{2-}$ describes the experimental data better than all another models. Within the framework of this model, the spectra of individual monomeric and dimeric palladium complexes were obtained (fig. 1).

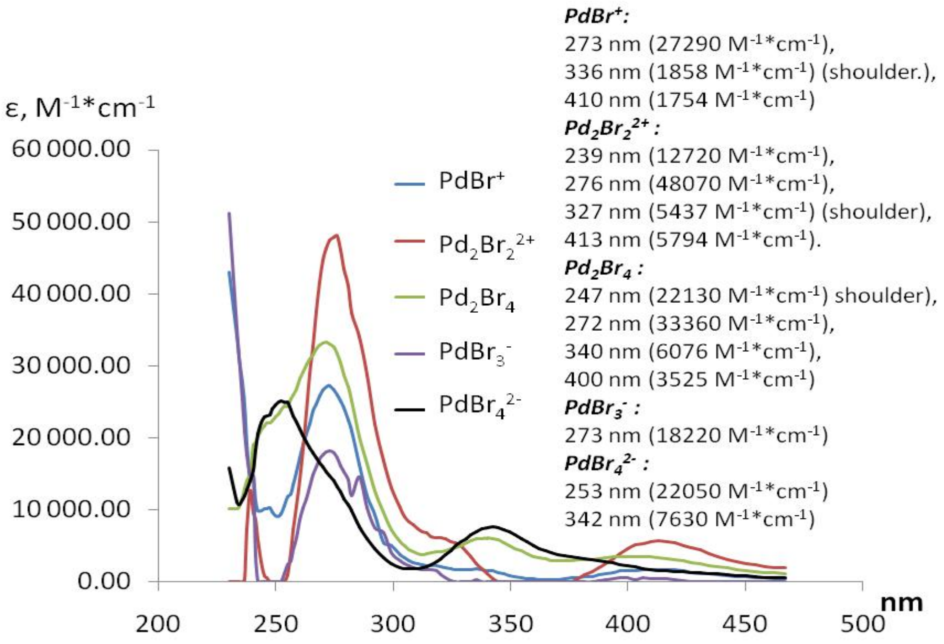
The state of complexes in $PdBr_2$ - LiBr – CH_3CN system was studied after purging by carbon monoxide. It was shown that the palladium(II) carbonyl complexes (the band at 2120 cm^{-1}) and the palladium(I) carbonyl complexes (the band at 1908 cm^{-1}) present in acetonitrile system under carbon monoxide atmosphere.

It was established that the initial catalytic system $PdBr_2$-LiBr-CH_3CN (c ($PdBr_2$) = 0.005M, c (LiBr) = 0.01M) contains mainly $PdBr^+$, $Pd_2Br_2^{2+}$ and Pd_2Br_4 complexes, from which the true catalyst (the complexes Pd(I)) is formed. During the process of carbonylation of acetylene, palladium is present in the form of a carbonyl complex of palladium (I), in the coordination sphere of which, probably, acetylene and maleic anhydride may be present.

Table 1. The considered models of the complexation

Stages of the complexation	Models of the complexation
(1) $Pd^{2+} + Br^- \leftrightarrows PdBr^+$	**«0, 1, 2, 3, 4»*** – stages 1, 2, 3, 4.
(2) $PdBr^+ + Br^- \leftrightarrows PdBr_2$	**«1, 2, 3, 4»** – stages 2, 3, 4.
(3) $PdBr_2 + Br^- \leftrightarrows PdBr_3^-$	**«2, 3, 4»** – stages 3, 4.
(4) $PdBr_3^- + Br^- \leftrightarrows PdBr_4^{2-}$	**«3, 4»** – stage 4.
(5) $2PdBr_3^- \leftrightarrows Pd_2Br_6^{2-}$	**The model with $Pd_2Br_6^{2-}$** – stages 2, 3, 4, 5.
(6) $PdBr_2 \leftrightarrows Pd_2Br_4$	**The model with Pd_2Br_4** – stages 2, 3, 4, 6.
(7) $2PdBr^+ \leftrightarrows Pd_2Br_2^{2+}$	**The model with Pd_2Br_4, $Pd_2Br_6^{2-}$**– stages 2, 3, 4, 5, 6.
	The model with $Pd_2Br_2^{2+}$, Pd_2Br_4, $Pd_2Br_6^{2-}$– stages 2, 3, 4, 5, 6, 7.

*digits in quotation marks indicate palladium-containing compounds: 0 – Pd^{2+}; 1 – $PdBr^+$, 2 – $PdBr_2$, 3 – $PdBr_3^-$, 4 – $PdBr_4^{2-}$



$PdBr^+$:
273 nm (27290 M^{-1}*cm^{-1}),
336 nm (1858 M^{-1}*cm^{-1}) (shoulder.),
410 nm (1754 M^{-1}*cm^{-1})
$Pd_2Br_2^{2+}$:
239 nm (12720 M^{-1}*cm^{-1}),
276 nm (48070 M^{-1}*cm^{-1}),
327 nm (5437 M^{-1}*cm^{-1}) (shoulder),
413 nm (5794 M^{-1}*cm^{-1}).
Pd_2Br_4 :
247 nm (22130 M^{-1}*cm^{-1}) shoulder),
272 nm (33360 M^{-1}*cm^{-1}),
340 nm (6076 M^{-1}*cm^{-1}),
400 nm (3525 M^{-1}*cm^{-1})
$PdBr_3^-$:
273 nm (18220 M^{-1}*cm^{-1})
$PdBr_4^{2-}$:
253 nm (22050 M^{-1}*cm^{-1})
342 nm (7630 M^{-1}*cm^{-1})

Fig. 1. Electronic spectra of $PdBr^+$, $Pd_2Br_2^{2+}$, Pd_2Br_4. $PdBr_3^-$ and $PdBr_4^{2-}$ complexes. Electron spectra of the complexes $PdBr_2$ and $Pd_2Br_6^{2-}$ were not restored because of the very low calculated concentrations of these compounds.

Acknowledgement. This work was supported by the Russian Foundation for Basic research, grant №16-33-00371.

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PP-II-9

Methanol Adsorption on Pt(111): *In Situ* Study by Polarization Modulation Infrared Reflection Absorption Spectroscopy

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Methanol adsorption is a prototypical reaction in the surface science because methanol is a small organic molecule containing different chemical bonds (C-H, C-O, and O-H). Furthermore, methanol is important as an alternative energy source, it can be applied for the development of fuel cells [1]. The fuel cell is an electrochemical cell that converts the chemical energy from a fuel into electricity through an electrochemical reaction. The simplest fuel cell uses hydrogen as a fuel and usually Pt-based catalysts use for hydrogen production by decomposition or partial oxidation of methanol. In spite of numerous studies of the adsorption and oxidation of methanol on platinum some questions are not clear yet because the most of these studies was performed in ultrahigh vacuum [2-3].

However, the data obtained cannot always be applied in real catalysis, which are known to be carried out at least at atmospheric pressure. With increasing pressure new intermediates can be formed, which are not observed in UHV. Furthermore, the state of the catalyst may change at elevated pressures.

Herein we present our results of the study of adsorption of methanol on the Pt(111) single crystal surface. The adsorption has been examined at temperatures from 100 to 500 K in a pressure range from UHV to 1 mbar. The monolayer and multilayer structures were observed *in situ* using polarization modulation infrared reflection adsorption spectroscopy (PM IRRAS). This method opens new possibilities for *in situ* studies of mechanisms of heterogeneous catalytic reactions and allows simultaneous obtaining the information about the adsorbed species and gas phase molecules, that is identifying reaction products and intermediates, and also determining the conversion of the reactants and the selectivity toward the main products [4]. It should be noted that this technique may be applied at pressures from UHV to elevated pressures and at temperatures from 77 K to 1200 K [5]. In addition, the surface chemistry of Pt(111) was examined by X-ray photoelectron spectroscopy before and after exposures in methanol.

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PP-II-10

Control of the Surface Structure of Bimetallic Pd-Ag Catalysts by the Adsorbate-Induced Segregation

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The catalytic performance of bimetallic palladium systems has been a subject of growing interest over the last decades [1]. Recently it has been shown that their superior catalytic properties are explained by the ability to form well-ordered single-atom structures, where the surface Pd atom is surrounded by other metal atoms. Thus the phase and chemical composition of the bimetallic particles surface in general differs from that in the bulk [2].

The method of adsorbate-induced segregation is based on the phenomenon of greater affinity of one element to an adsorbate than the other to induce surface segregation. This can cause modifications of the activity and the selectivity of the alloy catalyst. Efficiency of this method has been demonstrated nowadays for the Pd-Cu system [3].

The main focus of our research was to investigate the possibility of controlling surface structure of the bimetallic Pd-Ag systems by the adsorbate-induced segregation technique. Carbon monoxide and oxygen (synthetic air) were used as adsorbates. The selective hydrogenation of diphenylacetylene was used as test reaction to correlate the spectroscopic data and the catalyst performance. The diffuse reflectance infrared Fourier transform spectroscopy of chemisorbed CO (CO DRIFTS) was applied to monitor the transformation of the catalyst surface structure in the course of adsorbate-induced segregation.

A bimetallic 1.0%Pd-2.0%Ag/Al_2O_3 (wt.%, molar ratio Ag:Pd = 2) catalyst was prepared by incipient wetness impregnation with an aqueous solution of palladium and silver nitrates. The sample was dried in air at room temperature and pre-reduced in 5%H_2/Ar flow at 550 °C for 2 h. The reference sample was 1.0 wt.% Pd/Al_2O_3. The CO DRIFT spectroscopy was performed with a Tensor 27 spectrometer (Bruker, Germany) equipped with a high-temperature cell for in situ treatments at atmospheric pressure (Harrick, USA). The Pd-Ag/Al_2O_3 catalyst was re-reduced in high-temperature cell at 500 °C 1h and then treated in 30%CO/N_2 (200 °C, 30 min) or 20%O_2/N_2 flow (200 °C, 1h). After each step the spectra were recorded. The catalysts subjected to adsorbate-induced segregation were transferred from the cell to the reaction medium under argon flow to avoid from contact with air. The hydrogenation of diphenylacetylene (DPA) was carried out in a stainless-steel autoclave-type reactor at 5 atm of H_2, 25°C in n-hexane (98%, Merck) as a solvent.

Figure 1 shows the CO-DRIFT spectra for monometallic Pd/Al_2O_3 sample and bimetallic Pd-Ag_2/Al_2O_3 catalyst after different treatments. The single band centered at 2049 cm^{-1} indicates the presence of single-atom Pd sites on the surface of freshly reduced PdAg sample without any ensembles of neighboring palladium atoms, as also indicated by the absence of the band at 1900-2000 cm^{-1} typical for the bridged bond CO. The subsequent treatment of a freshly reduced sample with carbon monoxide or oxygen (synthetic air) leads to the appearance of a signal of bridge-bonded CO form (1970-1990 cm-1). The shift of the band of linearly bonded CO to higher wavenumbers indicates significant changes in the electronic state of bimetallic particles.

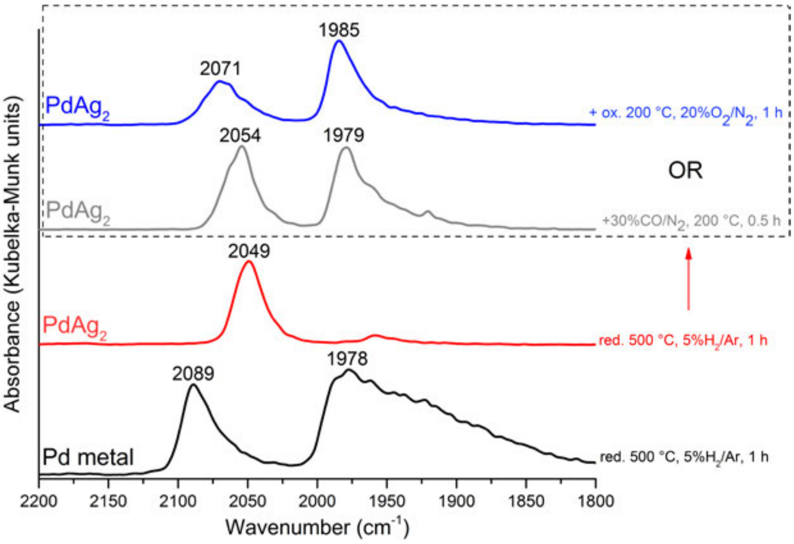

Fig.1. DRIFT spectra of Pd catalyst and bimetallic PdAg$_2$ samples after different treatments

The freshly reduced PdAg$_2$ sample demonstrates the lowest activity in the DPA hydrogenation. Treatment of freshly reduced sample by CO leads to increase in its activity and to minor decrease in diphenylethylene (DPE) selectivity. The oxidized bimetallic sample treated with synthetic air shows the highest activity, but the loss of selectivity in DPE formation is more pronounced.

The observed changes are associated with the surface enrichment of bimetallic PdAg$_2$ particles with palladium and the partial destruction of single-atom structure. As a result, more active sites are involved in the reaction and the catalyst activity increases. However, the formation of multiple adsorption centers promotes the strong adsorption of DPA and promotes full hydrogenation of triple bond leading to decrease in selectivity.

The data obtained indicates that the adsorbate-induced segregation may serve as the effective tool to tune surface structure of the bimetallic catalysts and their catalytic performance.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant no 16-29-10788.

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PP-II-11

Synthesis and Physicochemical Characterization of Vanadium-Containing Faujasite for Oxidative Dehydrogenation (ODH) of Light Alkanes

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In recent years, for energy and chemical production scientific community aims to exploit to the maximum compounds readily available and/or which are waste from existing industrial processes. One of the main objects of interest is the production of light alkanes, as they are in high demand by chemical industry. Oxidative dehydrogenation (ODH) of alkanes is becoming an alternative to olefin extraction by conventional methods, such as catalytic cracking or conventional dehydrogenation [1].

The investigated ODH process is associated with lower energy consumption, and less catalyst coking compared to conventional dehydrogenation of alkanes, which further promotes research on this subject [2]. The oxidative dehydrogenation itself is of wide interest, especially with vanadium active centers. Examination of specimens of active vanadium centers is essential to avoid the subsequent combustion reaction of the reaction products to carbon oxides (CO and CO2). The factors responsible for the catalytic properties of vanadium catalysts are, however, not entirely clear. The key issue remains what is the type of vanadium centers involved in the oxidative dehydrogenation of alkanes. Are they isolated, single vanadium centers, or polymeric V-O-V chains, or perhaps vanadium alone in tetrahedral or octahedral coordination? Microporous materials, such as zeolites, may serve as support for vanadium, being promising ODH catalysts. This is due to the fact that they combine unique textural, acid-base and redox properties, enabling alkanes to be activated at relatively low temperatures. Their developed surfaces make it possible to prepare catalysts with well dispersed vanadium centers.

Hence, an attempt was made to synthesize vanadium catalysts deposited on a standard microporous zeolite (faujasite, FAU), characterize obtained samples, and to investigate their activity in the ODH reaction.

Vanadium catalysts were obtained by two methods: classical impregnation and ion exchange, using FAU zeolite with Si:Al ratio of 31 as a support. The preparation was conducted in three pH conditions: 2.5; 5 and 7. These allowed for different catalysts with varying amounts and type of vanadium phase depending on the synthesis conditions. The catalysts were tested with a set of physicochemical methods. Their phase composition was confirmed by XRD, BET resulted in surface area, reducibility was measured with H_2-TPR method, NH_3-TPD gave information on the type of acid centers. The obtained samples were subjected to catalytic tests in oxidative dehydrogenation of propane in a bed gas flow reactor with a gas chromatograph to detect substrates and reaction products. Tests were conducted at a temperature range of 300 - 520 ° C, with varying bed contact times with the reaction mixture.

Acknowledgement. This work was supported by the National Science Centre, Poland within project no 2016/23/B/ST4/02854.

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PP-II-12

A Study of the Phase Composition of Copper-Cerium Oxide System

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We have previously shown that copper-cerium oxide catalysts exhibit high activity in the ethanol conversion reaction [1]. It was found that the activity of these catalysts depends on the atomic ratio of copper to cerium. In connection with this, in this paper we have studied the phase composition of copper-cerium oxide catalysts of various compositions.

Copper-cerium oxide catalysts were prepared by mixing aqueous solutions of copper and cerium nitrate. Synthesized catalysts was then calcined at 550°C for 10 hours. X-ray studies were carried out on an automatic powder diffractometer "D2 Phaser" firm "Bruker" (CuKα-radiation, Ni-filter, $5 \leq 2\theta \geq 75$ °). Thus, were investigated nine Ze-Cu-O catalysts prepared in various proportions of components satisfying the following conditions:

$$mZe:nCu, \text{ where } m, n = 1 \div 9, m + n = 10.$$

Investigations of the Ce-Cu-O system showed that except of the sample of Ce:Cu=1:9, all other samples contain phases of cerium (CeO2) and copper (CuO) oxides. On a sample with a ratio of the initial elements of Ce:Cu=1:9, cerium oxide CeO2 and elemental copper Cu are formed. It should be noted that in all samples the percentage ratio of components is preserved, which is indicated by a regular change in the intensities of reflexes in diffraction pictures.

We also on the "D2 Phaser" instrument using the DIFFRAC.EVA program calculated the degrees of crystallinity of all the phases formed, the results of which are presented in the table 1.

Table 1. Crystallinity of samples in the Ce-Cu-O catalyst system.

Ze:Cu ratio in the catalyst	1:9	2:8	3:7	4:6	5:5	6:4	7:3	8:2	9:1
Crystallinity,%	66.7	59.1	63	52.7	62.5	70.4	67.9	64.6	71.2

As can be seen from the table with a change in the copper content of the catalyst, the crystallinity of the samples varies from 52.7% on a sample of Ce: Cu = 4: 6 to 71.2% on a sample of Ce: Cu = 9: 1.

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PP-II-13

Investigation of the Influence of the Catalyst on the Morphology of Polyaniline

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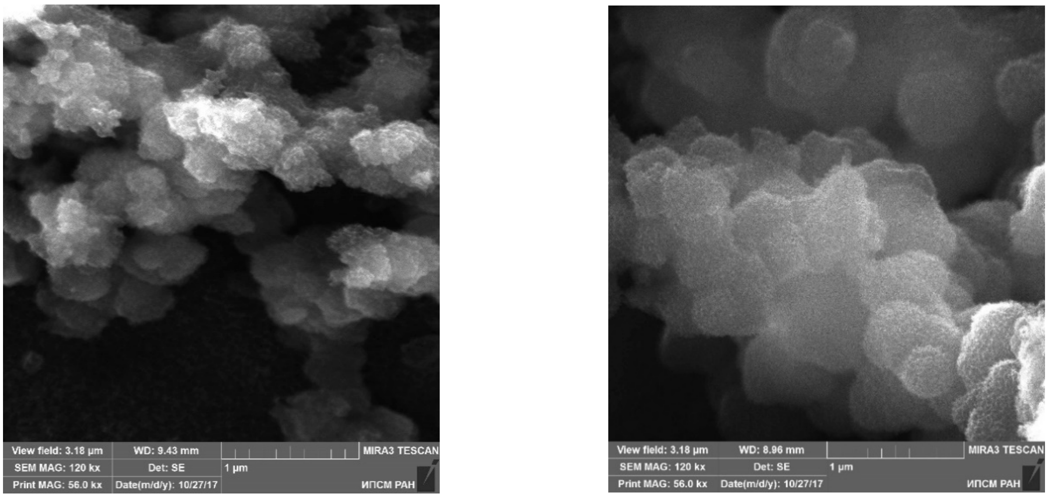
Polyaniline (PANI) is currently the most common electrically conductive polymer. Thanks to a wide range of useful properties, PANI finds application in many areas of the national economy. However, this high-molecular interaction can be achieved in typical organic solvents and adhesion to different substrates. Polyaniline is usually obtained by oxidative chemical polymerization of aniline for 24-48 hours, and the yield is 50 %.

To reduce the time of PANI obtaining in the present work, a synthesis was carried out with the addition of cobalt phthalocyanine as a catalyst. The reaction was completed in 1 hour with a quantitative yield of the product. The morphology of the isolated PANI was examined by scanning electron microscopy (SEM MIRA3 TESCAN) and the results were compared with the morphology of PANI obtained in the classical way (fig. 1).



a b

Figure 1. SEM image of PANI obtained in the classical way (a) and PAN obtained catalytically (b).

On SEM images we see that PANI obtained with the addition of a catalyst has larger agglomerates in the composition than PANI synthesized in the classical way. It is likely that in carrying out the polymerization process in the presence of a catalyst, the molecular weight of the desired product is higher than that in the absence of cobalt phthalocyanine.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-02-97008

PP-II-14

Stability of Supported Palladium Catalysts in Hydrogenation of p-Nitroaniline

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The applied catalysts based on metal nanoclusters are one of the main development trend in the field of catalysis and catalytic technologies in the 21st century. This type of material is a widespread catalyst, which is characterized a a highly disperse component (metal, oxide or salt) on the surface of the support. Such materials have their own set of characteristics, which can influence the catalyzed process in different ways. The most important characteristics of the catalyst are its catalytic activity, work stability and selectivity, which are directly related to the structure and physico-chemical properties of the material. The liquid phase hydrogenation is more safer and clean than the analogous reactions employing chemical compounds as the reducing agents, especially when hydrogenation is performed under high pressure and temperature. Products of hydrogenation are used in the manufacture of textile, paint and varnish, petrochemical, pharmaceuticals, in fine organic synthesis and in the production of plastic photostabilizers, etc.

However, the loss over time of catalytic activity and/or selectivity, is a problem of great and continuing concern in the practice of industrial catalytic processes. Thus, the purpose of this investigation was study of deactivation causes of palladium catalysts supported on various inorganic matrixes. In particular, the silica, coal and alumina were used as catalytic support.

The hydrogenation p-nitroaniline was performed in the temperature-controlled semi batch stirred reactor. The stirred reactor allows to perform of process without the effect of external diffusion. Method of the experiment included the five steps. The solvent and catalyst placed at reactor. The system was closed and thermostated and then the catalyst was saturated with hydrogen. After this, p-nitroaniline was placed at reactor via injector. The kinetic experiment was carry out under intensive mixing (3 000 rpm) and 298 K. The hydrogenation of p-nitroaniline was carried out over catalysts Pd/SiO_2, Pd/C, $Pd/\gamma\text{-}Al_2O_3$ in water solution of 2-propanol (0.68 mole fraction). The kinetics of reaction was measured using hydrogen uptake. Such the choice of research objects allowed to draw conclusions about the influence of both the structural characteristics of metal particles and the nature of the support. The analysis of reaction mixtures by UV-spectroscopy was showed, that the p-nitroaniline was completely converted to 1,4-phenylenediamine on all catalysts. Catalysts on a coal and gamma alumina are similar in activity, whereas palladium on silica is noticeably inferior to them. The curves example of hydrogen uptake are illustrated in figure 1.

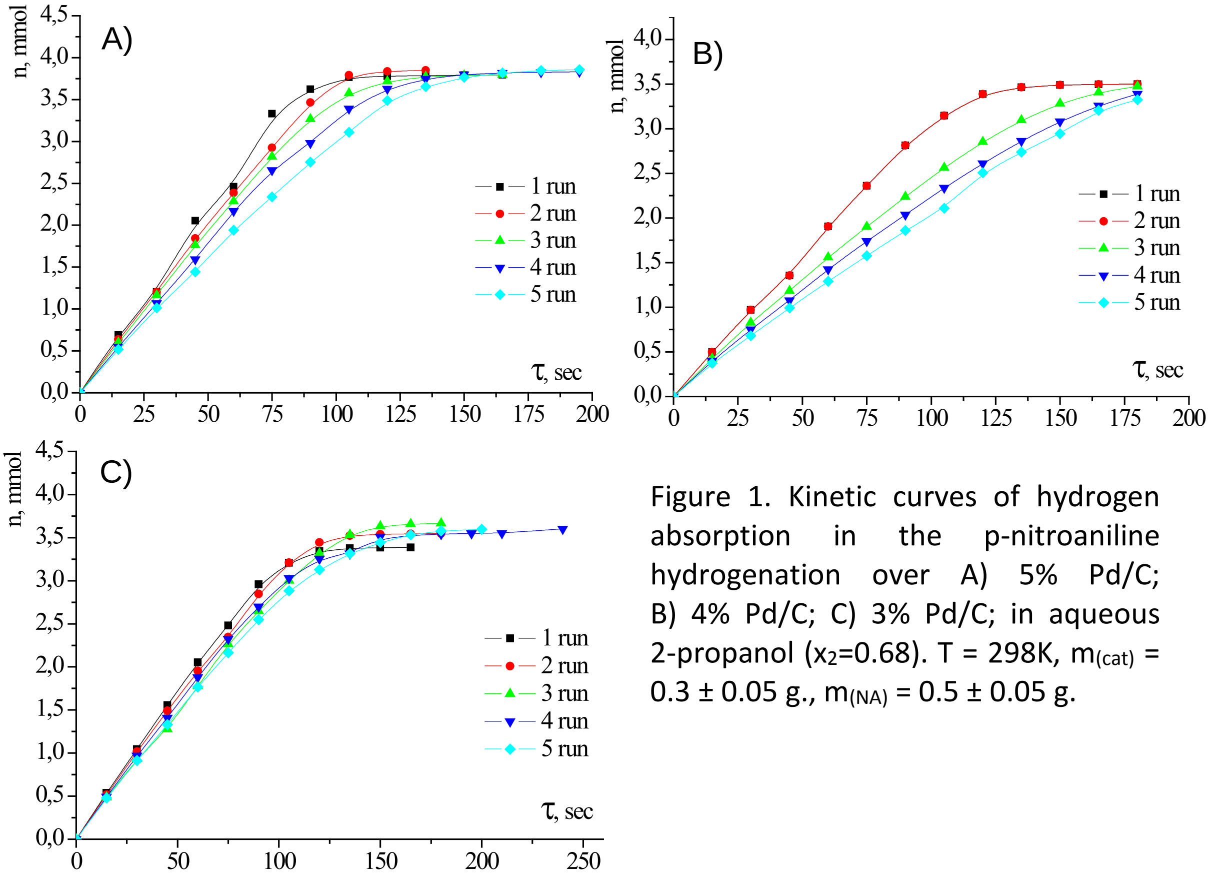

Figure 1. Kinetic curves of hydrogen absorption in the p-nitroaniline hydrogenation over A) 5% Pd/C; B) 4% Pd/C; C) 3% Pd/C; in aqueous 2-propanol (x_2=0.68). T = 298K, $m_{(cat)}$ = 0.3 ± 0.05 g., $m_{(NA)}$ = 0.5 ± 0.05 g.

A reaction is zero order if concentration data are plotted versus time and the result is a straight line. And the plots of amount of mole of substance vs. time gives a straight line (figure 1). The reaction rate per gram of supported metal increased with decreasing amount of palladium. The evaluation of the change in the activity of palladium catalysts on γ-Al_2O_3 under the conditions of repeated injections of 4-nitroaniline showed that the reaction rate on the 5% Pd catalyst decreased by 1.5 times after 3 runs and by 2 times after 5 runs. However, the reaction rate on 4% and 3% Pd / γ-Al_2O_3 decreased by 1.5 times only after 4 runs. Thus, the activity of the 5%, 4%, and 3% Pd//γ-Al_2O_3 catalysts declined by ~ 40%, ~ 32% and ~ 38% after 5 runs, respectively. The reaction rate per gram of supported metal did not significantly differ on 5% and 4% Pd/C catalysts and it increased by 1.5 times on 3% Pd/C. The comparison of palladium catalysts on coal showed, that the reaction rate on 5% and 4% Pd/C catalysts decreased by 1.5 times (36-38 percent) after 5 runs. The reaction rate on 3% Pd/C decreased by 10% only. Although 5, 4, 3% Pd/C catalysts more small activity than Pd /γ-Al_2O_3 and Pd/C catalysts, these have more catalyst lifetime. After 5 runs of reaction, these activity decreased by 20, 9 and 17 per cent only. For explanation of obtained results the XPS, TPR, TPD of ammonia and FTIR-spectroscopy studies were carried out. The defining factors of catalysts deactivation were acid-base properties and size of metal clusters.

PP-II-15

Supramolecular Catalysis in Solid Matrix. IR Experiment and Theory

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Traditionally, the theme of supramolecular catalysis was identified with biological systems and their inherent phenomena of enzymatic catalysis. However, with the development of supramolecular chemistry as a full-fledged direction in the chemical synthesis, one of its tasks became the creation of highly efficient and selective catalysts.In this aspect it is necessary to study the mechanisms of the catalysisin various modelling processes.This problem can be also important for chemistry of high-purity substances.

So, the present work shows that alkali metal halides can be effective catalysts for transformation of ammonia and carbon dioxide inhydration processes. A special technique of sample preparation for gaseous complexes for the investigation of the mechanism of these reactionsin IR spectral experiments was suggested [1]. Briefly it consists inco-condensation of water vapors and gases on a fine dispersionmaterial of the alkali metal halide with further pressing of solid matrix in shape of pellet.

A new band (3240 cm^{-1}) for ammonia-water system was observed in high frequencies region as well as for a heavy water complex (2460 cm^{-1}). In the region of middle frequencies we also have found new bandsfor H- and D-substituted systems (1495 and 1078cm^{-1}respectively). Because of good correlation of the isotopic shift values for the detected bands (νH/νD =1.32 for high frequency modes and 1.39 for middle frequency ones) we have assigned these bands to the OH-stretching of bonded water. Besides the middle frequency band (1495 cm^{-1}) locates in the same spectral range, where the absorption of ammonium salts is observed. Therefore this band can be assigned to the vibration within a cluster, in which the hydrogen atom transferred from water to ammonia molecule participates.

In the case of carbon dioxide-water system in high frequencies region two new bands (3120 and 2925 cm^{-1}) were observed, whereas for D-water complex only one new band (2455 cm^{-1}) was found. The isotopic shift (νH/νD =1.27) of this band agrees well with the theoretical value for the OH-stretching. In the 2600-2000 cm^{-1} region two new bands at 2140 and 2108 cm-^{1} were found which don't have any sufficient shift for heavy water cluster,and can be assigned to stretching of CO_2 molecule in the complex. In the middle IR region two overlapped bands (1395 and 1380 cm^{-1}) were revealed which also have no isotopic shift in the system with heavy water. Taking into account that the vibrations of carbonates locate in the presented range, we can interpret the mentioned absorption as the vibrations in (H_2CO_3)-fragment, arising in a cluster owing to the hydrogen atom transfer from water to the oxygen atom of carbon dioxide.

In our DFT calculations we have tested a set of clusters, including different ratios of interacted molecules. However for two shapes of clusters only the DFT treatment gives the optimized geometry along with the absence of negative frequencies, i.e. corresponding to the criteria of existence in quantum chemical approach.

The calculation gives the frequency of OH-stretching 3030 cm^{-1}. The big shift of this mode relatively free water OH-stretching is provided by the strong interaction between H-atom of water and N-atom of ammonia molecule. The relatively small transfer (0.05Å) of this H-atom to NH_3 fragment is almost barrier less, whereas the frequency of OH-stretching mode changes from 3030 up to 1698 cm^{-1}. An estimate of the total energy of the systems also shows a greater stability of the triple complex (27 kcal/moleversus 7 kcal/mole for binary one).

The oxygen atom of carbon dioxide can form hydrogen bond rarely, in contrast to nitrogen atom of ammonia, which is a classical donor in hydrogen bonded intermediates. Therefore in the case of the CO_2/H_2O complex formation in KBr matrix the mechanism of their interaction should be completely different. So, the optimized geometry of water complex with carbon dioxide contains not one, but two water molecule ($2H_2O/CO_2/KBr$). The calculations predict the hydrogen atom transfer from the proton active water cluster to the oxygen atom of carbon dioxide and following transformation of this system in H_2CO_3 molecule.

On the whole the presented DFT data agree with the effects observed in the IR spectra. The appearance of new bands is the manifestation of water bonding with ammonia or carbon dioxide accompanied by the hydrogen atom transfer from water to a partner molecule. The KBr matrix is not neutral in both cases and its role is to hold the components and to provide the decrease of the activation barrier of molecular transformation.

Acknowledgement. This work was supported by the Russian Foundation of Basic research, grant No 14-08-00898-a, and the Ministry of Education and Science of the Russian Federation, Basic Part of State Task, project No 2897.

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PP-II-16

Synthesis of Selective Pd Catalyst Supported on Nitrogen-Doped Carbon Nanotubes for Acetylene Hydrogenation

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Nitrogen-doped carbon nanomaterials (N-CNMs) are of great interest for application in catalysis due to their exceptional physico-chemical properties [1]. Doping of CNMs with nitrogen influences on acid-base, hydrophilic-hydrophobic and electro-physical characteristics of carbon nanomaterials. It was shown that using of N-CNMs as a catalyst support leads to the change of supported metal particles size, acceleration of electron transfer and formation of new adsorption sites on the carbon surface. Presently different N-CNMs (nitrogen-doped carbon nanotubes (N-CNTs), carbon nanofibers, nanowires, nanorods, activated carbon, graphene) are successfully synthesized and studied for catalytic applications. The goal of the present work is to study the N-CNTs as a support of palladium catalyst for the reaction of selective acetylene hydrogenation in ethylene-rich mixtures.

CNTs were synthesized by catalytic decomposition of ethylene, whereas N-CNTs – by decomposition of 40% C_2H_4/60% NH_3 mixture on iron-based catalyst [2]. It was found that nitrogen content in N-CNTs was 4,8 at.%. According to XPS data nitrogen is in 3 main electronic states: pyridinic, pyrrolic and graphite-like. TEM showed that CNTs have typical coaxial-cylindrical, whereas N-CNTs – bamboo-like structure.

Catalysts 2% Pd/CNTs, 2% Pd/N-CNTs and 0,2% Pd/N-CNTs were synthesized by precipitation from solution of $Pd(OAc)_2$ in the presence of triphenylphosphine (PPh_3) with molar ratio $PPh_3/Pd = 0.4$. The liquid-phase reduction of the samples was carried out in hydrogen flow at 40˚C. Catalytic activity of the catalysts was measured in the reaction of selective hydrogenation of acetylene to ethylene in a quartz flow reactor. The reaction mixture contained 99,2 % ethylene and 0,8 % acetylene.

TEM images show that the size of visible Pd particles in 2% Pd/CNTs и 2% Pd/N-CNTs decreases from 7-8 nm to 1,5 nm respectively. CO chemisorption data agree with the TEM results: CO/Pd for CNTs is 24 % and for N-CNTs – 38%. According to XPS data palladium was shown to be in two states: highly disperse metallic (Pd^0, 335.7-335.9 eV) and ionic ($Pd^{\delta+}$, 337.6-337.8 eV). The doping of CNTs with nitrogen leads to the increase of $Pd^{\delta+}$ fraction from 30 to 45 %. There are no visible palladium particles in 0,2% Pd/N-CNTs catalyst in TEM images, however CO/Pd did not exceed value of ~3-5%. XPS showed that Pd in this catalyst was only in the ionic state with the binding energy 337.8 eV. Therefore it can be concluded that Pd particles interact with pyridinic nitrogen (N_{Py}) sites near the carbon vacancy in the graphene layer of N-CNTs with the formation of subnanometer ionic particles invisible by TEM. As the concentration of palladium is increased up to 2% and the N_{Py} sites are consumed, Pd starts to interact with the N_Q sites with the stabilization of palladium nanoparticles in the metallic state (Pd^0). On the basis of these data it was concluded that nitrogen sites (N_{Py} и N_Q) have different reactivity.

The stability of $Pd^{\delta+}$ in the catalysts was studied by XPS. To avoid the contact with atmosphere the samples were heated in hydrogen from 50 to 700˚C in the preparation chamber of spectrometer. It was found, that in the catalyst 2% Pd/CNTs $Pd^{\delta+}$ is present only up to 200˚C and is formed due to the oxidation during sample storage. In 2% Pd/N-CNTs and 0,2% Pd/N-CNTs catalysts $Pd^{\delta+}$ is registered up to 500-600˚C confirming the interaction of Pd particles with pyridinic nitrogen sites of N-CNTs.

The catalysts 2% Pd/CNTs и 2% Pd/N-CNTs showed 100% conversion in the reaction of acetylene hydrogenation at 25˚C, but the ethylene selectivity doesn`t exceed 6-8 %. In the case of 0,2% Pd/N-CNTs selectivity increases up to 70% with simultaneous decrease of conversion down to 20%, fig. 1a. Increasing the temperature allows improving the conversion and conservation of the high value of selectivity: at 65˚C conversion of acetylene is 80 % and ethylene selectivity – 80%, fig. 1b. According to this data it can be concluded that subnanometer ionic palladium particles are highly selective sites in this reaction compared to nanosized Pd^o, and preservation of high selectivity with the reaction temperature grow is explained by the thermal stability of $Pd^{\delta+}$ state.

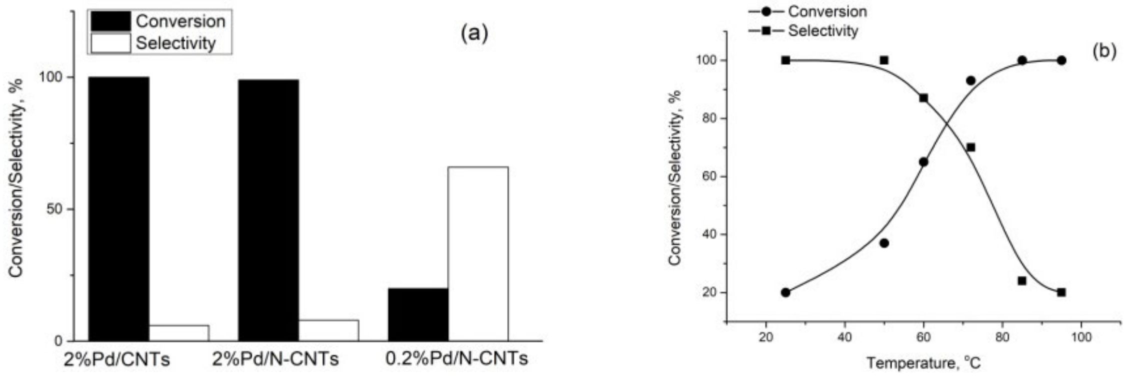

Figure 1. a) Dependence of acetylene conversion and ethylene selectivity on different catalysts at 25˚C; b) temperature dependencies of acetylene conversion and ethylene selectivity on the catalyst 0.2%Pd/N-CNTs.

Thus, it was shown that Pd particles interact with nitrogen sites of N-CNTs giving metal nanoparticles and ionic subnanoparticles. Thermally stable palladium subnanoparticles in ionic state stabilized by pyridinic nitrogen near the carbon vacancy in the graphene layer of N-CNTs were found to be selective in acetylene hydrogenation reaction.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 18-33-00764.

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PP-II-17

Silver-Containing Mixed Oxides as Catalysts for CO and C_2H_4 Oxidation

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The development of heterogeneous catalysis as the relevant field of modern science implies the synthesis, research and detail investigation of novel catalytic systems. Mixed oxides of Ib group metals are attractive objects for various catalytic applications including oxidative processes [1,2]. Such interest is caused by the modification of reaction/catalytic properties of oxygen within mixed oxide lattice owing to the coordination by two or more different metal types. In this work, the catalytic properties silver-containing mixed oxides such as $Ag_2Cu_2O_3$, $Ag_2Cu_2O_4$ and $AgNiO_2$ in CO oxidation and C_2H_4 epoxidation are presented.

All mixed oxides were synthesized from solutions of metal nitrates by co-precipitation in alkaline medium. Catalytic measurements were performed using an automatic setup equipped with a plug flow reactor and a mass-spectrometer for the analysis of gaseous mixtures. Both $Ag_2Cu_2O_4$ and $AgNiO_2$ demonstrated the activity in CO oxidation at room temperature (RT), while oxide $Ag_2Cu_2O_3$ interacted with CO starting from 50-60°C only. In case of the presence of H_2O vapors in reaction medium the full deactivation in RT CO oxidation was observed for $Ag_2Cu_2O_4$ and $AgNiO_2$. Oxides $Ag_2Cu_2O_3$ and $Ag_2Cu_2O_4$ were found to be unstable under C_2H_4 epoxidation conditions during heating in the range from 180 to 250°C. It resulted in the decomposition of silver-copper mixed oxides into Ag^0/CuO composites, which demonstrated the selectivity in partial C_2H_4 oxidation close to 15-25%. In case of $AgNiO_2$ the partial C_2H_4 oxidation activity was observed even at RT. Corresponding value of C_2H_4 selectivity near 60-70% was attributed to weakly bounded oxygen species on the surface of $AgNiO_2$. Additional studies concerning the nature of such oxygen are needed.

For characterization of structural features and element states on the surface of mixed oxides were studied by X-ray diffraction and X-ray photoelectron spectroscopy, respectively. Particularly, the catalytic properties of CO oxidation over $Ag_2Cu_2O_3$ were attributed to $Cu^{2+}\leftrightarrow Cu^{1+}$ surface transition. High oxidation activity of $AgNiO_2$ and $Ag_2Cu_2O_4$ oxides at RT is likely caused by the presence of unusual metal species like Ni^{3+} and Ag^{3+}/Cu^{3+}, respectively.

Mixed oxides are interesting model objects for studies in oxidative catalysis field.

Acknowledgement. The reported research was funded by Russian Foundation for Basic Research and the government of the region of the Russian Federation, grant № 18-43-540013

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PP-II-18

Synthesis and Photocatalytic Activity of Fibrous CeO_2 Nanostructures

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Nanocrystalline cerium dioxide is a widely used nanomaterial for applications in catalysts, fuel cell, microelectronics, optics and medicine [1]. The advantage of cerium dioxide nanostructures in comparison with other semiconductor particles is its low toxicity, long-term stability, oxygen non-stoichiometry, biological inertness, photocatalytic activity under the UV and visible light.

The purpose of this work is the synthesis of fibrous structures containing CeO_2 nanoparticles and studying their photocatalytic activity.

Fibrous CeO_2 nanostructures have been prepared by mixing ethanol solutions of cerium (III) nitrate $Ce(NO_3)_3 \cdot 6H_2O$ and bleached sulfate cellulose as a template. The sulfate cellulose modified with cerium(III) nitrate was calcined in a muffle furnace at a temperature of 600-800°C for 120 min in air.

Calcination of cerium (III) nitrate in air at a temperature of 600 °C without cellulose leads to forming particles of cerium dioxide:

$$2Ce(NO_3)_3 \cdot 6H_2O \xrightarrow{t} 2CeO_2 + 6NO_2 + O_2 + 12H_2O$$

the structural parameters of which were determined by X-ray diffraction. The diffraction peaks at 28.65°(111); 33.18°(200); 47.57°(220); 56.42°(311); 69.52°(400); 76,73°(331) corresponds to face-centered cubic crystal structure of "cerianite" [2].

Using cellulose as a template makes possible to obtain highly porous, fibrous structures consisting of cerium dioxide nanoparticles. Earlier a similar synthesis procedure was used in [3] to obtain mesoporous structures of titanium dioxide. Calcination of the sulfate cellulose which was modified by cerium nitrate removes template and leads to the formation of material that replicate the shape of the initial sulfate cellulose fibers. The diameter of fibrous CeO_2 structures is in the range from 9 to 5 µm. According to the results of X-ray diffraction analysis samples calcined at 600 and 800 °C have crystal structure of "cerianite". It follows from X-ray diffraction patterns that the degree of crystallinity of the samples increases with increasing calcination temperature. The samples of CeO_2 calcined at 600 °C have low-intensity and broad characteristic peaks, which indicates its amorphous structure. CeO_2 particles obtained by calcination at a temperature of 800 °C were characterized by high crystallinity, as evidenced by high intensity of the peaks and their small width. Diameter of the CeO_2 particles depends of annealing temperature and $Ce(NO_3)_3$ concentration and consists 18 – 30 nm as determined using the Scherrer formula.

PP-II-18

The results of IR spectroscopy studying of cerium dioxide samples obtained by the template synthesis on cellulose showed that calcination at a temperature of 800 °C led to disappearance of the bands at 741; 814; 896; 1112; 1203; 1467 cm^{-1}, attributable to deformation vibrations of C-O, C-C and C-H bonds, respectively, which is explained by complete combustion of cellulose upon calcination. At a temperature of 600 °C, absorption bands with a lower intensity are observed at 849; 954; 1539 cm^{-1}, which may indicate incomplete combustion of cellulose.

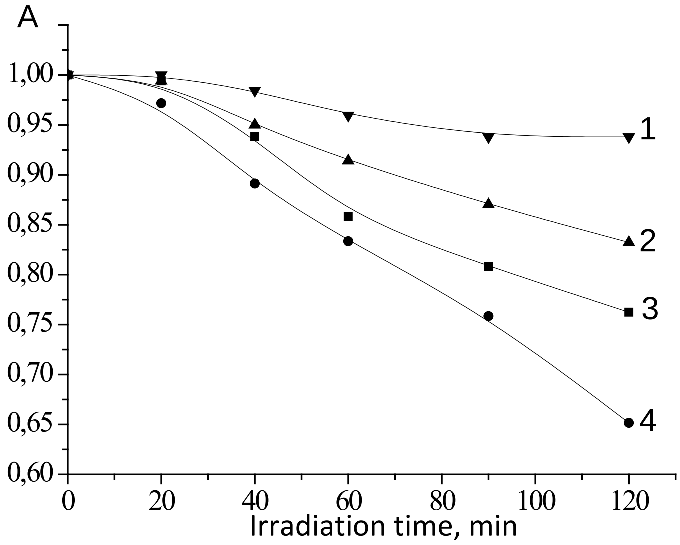

Fig. Kinetic curves of methyl orange (pH 3.5) photodegradation in the presence of:
1) fibrous CeO_2, calcination temperature 600°C
2) nonfibrous CeO_2, calcination temperature 600°C
3) nonfibrous CeO_2, calcination temperature 800°C
4) fibrous CeO_2, calcination temperature 800°C

The photocatalytic activity of CeO_2 nanostructures was investigated by photodegradation of the well-known organic dye methyl orange (MO) (pH 3.5, acetate buffer solution) under the influence of UV light with λ_{exc} 254 nm.

It was found that the samples obtained on calcination of $Ce(NO_3)_3$ on cellulose at a temperature 800 °C have better photocatalytic properties than samples annealed at a temperature of 600 °C (Fig.), which is connected with a smaller crystallite size of CeO_2 and possible presence of impurities due to incomplete decomposition of cellulose and cerium (III) nitrate at temperatures of 600 °C. The relative rate of photodegradation of MO in the presence of fibrous structures of CeO_2 annealed at a temperature of 800 ° C is two times greater than that of CeO_2 particles obtained without using a template.

The influence of CeO_2 dosage, initial pH of dye solution and the excitation wavelength on the photodegradation rate of methyl orange also were studied.

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PP-II-19

Supercritical Fluid Extraction Regeneration of LD-145 Catalyst

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The present work is devoted to the investigation of the possibility of regenerating the selective hydrogenation catalyst LD-145 by the method of supercritical fluid CO2 extraction (SCFE).

The process of regeneration of the catalyst samples was carried out at the facility [1] using pure SC-CO2 at pressures of 10, 20 MPa and temperatures of 343, 373, 433, 473 K. The change in the mass of the catalyst during the regeneration, depending on the mass involved in the extractant process, for four isotherms at a pressure of 20 MPa, is shown in the figure.

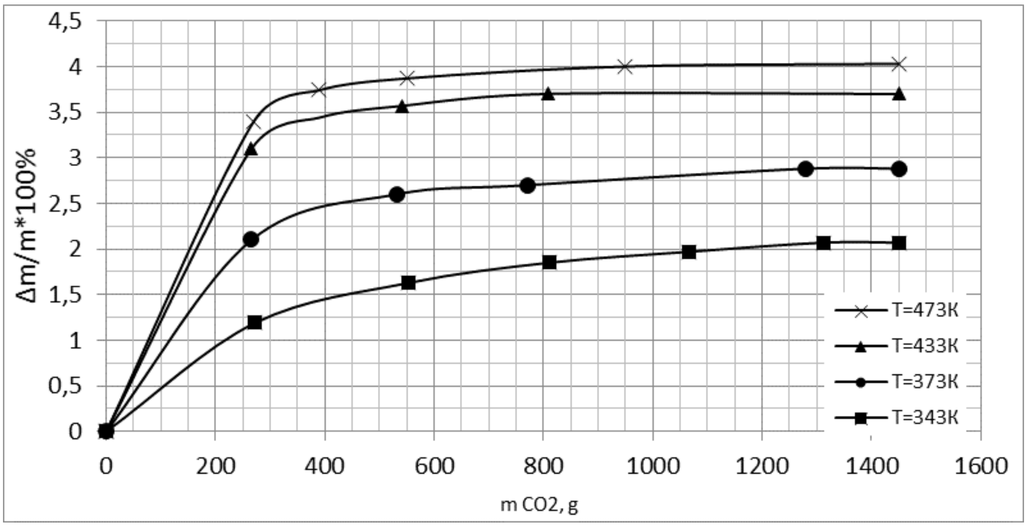

Figure 1 - The kinetics of SCFE regeneration process of LD-145 catalyst at P=20MPa

In order to determine the degree of recovery of the compaction products, the catalyst samples were weighed before and after the experiment on an electronic balance. Weighing results are shown in the table.

Temperature	Loss of mass of catalyst samples at pressures, %	
	10 MPa	20 MPa
343 K	1.92	2.07
373 K	2.50	2.88
433 K	3.57	3.70
473 K	-	4.03

As can be seen from the figure and the table, an increase in pressure and temperature has a positive effect on the process of catalyst regeneration. A similar effect of pressure and temperature is due to the fact that with increasing pressure, the density of CO_2 increases, and, consequently, its dissolving power. With increasing temperature, the pressure of saturated vapor of the compaction products increases and, as a consequence, their concentration in CO_2 increases [2]. In such conditions the temperature affects the change in mass more strongly. The greatest weight loss was 4.03% for a sample of the catalyst regenerated by the method of SCFE at a pressure of 20 MPa and a temperature of 473 K.

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PP-II-20

XPS Study of Oxidative Dehydrogenation of Propane over V_2O_5/TiO_2 Catalysts

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Propylene is one of the most important feedstocks in the chemical industry. It is a starting material for the synthesis of a wide variety of chemicals. Traditionally, propylene is produced along with other light olefins by steam cracking or fluid catalytic cracking of higher hydrocarbons. These methods are not ideal as the costs of the starting materials escalate and due to poor selectivity increasing production, purification, and energetic costs. An alternative way is to develop and to utilize one-step methods, in which propylene is the end product and is produced with high selectivity. One of the most promising processes is oxidative dehydrogenation of propane (ODP), which ideally produces just propylene and water. It is known that catalysts based on vanadium oxide demonstrate high activity in this reaction. Here, we report the first results of our mechanistic study of the gas-phase ODP over titania-supported vanadium oxide catalysts. We used X-ray photoelectron spectroscopy (XPS) to study the catalyst state during ODP. The XPS experiments were performed on a photoelectron spectrometer equipped with a high-pressure cell which enables to heat catalysts before analyzing in gaseous mixtures at pressures up to 0.5 MPa. The catalyst state was studied before and after treatment under flows of propane and O_2. Recently, such approach we have applied for study the oxidation of ethanol over V_2O_5/TiO_2 catalysts [1].

According to XPS data treating the fully oxidized V_2O_5/TiO_2 catalyst in the propane flow at 1 bar and 420°C for 30 min leads to full reduction of V^{5+} to V^{4+} and V^{3+}. This process is reversible and full oxidation of vanadium cations to the V^{5+} state occurs in oxygen even at 350°C. Following treatment in a flow of the propane/oxygen mixture at 420°C for 30 min leads to the partial reduction of V^{5+} to V^{4+}. It means that in the presence of oxygen in the gas phase, the fast oxidation of the V^{3+} cations takes place. The obtained data confirm that the ODP proceeds via redox mechanism.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 18-33-00431.

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PP-III-1

Transfer Hydrogenation Reactions in the Presence of a Chiral bis-Imine Rhodium (I) Complexes. Modelling and Experimental Study

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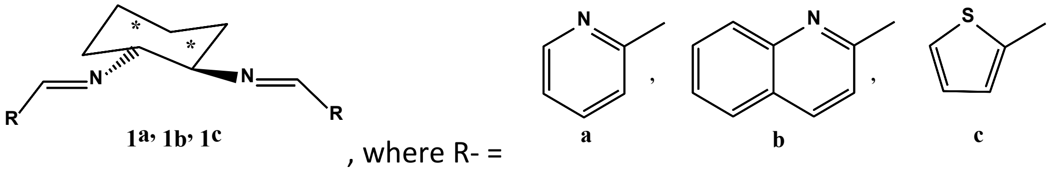
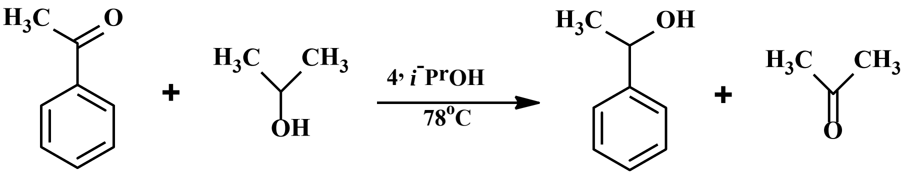
The aim of our study is a rhodium (1+) complexes generated *in situ* by the interaction of chloride dimeric complex [Rh(1,5-cod)μ-Cl]$_2$ with a small excess of optically active *N,N,N,N* - and *S,N,N,S*-ligands **1a**, **1b** and **1c** in transfer hydrogenation (TH) of acetophenone (APh).





(eq1)

The reaction proceeds according to the equation 1. Mechanisms of TH reaction studied in detail mainly for diamine complexes of transition metals. Based on NMR spectroscopy data we exclude the "metal-ligand bifunctional catalysis" proved for complexes with H-N-Me-H fragments, where the Me-transition metal [1]. The formation of d8 - monohydride rhodium complex is postulated in a several articles [2].Despite the lack of direct evidence (no hydride is observed by NMR investigations), the participation of hydride species as a key intermediate is possible.

Guiral et al.[3] found that for a Rh complex bearing a tertiary diamine ligand direct transfer of the α-hydrogen of metalalkoxide complex to prochiral ketone is also possible. This mechanism is commonly known as the Meerwein-Ponndorf-Verley reduction. Whether the mechanism is «migratory insertion» or «Meerwein-Ponndorf-Verley reduction» cannot be deduced from the results presented in our paper.

We proposed a scheme of mechanism for reaction of TH APh. It includes stages of successive formation of the active complex K$_a$ (NNNN) Rh-OiPr) during cyclooctadiene hydrogenation, rhodium hydride as a result of β-hydride transfer (eq.2), coordination of APh (eq.3) and "migratory insertion" (eq. 4), which are consecutive and each stage is in equilibrium. In the scheme of mechanism these stages are combined into one.

$$\mathrm{(NNNN)Rh - OiPr} \rightleftarrows \mathrm{(NNNN)RhH + (CH_3)_2C = O} \tag{2}$$

$$\mathrm{(NNNN)RhH + Ph(CH_3)C = O} \rightleftarrows \mathrm{(NNNN)RhH(re, si - Ph(CH_3)C = O)} \tag{3}$$

$$\mathrm{(NNNN)RhH(re, si - Ph(CH_3)C = O)} \leftrightarrows r,s - (NNNN)Rh - O - C^{*}HPh(CH_3)\,(\mathrm{K_a SHr}\ U\ K_a SHs) \tag{4}$$

The reaction products (R) and (S)-1-phenylethanol are formed with regeneration of K_a catalyst (eq.5). The equilibrium of this reversible reaction is strongly shifted to the right because of the large excess of reagent 2-propanol (i-PrOH/Rh ≈ (6÷20)*10^3).

$$r,s-(NNNN)Rh-OCHPh(CH_3)+iPrOH \rightleftarrows (NNNN)Rh-OCH(CH_3)_2+r,s-Ph(CH_3)CHOH \qquad (5)$$

To simplify the kinetic scheme reactions 2, 3 and 4 were also combined into one with k_1 and k_{-1}. Scheme shows the simplified catalytic cycle of asymmetric transfer hydrogenation of ketones, containing two cycles corresponding to two pathways of enantiomers forming.

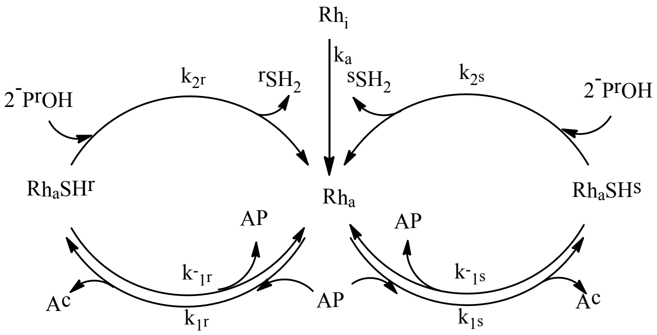


Figure. The proposed scheme for the transfer hydrogenation of AP

Formal kinetic rate laws for the formation of products were derived from the Scheme using the Bodenstein approach for the catalytic intermediates [Rh_aSH_r] and [Rh_aSH_s]:

$$r_{S\text{-}PE}=\frac{k_{2s}[Rh_0]k_{1s}[AP]}{(k_{-1s}[Ac]+k_{2s})\left(1+\frac{1}{k_a}+\frac{k_{1r}[AP]}{k_{-1r}[Ac]+k_{2r}}+\frac{k_{1s}[AP]}{k_{-1s}[Ac]+k_{2s}}\right)} \qquad (6)$$

$$r_{R\text{-}PE}=\frac{k_{2r}[Rh_0]k_{1r}[APh]}{(k_{-1r}[Ac]+k_{2r})\left(1+\frac{1}{k_a}+\frac{k_{1r}[AP]}{k_{-1r}[Ac]+k_{2r}}+\frac{k_{1s}[AP]}{k_{-1s}[Ac]+k_{2s}}\right)} \qquad (7)$$

The kinetic constants (k_a, k_{1s}, k_{-1s}, k_{2s}, k_{1r}, k_{-1r}, k_{2r}) were estimated in time from the curves for formation of R and S 1-phenylethanol enantiomers in 12 experiments by minimizing the average statistical deviations.

Table– Calculated constants for the proposed scheme

k_a×10^2, *L/ mol*min*	k_{1s}, *L/ mol*min*	k_{-1s} ×10, *L/ mol*min*	k_{2s}×10^2, *min^{-1}*	k_{1r}, *L/ mol*min*	k_{-1r}×10, *L/ mol*min*	k_{2r}×10^2, *min^{-1}*
1,60±0,15	19,50±1,98	1,57±0,37	1,14±0,11	41,89±1,51	3,02±0,7	2,23±0,11

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PP-III-2

DFT Study of Pd Catalyzed Carbon-Carbon, Carbon-Heteroatom and Heteroatom-Heteroatom Bonds Formation

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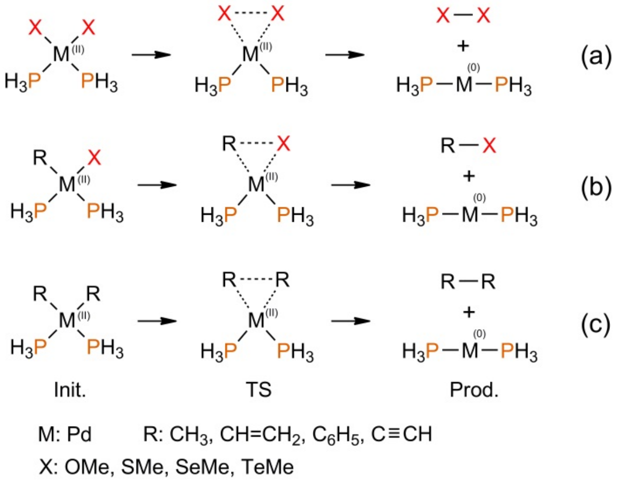
Reductive elimination process is one of the main stages in the metal-catalyzed cross coupling reactions. Key features of reductive elimination processes for various substrates are currently in the focus of experimental and theoretical research [1,2]. However, those cases of reductive elimination that involve heteroatoms and result in C-X, X-X, and X-Y bonds formation are studied much less than C-C bond formation.



Scheme 1. Symmetric (a), (c) and non-symmetric (b) couplings on Pd complexes.

In this study we demonstrate that the energy parameters (activation energies, reaction energies) of symmetric and non-symmetric reductive elimination reactions (Scheme 1) are mutually correlated. For chalcogenide groups (X), the energy values for non-symmetric reactions, resulting in formation of R-X bonds, are intermediate between the values for symmetric reactions leading to X-X and R-R products. For example, the energy of Me-OMe non-symmetric bond formation constitutes -15.1 kcal/mol thus occupying an intermediate position between symmetric Me-Me (-31.4 kcal/mol) and MeO-OMe (35.6 kcal/mol) reductive elimination energies. We also show a possibility to apply the observed correlations to the RX homolitic dissociation reactions, given that bond dissociation energy (BDE) values for non-symmetric R-X bonds occupy intermediate positions between the values for symmetric R-R and X-X bonds.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 17-03-01148.

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PP-III-3

The Role of Confinement on the Reactivity of Fe-ZSM-5 Zeolite in the Selective Methane Oxidation

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Selective large-scale functionalization of alkanes is considered so promising nowadays that it is perceived as a “Holy Grail in Chemistry” [1]. Among many viable processes, the selective catalytic conversion of methane to methanol at a low temperature represents a particular challenge that attracts much attention nowadays from researchers both in industry and in academia. Recent studies have identified zeolites modified with earth-abundant Cu- and Fe-ions as the effective heterogeneous catalyst enabling such a low-temperature oxo-functionalization of methane [2]. Recently, many theoretical studies have focused on analyzing structure-activity relations for such catalytic sites and they led to a proposal on the existence of linear-type relationships between the basic thermodynamic properties and their kinetic behavior towards C-H activation [3]. We propose that such simplified relationships can be largely disrupted when the details of the chemical environment of the active site are taken into account in the computational model [4]. To verify this hypothesis, we have carried out in this work a detailed periodic DFT study on the C-H activation of methane at representative sites of ZSM-5 zeolite functionalized with a Fe_2O_2-center.

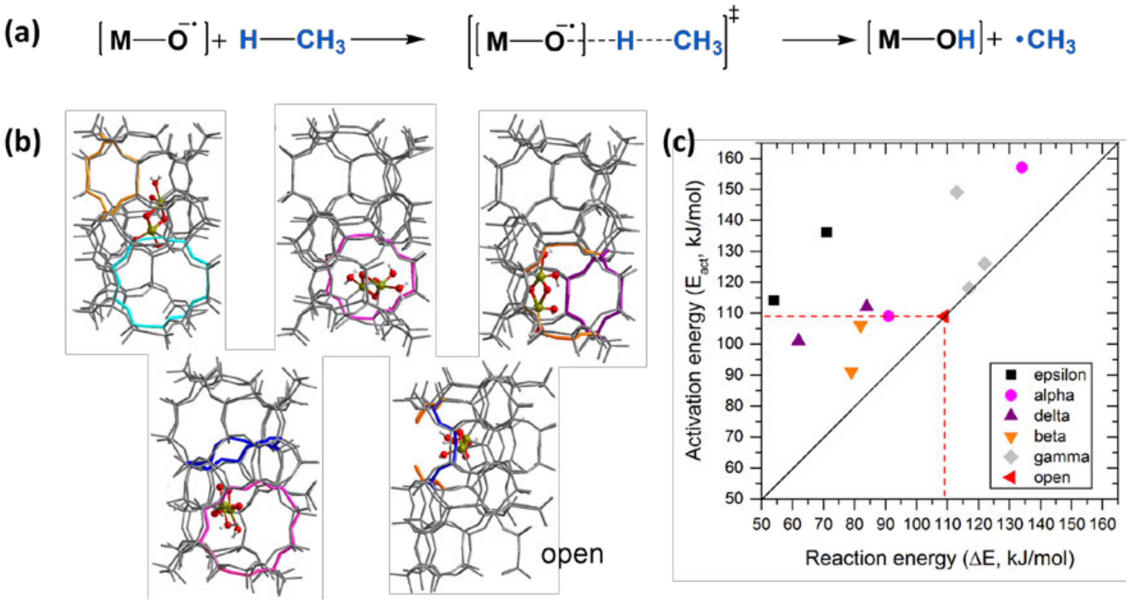

Figure 1. (a) The homolytic activation of methane by a M-O fragment of a more complex reactive species. (b) Representative configurations of Fe_2O_2 active site stabilized in periodic ZSM-5 zeolite models and (c) the respective DFT-computed C-H activation barriers plotted against the associated reaction energies.

All calculations were carried out with the PBE exchange-correlation functional using VASP 5.2. Plane-wave basis set with the cut-off energy of 400 eV in combination with PAW method was employed. Fully periodic MFI unit cell with two lattice Al substitutions was used as a model. The negative lattice charge was balanced by the binuclear iron complex. The representative radical homolytic C-H cleavage mechanism only was considered (Figure 1(a). The locations of the complex were selected such that distinct confinement environment at the active site could be realized. External surface sites were represented by a slab MFI mode (Figure 1(b).

Our results clearly show that the size and the shape of the pore environment surrounding Fe_2O_2-center influences both the barriers and the enthalpies of C-H-bond activation significantly (Figure 1(c). Depending on the model, the C-H cleavage barrier varied from 90 up to 160 kJ/mol with the more confined sites being generally less reactive. More important is the apparent lack of the correlation between the reaction enthalpy and the activation barrier. Because the homolytic C-H cleavage (Figure 1(a)) involves the formation of a free CH_3 radical species only weakly bound with the zeolite lattice, one expects that both the reaction energy and its barrier depend mostly on the hydrogen affinity of the extraframework basic site and therefore scale linearly with each other. Indeed, a very close dependence of the two parameters is identified for the most open γ-site located at the intersection of the sinusoidal and straight MFI channels and for the model mimicking the external surface environment. For other sites, the effects of confinement can have both the stabilizing effect on the final radical product and destabilizing influence of the transition state giving rise to a substantial deviation from the linear relation between the thermodynamic and kinetic parameters. Furthermore, our calculations demonstrate that the electronic structure of the active site evolves along the reaction path for the C-H activation making the construction of any linear relationships for the prediction of reaction barriers from thermodynamic parameters impossible.

Acknowledgement. This work was supported by the Ministry of Education and Science of Russian Federation, goszadanie no 11.1706.2017/4.6.

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PP-III-4

Reactivity of Methane Activation Intermediates Formed on Cu-ZSM-5, Contained Different Copper Sites

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1. Scope

Cu-containing zeolites are believed to be promising catalyst for selective conversion of methane under mild conditions [1]. Spectroscopic characterization of the zeolites showes the formation of Cu-sites of different structure and composition is possible. There have been detected isolated Cu^+ and Cu^{2+} cations, dimmer CuOCu species, various oxoclusters, etc. [2]. However, there is no proper understanding of the role of different Cu-sites in methane activation yet. Also, there is no data about the link between the structure of active sites and the mechanism of methane activation. Thus, the investigation of methane activation on the Cu-containing zeolites modified with Cu-sites of different structure and composition is very important fundamental objective. To address this problem, the study of different Cu-containing zeolites with respect to methane activation has been performed: ^{13}C CP/MAS NMR technique has been aplied for the characterization of the nature and reactivity of the intermediates formed from methane when interacting with Cu-sites.

2. Results and discussion

The samples of Cu-containing zeolites with two different Cu-sites have been synthesized. The treatment with oxygen for both samples has been performed prior the reaction with methane. UV-vis and NMR spectroscopy characterization of the Cu-sites has been carried out: samples Cu^{2+}/H-ZSM-5 and CuO/H-ZSM-5 contain isolated Cu^{2+}cations and small oxide CuO clusters respectively.

Figure 1a,b demonstrates the ^{13}C CP/MAS NMR spectra of surface methoxide intermediates formed from methane after the interaction with different Cu-sites. The signal at 63 ppm has been previously assigned to methyl group attached to Cu^{2+}–O–Cu^{2+} site which has been proposed to provide methanol formation [3]. The signals at 59 ppm and 53 ppm correspond to methyl groups attached on different types of bridge groups SiOAl. The fact that all these species survive evacuation under vacuum at 473K points that they are strongly adsorbed on the zeolite surface.

To provide more information on the difference of Cu-sites properties with respect to methane activation, the reactivity of the intermediates has been examined in the reaction with benzene. Figure 1c shows ^{13}C CP/MAS NMR spectra of Cu^{2+}/H-ZSM-5 after benzene adsorption and heating to 523 K. As it is seen, the intensity of the signal at 63 ppm becomes

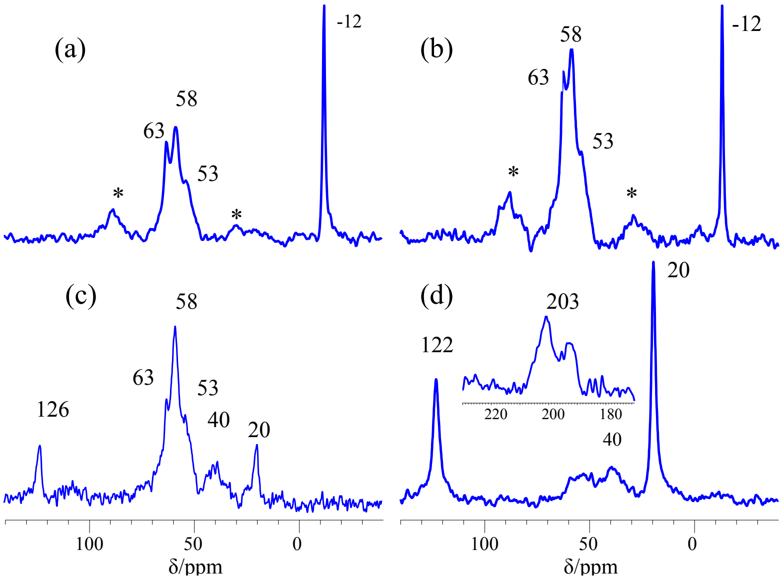

Figure 1.^{13}C CP/MAS NMR spectra of the surface intermediates formed from methane-^{13}C at 523 K adsorbed on Cu^{2+}/H-ZSM-5 (a), CuO/H-ZSM-5 (b). ^{13}C CP/MAS NMR spectra of the surface intermediates formed from methane-^{13}C and adsorbed benzene on Cu^{2+}/H-ZSM-5 (c), CuO/H-ZSM-5 (d). Asterisks (*) denotes spinning side bands.

lower and signal at 20 ppm, which corresponds to methyl groups of toluene, are observed. This indicates that only methoxide species detected by the signal at 63 ppm provides methylation of benzene.

Figure 1-d demonstrates ^{13}C CP/MAS NMR spectra of CuO/H-ZSM-5 after benzene adsorption and heating to 523 K. Clearly, there is a remarkable difference as compared to figure 1-c. The signals from surface methoxides almost completely disappear; the intensity of the signal at 20 ppm is much higher and a new signal at 200 ppm, that may correspond to benzaldehyde, can be observed. Thus, it is clear that Cu-containing zeolites can demonstrate different properties for methane conversion depending on the structure and composition of active Cu-sites.

3. Conclusions

Methane activation by two Cu-modified H-ZSM-5 zeolites containing exclusively either Cu^{2+} cations or small oxide CuO clusters has been studied. Reactivity of surface intermediates has been checked through reaction with benzene. The results have demonstrated higher conversion of surface methoxides, and thus methane to methyl group of toluene for CuO/H-ZSM-5 as compared to Cu^{2+}/H-ZSM-5. Also, formation of benzaldehyde observed on CuO/H-ZSM-5.

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PP-III-5

Selective CO Methanation in the Hydrogen-Rich Gas over the Halogen (F, Cl, Br) Promoted Ni/CeO_2 Catalysts

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The process of selective CO methanation in hydrogen-rich gas mixtures in the presence of CO_2 is a promising way for deep CO removal designed for low-temperature proton-exchanged membrane fuel cell feeding applications, as well as a challenging fundamental problem of substrate-selective hydrogenation. In addition to the target CO methanation reaction (1), undesirable CO_2 methanation (2) and reverse water-gas shift (3) reactions may occur, causing considerable hydrogen losses and increasing CO outlet concentration:

$$CO+3H_2 = CH_4 + H_2O; \qquad \Delta H^o = -206 \text{ kJ/mol} \qquad (1)$$

$$CO_2+4H_2 = CH_4 + 2H_2O; \qquad \Delta H^o = -165 \text{ kJ/mol} \qquad (2)$$

$$CO_2 + H_2 = CO + H_2O; \qquad \Delta H^o = 41 \text{ kJ/mol} \qquad (3)$$

Recently, we have shown that Ni/CeO_2-based systems are efficient catalysts for selective CO methanation [1,2]. The positive effect of chlorine additives on Ni/CeO_2 catalyst's selectivity was discovered [2]. However, the origin of the effect is yet not fully cleared.

In this work we show the results on the comparative study of the CO selective methanation in the realistic H_2-rich gas mixture containing 1 vol.% CO, 10 vol.% H_2O and 20 vol.% CO_2 over free and halogen (F, Cl, Br) promotion Ni/CeO_2 catalysts. Catalytic performance of the Ni/CeO_2, Ni(F*)/CeO_2, Ni(Cl*)/CeO_2 and Ni(Br*)/CeO_2 catalysts were studied in the reaction. BET, XRD, HRTEM, EDX, XPS and CO chemisorption techniques were used for catalysts characterization.

The effect of halogen additives was studied on Ni/CeO_2 catalyst prepared from a nitrate precursor. Halogen-promoted Ni(F*)/CeO_2, Ni(Cl*)/CeO_2 and Ni(Br*)/CeO_2 catalysts were prepared by treatment of Ni/CeO_2 by the aqueous solutions of NH_4F, NH_4Cl and NH_4Br, respectively. It is seen (Fig. 1) that halogen ions strongly influence on the catalytic properties in the CO preferential methanation: fluorine does not change catalytic activity; chlorine inhibits CO_2 methanation activity providing high selectivity towards CO methanation; while bromine totally inhibits both CO and CO_2 methanation activity. This phenomenon was associated with the formation of halogen-containing surface species and bulk phases in the halogen-promoted Ni/CeO_2 catalysts [3]. The kinetic and FTIR in situ study showed that for Ni/CeO_2 catalyst the CO methanation reaction proceeds over the Ni surface via CO and H_2 chemisorption. The CO_2 methanation reaction over Ni/CeO_2 proceeds via CO_2 adsorption over ceria surface and stepwise hydrogenation to hydrocarbonates and formates by the hydrogen spilled over from Ni. While for Cl-containing catalyst CO_2 methanation reaction is locked by chlorine, providing inactivity in CO_2 methanation and therefore high efficiency in selective CO methanation [2].

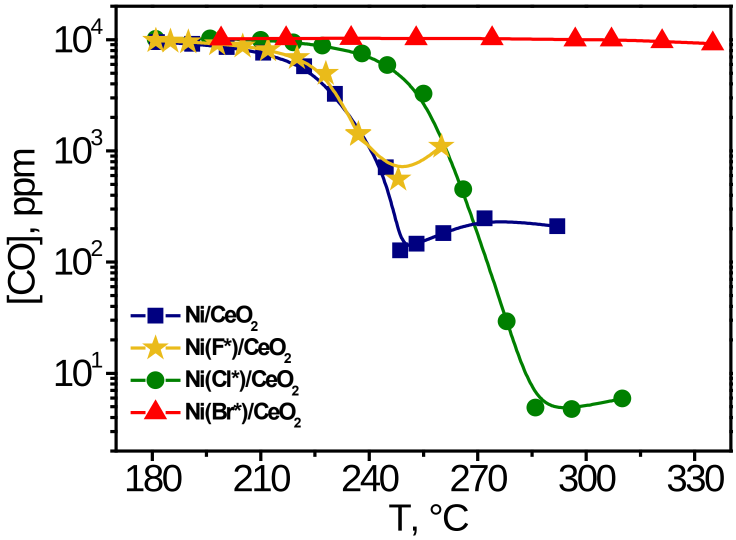

Figure 1. The temperature dependencies of the CO outlet concentration over the Ni/CeO_2, Ni(F*)/CeO_2, Ni(Cl*)/CeO_2 and Ni(Br*)/CeO_2 catalysts. Feed gas composition (vol. %): 1.0 CO, 65 H_2, 10 H_2O, 20 CO_2 with He as balance. WHSV: 29 $L \cdot g^{-1} \cdot h^{-1}$.

The advanced performance of Ni(Cl*)/CeO_2 was associated with preferable ceria surface blocking by chlorine species. Ni(Cl*)/CeO_2 catalyst showed sufficient performance in selective CO methanation, in contrast to Ni(F*)/CeO_2 and Ni(Br*)/CeO_2. Ni(Cl*)/CeO_2 catalyst showed much higher CO cleanup efficiency and provided CO removal from reformate gas to the level of ≤ 10 ppm. In particular, [CO]out ≤ 10 ppm and selectivity 90÷50% were reached at at 280÷335 °C for Ni(Cl*)/CeO_2.

Acknowledgement. This work is conducted within the framework of budget project No. 0303-2016-0011 for Boreskov Institute of Catalysis in the part of catalytic performance study and RFBR research project № 18-33-00702 -a in the part of catalysts characterization.

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PP-III-6

Theoretical Study and Modelling of Solvent Effect in Pd Catalysed C=C Double Bond Hydrogenation of Carboxylic Acids

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Catalytic conversions of biomass-derived molecules (oxygenates, functionalized aromatics) are mainly carried out in the liquid-phase because of the low volatility of these compounds. The presence of a heterogeneous catalysts in such a system creates an interface where adsorption modes of reacting molecules are determined by interactions with solvent molecules and the catalyst surface. Previous studies showed that H-bond stabilization of transition state [1], H_2O-mediated H-shuttling [2], or H_2O-assisted deprotonation [3] can decrease the activation barriers (ΔE_{act}) or create other low-energy reaction routes in aqueous systems. Here, we use alkenes with carboxylic groups (e.g., dibasic maleic acid) to investigate the effect of water on Pd-catalyzed C=C bond hydrogenation. The work also compares the implicit and explicit solvation models for the description of aqueous-phase heterogeneous reactions.

Periodic plane-wave DFT calculations were carried out using the Vienna *ab initio* simulation package (VASP). The planewaves were constructed using projector augmented-wave (PAW) potentials and the revised Perdew-Burke-Ernzerhof (RPBE) form of the generalized gradient approximation was used to determine exchange and correlation energies. The catalyst surface was modeled as a 4 × 4 Pd(111) closed-packed periodic lattice with four layers in the orthogonal direction and a 15 Å vacuum between slabs. Transition state (TS) structures were obtained for each elementary reaction by using the nudged elastic band (NEB) and the dimer methods. Vibrational frequency calculations were performed on reactants, TSs and products, to estimate enthalpies (H) and free energies (G) for each state.

The impact of $-CH_3$ and -COOH functional groups on alkene hydrogenation pathways were determined by comparing ethene, propene, and 2-butene, as well as acrylic, crotonic, isocrotonic, and maleic acids. The first hydrogen addition step was the rate determining step for all C=C double bond hydrogenations. Intrinsic activation enthalpies of both hydrogenation steps varied weakly with the change in alkene structure; with averages of 85 ± 12 kJ mol^{-1} for the first hydrogen-addition and 67 ± 6 kJ mol^{-1} for the second hydrogen-addition (where ± describes the range of activation enthalpies across all seven molecules). For reagents with -COOH substituents, the first hydrogen addition occurs with enthalpy barriers 7 kJ mol^{-1} higher when added near the -COOH group (on average). Free energy barriers ($\Delta G^{\neq}$) suggest that O–H bond activations of the carboxylic acid are only favorable for crotonic and isocrotonic acid. The first C=C hydrogenation step of the product carboxylate, however, has at least 50 kJ mol^{-1} higher $\Delta G^{\neq}$ values than in the carboxylic acid, indicating that C=C hydrogenation does not occur in carboxlyates. Maleic acid (MA) has two proximal carboxyl groups forming an intramolecular H-bond, which stabilizes specific adsorption modes and decreases activation free energies for hydrogenation by 15 kJ mol^{-1}. When dissolved in water, MA can lose protons through H_2O-mediated H-shuttling pathways but our calculations indicate that H_2O^*-assisted deprotonation has higher free energy barriers than the non-assisted reaction with Pd surface. These data indicate that hydrogenation of MA occurs in the carboxylic acid (not the carboxylate or dicarboxlyate) and is stabilized by the intramolecular H-bond.

A continuum solvation model implemented in VASPsol was also used to introduce water as a solvent in the maleic acid hydrogenation reaction. The geometries of gas phase molecules, adsorbates, and TS structures were not affected when the solvent model was added except for the angle of the -COOH group. Free energies vary significantly among species with polar groups exposed to the solvent. The solvent model predicts a decrease in free energy barriers for both H-additions in MA hydrogenation by ~20 kJ mol^{-1} (Fig. 1), while reactants and products adsorption energies are not significantly affected.

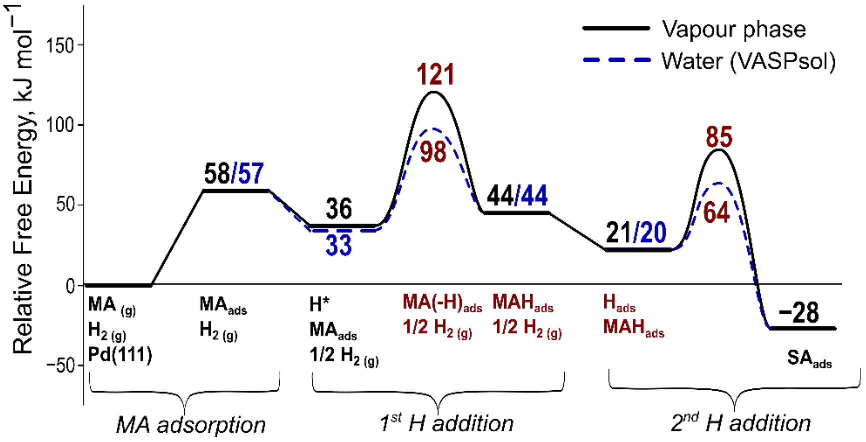

Figure 1 — Reaction coordinate diagram of MA hydrogenation in vapor phase and in implicitly modeled water solution.

An explicit solvation model was also constructed using a 6 x 3 Pd unit cell and water in an I_h crystal epitaxially placed above it. Two water molecules close to the surface were removed to adsorb reacting species. The presence of water molecules around the reactants does not affect intrinsic activation energies of the hydrogenation steps because none of the atoms involved in bonds rearrangement form H-bond with water. The network of H-bonds in the ice, however, facilitates deprotonation of carboxyl groups ($\Delta E_{act} \approx 25$ kJ mol^{-1}), thus hydrogenation of adsorbed carboxylates is more plausible in real aqueous solution. The completion of this network with intermolecular H-bonds with carboxyl groups makes this kind of adsorbed MA configuration more stable than the structure with intramolecular H-bond.

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PP-III-7

The Simulating of Oxygen Interaction with Thiolate-Protected Gold Clusters by DFT

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Thiolate-protected gold clusters are used in catalysis, biomedicine, electronics and other fields. Despite extensive research of $Au_n(SR)_m$, some issues are still being actively discussed, including their interaction with simple molecules, for example, molecular oxygen, and how this affects different processes: formation, reconstruction, catalytic processes.

The aim of the work is to simulate the interaction of O_2 with $Au_{20}(SCH_3)_{16}$ [1] and its fragments by DFT. The DFT/PBE and SBKJC basis set were used in PRIRODA programs.

The interaction of oxygen in ground state of thiolate-protected gold clusters is very weak. Results show that the interaction between oxygen and thiolate-protected gold clusters is possible with the preactivation: using singlet oxygen and removing ligand of the cluster. The reactions of singlet oxygen and $Au_{20}(SCH_3)_{16}$, $CH_3S(AuSCH_3)$, $CH_3S(AuSCH_3)_3$, $(AuSCH_3)_8$ cluster are favorable. The oxidation by singlet oxygen depends on the location of gold atom relative to the end of staple motif: O_2 dissociation in $CH_3S(AuSCH_3)O_2$, $CH_3S(AuSCH_3)_3O_{2\_end}$ and $CH_3S(AuSCH_3)_3O_{2\_medium}$, $(AuSCH_3)_8O_2$ proceeds through three and two transition states, respectively. The high dissociation barriers indicate that the oxygen on the cluster remains in molecular form. The electron-donor groups with respect to sulfur (some groups containing nitrogen) in the ligand increase the energies of $^1O_2$ interaction with the cluster in contrast to the electron-acceptor ones (a phenyl ring or carboxyl, hydroxyl groups). At thermal activation only with the certain amount of removed thiolate ligands, oxygen adsorption becomes favorable. The de-thiolation with three ligands from various staple motifs makes possible the $^3O_2$ adsorption. The $^3O_2$ adsorption energies at de-thiolation with three ligands decreases in the order $CH_3S(AuSCH_3)_3^- > (AuSCH_3)_8 > CH_3S(AuSCH_3)_2^-$. This indicates that a negative charge does not play a significant role in the oxygen adsorption.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 17-03-00962.

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PP-III-8

Analysis of the Effect of Radiation and Catalysts on Methane Activation

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Methane is a major component of natural gas and shale gas [1]. The current method of methane conversion into syngas ($CO+H_2$) is energy intensive and costly, so it would be useful to reduce the reaction temperature for the transformation of methane into chemicals [2]. Direct conversion of methane to different derivatives (methanol, high hydrocarbons and others) is alternative way to activate CH_4. However, the process of methane activation is limited by the rupture of C-H bond (E_{bond} = 413 kJ/mol).

Thus, to optimize the process of methane conversion it is necessary to reduce the dissociation energy. The C-H bond activation of CH_4 by transition metal nanoparticles have received a great deal of attention both experimentally and theoretically [3]. It was shown that this reaction is structure and charge sensitive [4,5] and their influence on the reaction mechanism is unclear. On the other hand, the non-thermal radiation or plasma can efficiently activate methane with a low density of highly energetic electrons and photons. But the methane activation using only the exposure by non-equilibrium environment suffers from low product selectivity [6]. A promising alternative method is hybrid system of plasma and catalysts for methane conversion. However, the synergetic effect of these systems is not understood yet. Thus, in order to successfully design a hybrid system, it is necessary to evaluate the separate effects of non-equilibrium conditions and catalyst.

The impact of catalysis on the C-H dissociation was investigated using density functional theory DFT/PBE in NWChem 6.6. program [7]. As a model of catalyst, we used neutral and charged silver, gold and copper cluster, which contain twenty atoms. The methane adsorption is most favourable on the atoms with low coordination number. Presence of charge on the catalysts leads to lower of activation energy of C-H bond dissociation.

Effect of non-equilibrium conditions was modelled by the theoretical kinetic analysis of reaction pathways of methane conversion at gas phase under effect of radiation. Simulations were performed at temperature of 500-700 K and pressure up to 100 atm with energy input up to 0.1 eV/molecule. The Chemical WorkBench software [8] was used for kinetic modelling. The analysis have shown, that photons are able to accelerate the rate of methane conversion. On the other hand, due to specific peculiarities of kinetics only limited increase of the selectivity of the overall process can be achieved.

The results of this investigation might be useful for the further understanding the process of methane activation in hybrid systems and possible development of industrial applications.

Acknowledgement. This work was supported by the Kurchatov Institute, NRC KI order №1388 23.08.2017. This work has been carried out using computing resources of the federal collective usage center Complex for Simulation and Data Processing for Mega-science Facilities at NRC “Kurchatov Institute”, http://ckp.nrcki.ru/.

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PP-III-9

Novel CuFeAl-Composite Catalysts for CO Oxidation

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The CuFeAl-composite catalysts are perspective for catalytic oxidation of CO and water-gas shift reaction for hydrogen producing. Here we present the result of investigation by complex physicochemical methods of CuFeAl-composite catalysts. The catalysts were synthesized from hydrates of $Cu(NO_3)_2$, $Fe(NO_3)_3$, and $Al(NO_3)_3$; the mix of hydrates was dried at 200°C and calcined at 450 or 700°C. The catalysts with 0%, 3%, 5%, 8%, and 10% of Cu were synthesized and tested in catalytic oxidation of CO. It was shown that catalytic properties depend on the Cu content and the calcination temperature. The catalysts calcined at 450°C demonstrate the better activity in the oxidation of CO then ones calcined at 700°C. It should be noted that they have the same surface area and the Cu content. The fresh catalysts were characterized by XPS, XRD, XANES/EXAFS, and FTIR. [Cu]/[Fe], [Cu]/[Al], and [Fe]/[Al] surface ratios of synthesized catalysts were controlled by XPS to guarantee the homogenous distribution of elements. Applying XANES allows us to establish the chemical states of copper and iron. X-ray diffraction techniques allow us to study the phase composition, but, unfortunately, the technique cannot identify nanoparticles and amorphous phases. This shortcoming was eliminated by EXAFS that clarifies the structure of local environment of copper and iron. We found that fresh CuFeAl-composite catalysts consist of CuO, Fe_2O_3, $CuFe_2O_4$, and Al_2O_3. XANES/EXAFS allows establishing the presence of amorphous $CuFe_2O_4$, containing of $CuFe_2O_4$ correlate with catalytic properties. FTIR data elucidate the catalyst structure.

Thus, the use of complimentary methods allows us to determine the chemical state of copper and iron and the phase composition during the oxidation of CO. The data presented can facilitate to clarify the mechanism for the oxidation of CO.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 17-73-20157.

PP-III-10

Electrocatalytic Properties of Nickel-Rhenium Alloys Prepared by Electroless Deposition

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Hydrogen evolution reaction (HER) is one of the best studied electrochemical reactions; it was chosen as a model reaction in electrochemistry kinetic studies many years ago. The interest in studying HER is due to the importance of this electrode process for theoretical electrochemistry as well as for hydrogen energy technologies (such as production of extra-pure hydrogen). The alloys of refractory metals such as Re, Mo, W with iron group elements (Fe, Co, Ni) were proposed as HER catalyst due to their low overpotential in HER. However, there are only a few studies devoted to the electrocatalytic activity of Nickel-Rhenium alloys prepared by electroless (catalytic) deposition towards the HER.

This study provides a new experimental data for the HER on Ni-Re (30-50 at.%Re) electrodes prepared by electroless deposition from pyrophosphate solution on cooper foil.

Mathematical processing of experimental data were proceeded by means of nonlinear regression and fitting of electrohemical impedance spectroscopy (EIS) data. It was shown that HER on rhenium-nickel alloys proceeds through Volmer-Heyrovsky mechanism. Exchange current densities for Volmer and Heyrovsky reactions and equilibrium coverage of the alloy surface by atomic hydrogen (θ^e) were calculated. The dependence of elecrocatalytic activity alloys upon the rhenium content was studied. The equilibrium coverage of the alloy surface was equal to 0.995. The increase of cathode overpotential resulted in decrease of θ^e. Calculated values of kinetic parameters were confirmed by results of EIS. The equivalent circuit of HER was proposed. Parameters of its structural elements were calculated. It was shown that catalytic activity of Ni-Re alloys for the HER in 1M H_2SO_4 is slightly lower when compared to catalytic activity of pure platinum. High corrosion resistance of Re-Ni alloys in alkaline media is established.

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PP-III-11

Catalysis of Carbon Monoxide Isotope Exchange Reaction by Highly Dispersive Tb-Zr-O Compositions

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The homomolecular exchange reaction : $^{12}C^{18}O+^{13}C^{16}O\leftrightarrow^{12}C^{16}O+^{13}C^{18}O$ occurs readily at around room temperature or below on many oxides. Refractory oxides (Nd_2O_3,SiO_2, Al_2O_3)and also Na_2O,TiO_2 and GeO_2 are of low or zero activity but many others are highly active. The activity of NiO depends on the method of its preparation and upon the lithium or chromium content;superficial films of oxide upon the metal Ni-NiO,Cu-Cu_2O,or Fe-Fe_2O_3,are abnormally active.[1]

In this paper we report our results regarding the isotopic exchange reaction $^{12}C^{18}O+^{13}C^{16}O\leftrightarrow^{12}C^{16}O+^{13}C^{18}O$ over Tb-Zr-O catalyst between -50^{0}C and +330^{0}C.

The Tb-Zr-O catalyst precipitated from terbium nitrate(0.2M) solution with zirconium nitrate(2M) and ammonium hydroxide(25%mass). Full deposition of the components occurred at pH=9. Before the research powder of Tb-Zr-O catalyst ($[Tb^{3+}]/[Zr^{4+}]=0.1$) was tableted and thermal decomposed at 400^{0}C. The specific surface area measured by the BET krypton adsorption method was 65 m^2/g. According to the X-ray phase analysis made on a diffractometer the Drone-2, Tb-Zr-O catalyst represented by solid solution with zirconium dioxide cubic modification. For studying of texture of a surface used the scanning supermicroscope of BS Tesla-440. According to a submicroscopy average pore size makes 0,8mkm, and the exemplar of Tb-Zr-O catalyst consists of ungeometrical units, average particle size which 10-12mkm.

The technique of carrying out experiences and processing of the experimental results is given in [2]. The reaction was studied at 20mm pressure of CO. The reaction vessel was of glass suspended vertically so that it could be surrounded by a furnace or by a Dewar flask containing a freezing mixture. The catalyst was into the reaction vessel which was then sealed on to the apparatus. A convenient amount was 0.2-3g, depending on the reactivity. The furnace was placed around the specimen and the temperature raised to about 400^{0}C, and the catalyst pumped over 3-4 hour. After that the pressure was usually less than 10^{-6} mm. The sample was then isolated from the pumps and cooled to the reaction temperature. This treatment repeated between each run when several experiments were performed on the same catalyst.

The rate of isotopic mixing reaction: $^{12}C^{18}O(M30)+^{13}C^{16}O(M29)\leftrightarrow^{12}C^{16}O(M28)+^{13}C^{18}O$ (M31)was followed by continuous measurements of ratio M30/M31 when an approximately equimolar mixture of $^{12}C^{18}O$ and $^{13}C^{16}O$ was allowed to contact the Tb-Zr-O catalyst. The maximal interval of temperatures at which the research was conducted: - 50-+400^{0}C. Results of a research showed that the kinetics of exchange is well described by the equation of first order. A plot of ln(1-F) against time (t) should give a straight line, the slope of which will give the experimental rate constant.

$$K = -\frac{N}{St} ln(1 - F)$$

Where *S* is the area in m^2 of catalyst surface, F-extent of exchange

$$F = \frac{c - c^0}{c^\infty - c^0} \quad \text{and } 1 - F = \frac{c^\infty - c}{c^\infty - c^0}$$

c^0 – numbers of molecules of $^{16}O^{18}O(C_{34})$ or $^{13}C^{18}O(C_{31})$ at initial time.

c^∞ – numbers of molecules of $^{16}O^{18}O(C_{34})$ or $^{13}C^{18}O(C_{31})$ at the end of the reaction.

c – numbers of molecules of $^{16}O^{18}O(C_{34})$ or $^{13}C^{18}O(C_{31})$ at any time.

N – numbers of molecules of carbon monoxide in the reaction vessel. Is dependent upon the pressure of carbon monoxide.

The isotopic exchange reaction occurs with an activation energy of 18kJ/mol in the measured temperature range -50 – +25^{0}C. In the same temperature range, both CO dissociation and CO disproportionation reactions are absent. This observation supports a nondissociative mechanism for CO isotopic exchange on Tb-Zr-O catalyst .

In the field of temperatures + 120^{0}C–+330^{0}C the speed of gomomolekulyarny isotope exchange goes down .

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PP-III-12

Bimetallic Zr,Al- Hydride Complexes as Probes for Methylaluminoxane Structure

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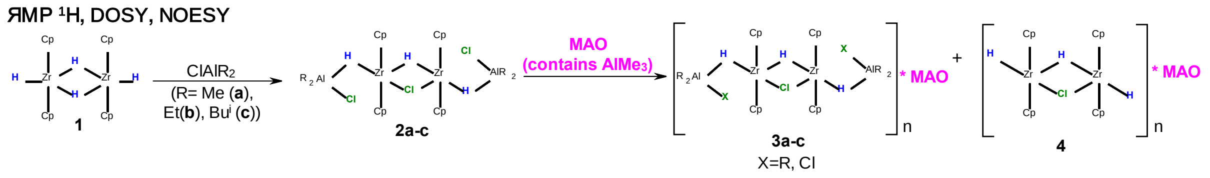
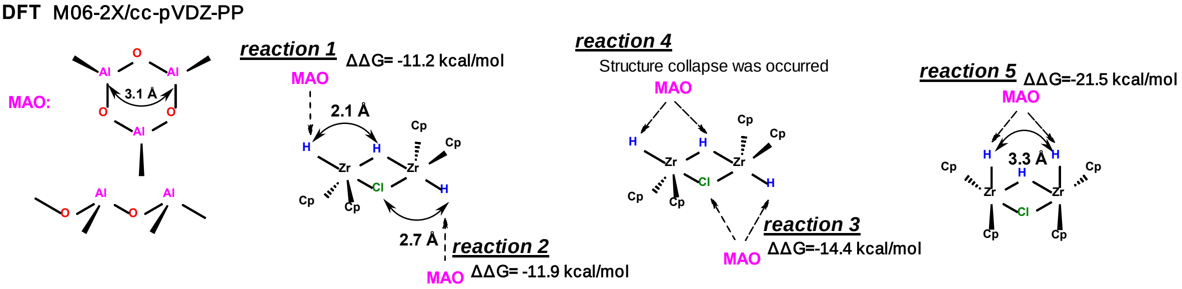
The use of metal complex catalysis in the chemistry of organoaluminum compounds made it possible to develop efficient methods for the alkene functionalization, di-, oligo- and polymerisation. Hydride complexes can serve as the active centres of these reactions, which role has been repeatedly discussed in the literature [1]. NMR studies of the reaction of L_2ZrX_2 (X=H, Cl) with $HAlBu^i_2$ ($AlBu^i_3$) showed the formation of Zr, Al-hydride clusters, the intra- and intermolecular dynamics of which determine the activity of catalytic systems in the alkene hydrometalation [2]. In the reaction of $[Cp_2ZrH_2]_2$ with $ClAlR_2$ (R= Me, Et, Bu^i) we found new complexes **2a-c**, characterized by the upfield ^1H NMR signals for the bridging Zr-H-Zr hydride in the -7 to -6 ppm range. The complexes showed high affinity towards methylalumoxane (MAO) and gave soluble (**3a-c**) and insoluble (**4**) in toluene adducts. DFT modelling of MAO binding with the new complexes demonstrated the possible involvement of simple chains with $(MeAlO)_n$ groups and/or hexagons with a $(MeAlO)_3$ units. Thus, the new hydride bimetallic clusters can function as a sort of probes for MAO, which apparently comprises a rather large proportion of linear or hexagonal fragments.





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PP-III-13

Theoretical Study of Catalysts for the Process of CO_2 Fixation by Epoxide with the Formation of Cyclocarbonate

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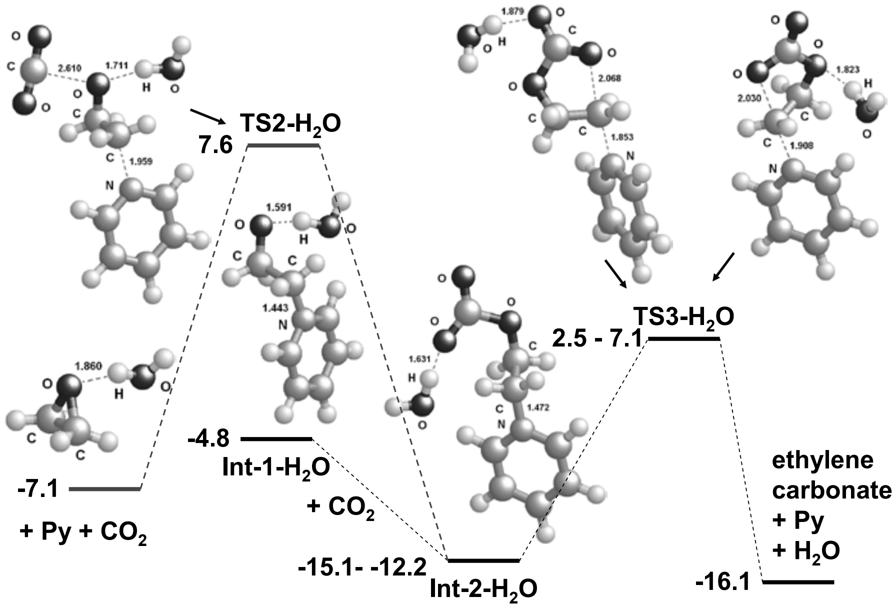
The chemical fixation of carbon dioxide is a very attractive subject in view of resource utilization and environmental problems. One of the most promising recycling methods is the synthesis of cyclocarbonates from epoxides and CO_2. Cyclic carbonates have found applications as polar aprotic solvents, electrolytes for lithium-ion batteries, as intermediates in the manufacture of fine chemicals, and as monomers for polycarbonates and polyurethanes production. However, due to the low activity of CO_2, development of new efficient catalysts is necessary.

We investigated the mechanism of the catalysis of the reaction of ethylene oxide with CO_2 in presence of different catalysts (BF_3, $SbCl_3$, $SbCl_5$, H_2O, Py, Py/H_2O (shown on the scheme below), Py/PhOH, Py/$ZnBr_2$, Py/Py_2ZnBr_2, PMe_4Br, PMe_4Br/H_2O, MmimBr, MmimBr/H_2O) using the DFT method (PBE/TZ2P). The most effective catalyst according to the calculation (and experiment) is a combination of ionic liquid and water (MmimBr/H_2O).



It was found that a binary system acid + base effectively catalyzes the process, and a major role in this transformation is played not the activation of CO_2, but the activation of ethylene oxide by conversion of the latter into an active intermediate anionic type, which in turn attacks the CO_2. The calculated activation energies are in good agreement with the experimental relative activities of the catalysts, derived on the basis of the reaction conditions (temperature, pressure, time, and yield), that allows to theoretically predicting the most effective catalyst in this process.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 17-03-00146-a

PP-III-14

Catalytic Conversion of Glycerol to Lactic Acid over Cu-Based Catalysts

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Lactic acid (LA) is an important product that is widely used in various industries such as food, chemical, cosmetics, and pharmaceuticals [1]. One of the most promising applications of LA is its use for biodegradable and biocompatible polymeric materials [2]. Nowadays, LA is commercially produced through the fermentation of natural raw materials [3]. Currently, a large amount of glycerol is produced as by-product in biodiesel industry which resulted in a price decline of crude glycerol [4]. It became attractive to use glycerol for the production of LA as an alternative to the traditional fermentative methods.

The aim of the present work is to study the liquid phase hydrothermal conversion of glycerol water solutions into LA over various copper-based catalytic nanoparticles in alkaline medium. Catalysts CuO, CuO/ZrO_2 were prepared by the precipitation method. Water solutions of $CuSO_4 \cdot 5H_2O$ and $ZrClO_2 \cdot 8H_2O$ were used as Cu and Zr precursors, respectively. Aqueous solution of NH_4OH was used as a precipitating agent. After that the samples were filtrated, washed by water for pH 7 and dried at 330 K for 6 h in vacuo. Cu_2O were prepared using reductants such as glucose (Cu_2O-1) and ascorbic acid (Cu_2O-2). The influence of the precipitation conditions (temperature, time, molar ratio) and type of reducting agent for Cu_2O on the properties obtained catalysts (composition, structure, physicochemical properties and the average particle sizes) were investigated using FTIR, BET, SEM-EDS, TEM and XRD techniques.

It was shown that Cu_2O-1 had more catalytic activity when Cu_2O-2 and Cu(II) oxides. The effect of the reaction conditions (temperature, the initial glycerol and NaOH concentration) on the conversion and selectivity of LA in the presence of Cu_2O-1 were studied. Under the optimized conditions, 91.3% glycerol conversion and 72.1% selectivity for LA were obtained over Cu_2O-1 when reacting 100 ml of 0.9 M glycerol solution, using 0.7 g Cu_2O-1 at 513 K for 6 h (carbon balance = 99%, ratio NaOH/Gly = 1.1).

Using GC-MS, HPLC, ^1H and ^{13}C NMR techniques, reaction by-products at various temperatures were reliably identified and quantitated, as a result a reaction mechanism for the conversion of glycerol was proposed. A synergistic catalytic effect of Cu atoms and base was found. Cu(I) oxides had more catalytic activity when Cu (II) oxides, because Cu(I) with hydroxyl accelerate the first stage of dehydrogenation of glycerol into glyceraldehyde. The base is necessary for the intramolecular Cannizzaro rearrangement of pyruvaldehyde into lactate.

PP-III-14

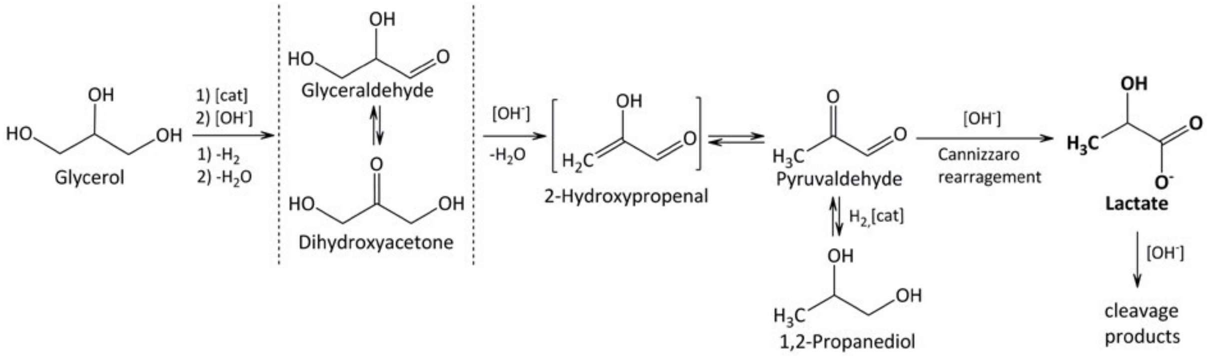

Figure 1. Proposed mechanism of conversion glycerol to lactic acid over Cu-based catalysts in alkaline media.

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Ethylene Adsorption onto Natural and Metal Oxide Modified Chilean Zeolites: an Operando DRIFTS Approach

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Ethylene is a plant growth regulator that induces accelerated softening and ripening of fruits and senescence of flowers during transport and storage [1]. Among the most applied methods for ethylene control at the environment level actions, adsorption appears as a cheap and efficient technique [2]. Various cation-exchanged forms of clinoptilolite-type zeolites have been claimed to produce significant differences in the adsorption of ethylene due to the location and size of the compensating cations which affect the local electrostatic field, and the polarization of the adsorbates [3, 4]. Unfortunately, there is still a lack of information related to the influence of active sites of zeolite surface on ethylene adsorption. In this work, the effect of the incorporation of transition metals into natural Chilean zeolite on ethylene adsorption is investigated.

Chilean natural zeolite mainly composed of clinoptilotite and mordenite was chemically and thermally modified by a sequence of ion-exchange treatments. Firstly, compensating cations initial present in natural zeolite were removed by ion-exchange using ammonium sulfate (0.1 M). Then, loads of 8% of copper, 8% of zinc, and 4% of both metals were incorporated into the ammonium modified natural zeolite, generating three different metal oxide modified zeolites, using copper and zinc nitrate solutions (0.13 M). Finally, prior ethylene adsorption, samples were calcined under oxygen flow (100 cm^3 min^{-1}) at 623 K.

Natural and metal oxide modified zeolite samples were characterised by X-ray diffraction, X-ray fluorescence spectroscopy, nitrogen adsorption at 77 K. Hygroscopic characteristics were examined according to ISO12571 methodology at 293K [5]. Chemical variations of zeolite surface during ethylene adsorption assays were monitored by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). DRIFTS *operando* experiments were conducted in a Thermo Scientific Nicolet iS50 FT-IR spectrometer equipped with a commercial PIKE DiffusIR™ accessory. Ethylene adsorption isotherms were carried out in a quartz fixed-bed flow adsorber. Ethylene concentration was followed by gas chromatography using an analytic method reported elsewhere [6].

XRF results reveals the incorporation of Cu^{2+} and Zn^{2+} into the zeolite structure at the desired levels, as new compensating cations. Previous studies suggest that Na^+ cations are weakly bonded to clinoptilolite framework; being easily removed by ion-exchange treatments [7]. Additionally, results of transmission electron microscopy indicate the formation of metal oxide nanoparticles of 5-10 nm in all modified zeolite samples. Modified samples with Zn^{2+} result forming oxide particles of bigger size. Nitrogen isotherms reveal a lower microporous surface area of Zn-exchanged samples. Hygroscopic and DRIFTS assays show that zeolites exhibit hydrophilic characteristics. IR vibration bands at 1635 cm^{-1} and 3000-3500 cm^{-1} (see Fig. 1) vary even at very low water concentration.

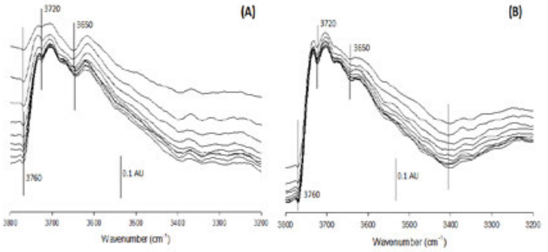

Figure 1: DRIFTS spectra of Cu-exchanged zeolite during ethylene adsorption: (A) in the absence of moisture, (B) in the presence of moisture.

Ethylene adsorption isotherms indicate an enhancement on the adsorption capacity of Cu-exchanged zeolite. This result could be not only associated to the higher micropore surface area of this sample, but also to bigger affinity of ethylene molecules to copper oxides formed on this zeolite. Ethylene could interact with copper cations *via* π-electrons of C=C bond, leading to strong adsorption [8, 9]. DRIFTS *operando* experiments of ethylene adsorption in the absence and in presence of moisture reveal that OH groups are also involved in ethylene adsorption. IR vibration bands of Si-OH-Al bridges at 3650 cm^{-1}, OH at 3717 cm^{-1} and silanol (SiOH) at 3750 cm^{-1} are modified during ethylene adsorption. Water molecules appear to compete with ethylene for OH sites, that could become rapidly occupied (see Fig 1-B) when moisture content is present.

Natural chilean zeolite exchanged with transition metals could be effectively applied as a low cost adsorber for ethylene elimination from closed atmospheres during fruit and flowers storage, transportation and distribution. OH groups present at zeolite surface appear to be involved in the adsorption mechanism. The presence of moisture reduces the adsorption capacity towards ethylene. Ethylene molecules seem to compete with water for similar sorption active sites.

Acknowledgement. The authors wish to thank CONICYT-PCHA/Doctorado Nacional/2015-21150082 and CONICYT-FONDECYT/Regular/2017-1170694 for their financial support.

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PP-IV-2

The Results of Testing New Materials for Primary N_2O Emission Reduction in Catalytic Ammonia Oxidation Process

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With fast development of the industry in the past 30 years environmental issues have become more and more important. Among them the problem of greenhouse gases emission reduction is of high priority especially in the European countries who ratified the Kioto Protokol.

Nitrous oxide (N_2O) is a greenhouse gas with a global warming potential of 310 [1] for the time horizon of 100 years. The main source of N_2O emission is the chemical industry where great amount of N_2O is formed as a by-product of the side reaction (2) of catalytic ammonia oxidation process in nitric acid plants [2]:

$$4NH_3 + 5O_2 = 4NO + 6H_2O + 904\ kJ \qquad (1)$$

$$4NH_3 + 4O_2 = 2N_2O + 6H_2O + 1104.4\ kJ \qquad (2)$$

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O + 1268.8\ kJ \qquad (3)$$

Depending on the type of the plant and operating conditions (mainly temperature and pressure) the amount of N_2O generated during the process varies from 1000 to 2500 ppmv. Taking into account that chemical industry belongs to large scale production with over 20 million tonnes of nitric acid yearly produced only within European countries N_2O emission would reach a significantly high level without abatement systems of more than 30 million tonnes of CO_2 equivalent.

To reduce N_2O emission in nitric acid plants 2 conventional methods are commonly used. They are secondary (the baseline Methodology AM0034) and tertiary (the baseline Methodology AM0028) catalytic N_2O destruction. Both methods require additional bulk or honeycomb catalyst to be used for N_2O decomposition: the former requires secondary catalyst to be installed inside the ammonia burner, the latter requires tertiary one to be placed in the separate vessel downstream the tail gas flow. The efficiency of N_2O reduction is within the range of 85-97%.

To reach high efficiency in N_2O removal the catalyst bed should have a significant thickness that in its turn leads to pressure drop increase and the plant capacity decrease. That is why it is highly important to primarily reduce the amount of N_2O generated by the platinum gauzes.

It is known [1,3] that N_2O concentration in the NOx-gas can be changed by varying operating parameters. For example, the amount of N_2O significantly decreases with the oxidation temperature increase and on the contrary primary N_2O emission increases with the increase of oxidation pressure. But process parameters (temperature, pressure, ammonia concentration, mix-gas temperature) are limited by certain values as explosive substances are used in the ammonia oxidation process. Moreover, elevated oxidation temperatures result in increase of platinum losses during the campaign.

In the present work results of testing of different additives in the primary platinum gauze pack are discussed. Theoretical value of these experiments is to find, prepare and test catalytically active chemical compounds that can be deposited on the gauze surface to selectively decompose N_2O without influencing NO yield. Practical value of the tests is to design a highly efficient primary catalyst pack with low N_2O generation levels that allows to operate under optimal operation conditions without capacity decrease. The chemical components under investigation comprise precious metals and their alloys and different metal oxides.

Acknowledgement. This work was supported by OJSC Krastsvetmet and EcoStream LLC.

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PP-IV-3

Hydricity of Fe- and Ru-Tetrahydrides with PNP-, CNC- and NNN-Pincer Ligands

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The chemistry of transition metal polyhydrides offers new ways for conversion and storage of energy, renewable energetics, and fine organic synthesis. Particularly, the polyhydrides readily donate hydride species to easily reduce esters, nitriles, ketones, and carbon dioxide thus allowing for an efficient synthesis of fine organic chemicals [1].

The reactivity of a metal hydride in reduction reactions can be predicted by its hydricity value. Hydricity of a compound or, rigorously, thermodynamic hydricity is the free energy needed to detach a hydride ion from M−H bond of the complex [2]. From the perspective of computational chemistry, hydricity calculation is a straightforward way to make a universal and experimentally verifiable prediction of a transition metal reactivity in the reduction reactions.

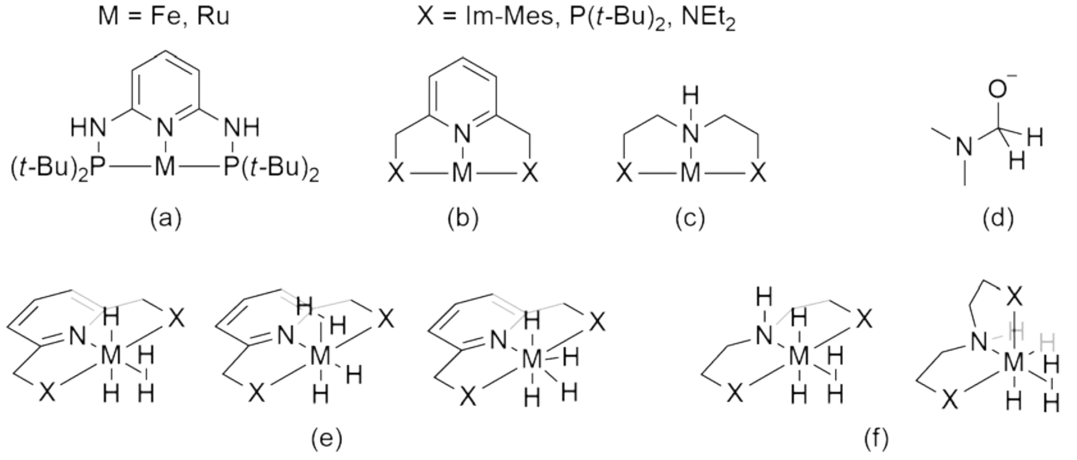

Figure 1. (a)-(c) – structures of the modeled tetrahydride complexes; (d) – structure of DMF-H$^-$ anion; (e) – from left to right: equatorial and axial H_2 molecules coordination, classic tetrahydride complex; (f) – “mer” and “fac” coordination of ligands (c)

In present work, we calculated hydricity values of Fe- and Ru-tetrahydrides with PNP-, CNC-, and NNN-pincer ligands (Figure 1*a-c*) with DFT methods. The values correspond to Gibbs free energies of hydride transfer from the metal complex to the solvent (DMF, Figure 1d):

$$[complex]^{+}H^{-} + DMF \rightleftharpoons [complex]^{+} + DMF{-}H^{-}$$

We used ORCA 4.0.0.2 program package [3] to perform unrestricted Kohn-Sham calculations with B97-3c method and at RI-TPSS-D3(BJ)/ma-def2-SVP level of theory. Continuum solvation model (C-PCM) was used to account for solvation effects. Vibrational frequencies were calculated numerically to validate the optimized geometries as true minima as well as to include the thermochemical terms in hydricity value calculations.

Table 1 – Hydricity of pincer complexes (for the cases of singlet and triplet cation species formation). The values were computed with B97-3c method.

Entry	Ligand*	M	X	Tetrahydride geometry*		Hydricity [kcal/mol]		
						singlet cation formation	triplet cation formation	
1	(a)	Fe	P(tBu)$_2$	H_2-axial		9	9	
2		Ru		classic hydride		42	43	
3	(b)	Fe	Mes-Im	H_2- equatorial		8	4	H_2 elimination
4			NEt$_2$	axial		10	-6	
5			P(tBu)$_2$	axial		10	8	
6		Ru	Mes-Im	classical		23	43	
7			NEt$_2$	axial		16	41	
8			P(tBu)$_2$	classical		40	48	
9	(c)	Fe	Mes-Im	mer	equatorial	13	0	
10			NEt$_2$	mer	classical	-2	-12	H_2 elimination
11			P(tBu)$_2$	mer	classical	23	10	
12		Ru	Mes-Im	mer	classical	9	36	
13			NEt$_2$	fac	classical	41	45	
14			P(tBu)$_2$	fac	classical	8	57	

*See Figure 1 for the ligand and tetrahydride structures.

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PP-IV-4

Cobalt-Carbon Nanocomposites for Chlorobenzene Hydrodechlorination

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Hydrodechlorination (HDC) is a promising disposal method for organochlorine wastes due to the absence of dioxins in products and possibility of HDC products reuse. Supported metal nanoparticles (Pd, Ni, Fe etc.) demonstrate good performance in HDC [1]. However, they are easily deactivated under the influence of reaction by-product, HCl.

To prevent or decrease deactivation, Me@C core-shell composites comprising carbon-coated metal nanoparticles of about 5 nm in size coated with a few layers of graphene-like carbon were proposed for the use as HDC catalysts. The preparation technique was based on the evaporation of overheated liquid drop of Me in the flow of inert gas containing a hydrocarbon. Indeed, in [2, 3] Fe@C and Ni@C demonstrated high efficiency in the gas-phase HDC of chlorobenzene (CB) at 200-300 °C, and long-term stability in continuous-flow system. But similar Co-containing composites were never tested in catalytic processes.

To prepare carbon-wrapped metal particles another way can be used. In [4] Pd nanoparticles imbedded in carbon support were produced by pyrolysis of sawdust impregnated with $Pd(NO_3)_2$. Interesting that pyrolysis provides only reduced form of Pd. Such Pd/C system also shows high efficiency in gas-phase HDC of CB at 150-300 °C.

Therefore, in this work cobalt-carbon nanocomposites were prepared by two methods described above and compared in CB HDC. Characteristics of catalysts are presented in Table 1.

Table 1. Characteristics of Co-C composites

Sample	S_{BET}, m^2/g	Co loading, mass.% (AAS data)
Co@C	62	≈80
Co/C	261	1.3

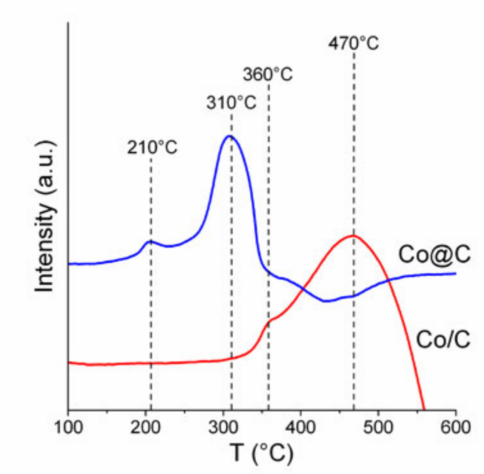

Figure 1. TPR profiles of Co@C and Co/C

TPR profiles of catalysts (Fig. 1) are different. The profile of Co@C comprises peak at 210 °C that can be attributed to the reduction of surface CoO to Co, or Co_3O_4 reduction to

CoO. Peak at 310 °C reflects the reduction of bulk CoO to Co. The total amount of absorbed H_2 is small with respect to total Co loading (≈80 mass.%), i.e. most of the Co is present in the metallic state, and only small fraction as CoO. XRD data confirm this conclusion. The profile of Co/C comprises the small peak at 360°C reflecting low Co loading (1.3 mass.%), and intensive peak at 470 °C, which appears due to methane formation in the reaction between carbon material and hydrogen. No reflexes were found in diffractogram of Co/C confirming small particle size found by TEM (d_n = 3.9 nm). Only CoO was found on the surface by XPS, in contrast to similar Pd/C system, where Pd is totally reduced.

Preliminary tests in CB HDC were performed in the fixed bed continuous flow system (H_2 flow 12 ml/min, CB feed 0.01 mmol/min). The results are presented in Fig. 2 and 3. Both catalysts are active in CB transformation to produce mainly benzene (B) on Co/C (≈100% at 150-250 °C and 74% at 300 °C), and mainly cyclohexane (CH) on Co@C (47% at 250 °C and 98% at 300 °C), see Fig. 3. Co@C demonstrates nearly 100% CB conversion at 200-300 °C; at these temperatures CB conversion on Co/C is lower (87-88%), but at 150 °C Co/C provides 96% CB conversion. Note, that Co loading in Co/C is approx. 60 times less than in Co@C, Co^0 was not found on the surface by XPS, and no Co oxides reduction can proceed at 150 °C.

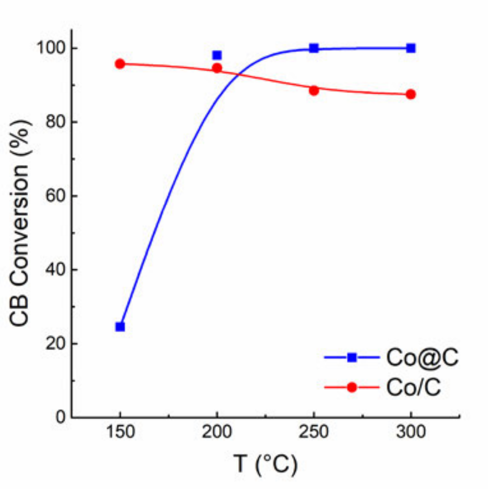

Figure 2. Chlorobenzene conversion vs temperature on Co@C and Co/C

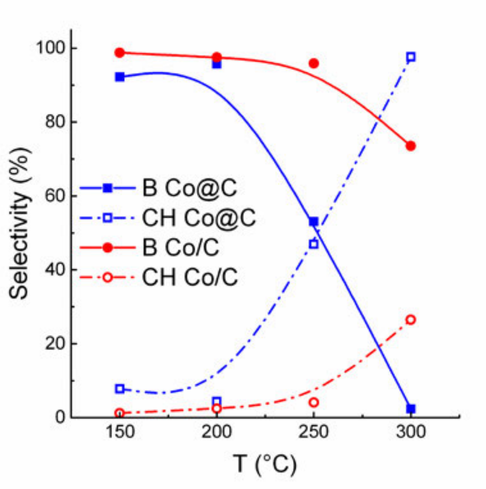

Figure 3. Selectivity to benzene (B) and cyclohexane (CH) vs temperature on Co@C and Co/C

It seems that cobalt oxide can provide CB HDC, at least at 150 °C. High efficiency of Co@C can be explained by activation of carbon shell due to the presence of defects and Co in subsurface layer, as in [3] for Ni@C and Fe@C.

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PP-IV-5

Design of Ag-CeO_2/SBA-15 Catalysts for Volatile Organic Compounds Oxidation

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Volatile organic compounds (VOCs) are among the major air pollutants that cause photochemical smog, ground-level ozone, sick building syndrome, and chemical sensitivity [1]. Thus, it is of vital importance to find effective methods for VOCs abatement in indoor air, chemical factories, gas wastes of vehicles and industry. There are many ways to solve this challenge, e.g. high-temperature oxidation, adsorption, photocatalytic decomposition, catalytic oxidation, etc. [2]. The catalytic deep oxidation of VOCs to CO_2 and H_2O is one of the most promising and effective ways for practical application. The most active catalysts are based on noble metals (Au, Pd, Pt, Ag). The highest practical interest in silver-containing catalysts is caused by their high stability (including in the presence of water vapor) and a relatively low cost in comparison with other noble metals [3].

The aim of the present work is to study the influence of conditions of introduction of silver and CeO_2 on their distribution in the porous structure of mesoporous ordered silica SBA-15 as well as to study the activity of the Ag-containing catalysts in low-temperature oxidation of VOCs. SBA-15 is used as a support with high specific surface area (>600 m^2/g) and unique porous structure comprising a system of ordered cylindrical pores with a diameter of 6-8 nm. The idea of this work is to use unique porous structure of SBA-15 as nanoreactors for synthesis and stabilization of small Ag and CeO_2 particles (< 5 nm).

Mesoporous ordered silica SBA-15 was synthesized by template method using Pluronic P123 (triblock copolymer PEO-PPO-PEO) as a soft template [4]. Ag and Ag-CeO_2 supported on SBA catalysts were prepared by incipient wetness impregnation technique using water solutions of $Ce(NO_3)_3$ and $AgNO_3$. The supports and catalysts were characterized by low-temperature N_2 adsorption, XRD, TEM (including TEM HR and STEM), TPR, UV-visible and Raman spectroscopy. Activity of catalysts was studied in deep oxidation of VOCs (methanol and formaldehyde).

Structure of the obtained SBA-15 was studied by low-temperature N_2 adsorption and TEM. The structure of the synthesized silica was shown to correspond to the one of the ordered mesoporous SBA-15 material. The porous structure was relatively stable up to 700 °C, while calcinations of the SBA-15 at 900 °C led to dramatically decrease of S_{BET} from 780 to 270 m^2/g. It was shown by N_2sorption, XRD, TEM and TPR that the addition of citric acid to impregnating solution of $Ce(NO_3)_3$ led to formation of CeO_2 particles with size of about 3 nm, uniformly distributed on the SBA-15 surface. The STEM image of the Ag/SBA-15 catalysts pre-reduced at 500 °C is presented in Fig. 1a. A bimodal particle size distribution is observed: small silver particles with sizes below 2 nm are located inside the SBA-15 pores and a small amount of silver particles with sizes of 4-8 nm are located on the external surface of SBA-15. This was also confirmed by XRD. The interaction of Ag and CeO_2 particles in Ag-CeO_2/SBA-15 catalysts was shown by TPR H_2. The Ag–CeO_2 interaction influences on the red-ox and catalytic properties of the catalysts.

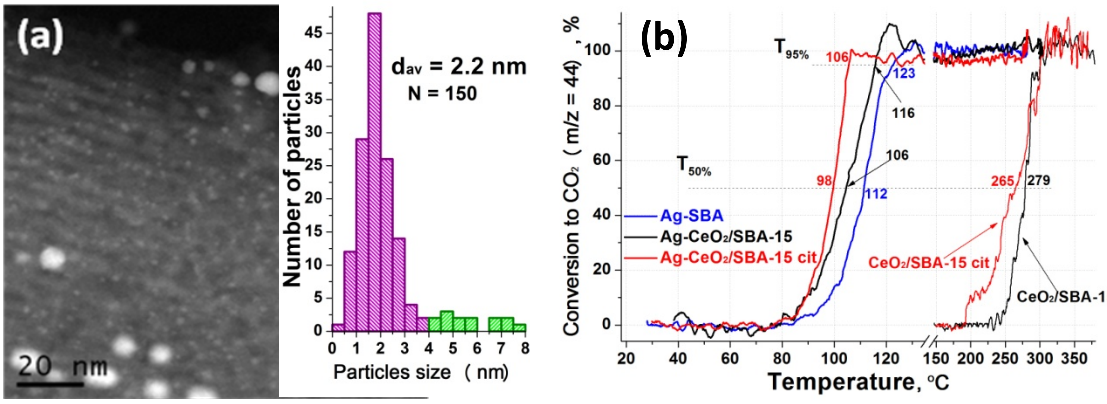

Figure 1. STEM image and particle size distribution for Ag/SBA-15 catalyst (a) and activity of catalysts in methanol oxidation (b)

The curves of methanol conversion to CO_2 (mass spectrometric signal m/z=44) from room temperature for the synthesized catalysts are presented in Fig. 1b. The Ag-containing catalysts are active in methanol oxidation at temperatures above 80 ^oC. The 100 % conversion is achieved at temperatures below 130 ^oC. As can be seen from the presented data the activity of the Ag-CeO_2/SBA-15 catalysts is higher than the one of the Ag/SBA-15 catalyst. The addition of citric acid to stabilize the ceria precursor in the impregnating solution leads to increased activity of Ag-CeO_2/SBA-15 cit catalyst in comparison with the catalyst prepared without citric acid (Ag-CeO_2/SBA-15 catalyst). The small size of ceria particles (about 3 nm) and enhanced interaction with Ag particles in Ag-CeO_2/SBA-15 cit catalyst causes this increased activity in methanol oxidation.

Thus, it was shown that a combination of citric acid to stabilize ceria precursor and unique porous structure of SBA-15 as nanoreactors allowed synthesizing Ag-CeO_2/SBA-15 catalysts with interacting small Ag and CeO_2 particles (<5 nm) that provide an increased catalytic activity in deep methanol oxidation. Thus, the prepared Ag-containing catalysts are promising materials for VOCs abatement.

Acknowledgement. This work was supported by the Grant of President of the Russian Federation
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PP-IV-6

Dual-Bed Catalyst for NO_x Abatement

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Emission of nitrogen oxides (NO_x: NO, NO_2) is a major global pollution problem. The most efficient method for NO_x abatement is the selective catalytic reduction by ammonia (NH_3-SCR):

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$

Moreover, when NO and NO_2 coexist the SCR reaction proceeds much more rapidly (so-called "Fast" SCR):

$$NO + NO_2 + 2NH_3 \rightarrow 3H_2O + 2N_2 \qquad (2)$$

Thus, two catalytic functions, oxidation of NO and reduction of both NO and NO_2, are required for effective NO_x conversion to N_2 and H_2O. Several papers [1–3] reported that using combined catalyst prepared by mechanical mixing of oxidation (*e.g.* $Mn/Ce_xZr_{1-x}O_2$ or Mn-$Ce/Ce_xZr_{1-x}O_2$) and SCR (*e.g.* Fe-zeolites) components is the promising solution. However, the operating temperature window of such catalysts is limited by unselective oxidation of NH_3 to NO and N_2O at T_{react} > 350–400 °C.

In this study we attempt to develop dual-bed catalytic system providing high SCR performance in a wide temperature range. The main idea was to extend operating temperature window through combination of two catalytic beds: (1) FeBeta zeolite (high-temperature SCR) and (2) [Mn-Ce/CeO_2-ZrO_2+FeBeta] combined catalyst (low-temperature SCR).

Upstream bed: FeBeta ("Zeolyst"; Si/Al=12.5; 0.9 wt% Fe) is commercially available zeolite. Downstream bed: [Mn-Ce/CeO_2-ZrO_2+FeBeta] combined catalyst was prepared by mechanical mixing of Mn-Ce/CeO_2-ZrO_2 (8 wt% Mn and 8 wt% Ce, incipient wetness co-impregnation) with FeBeta at a volume ratio 3/1 as described in [3]. Catalytic activities of FeBeta, combined catalyst, and dual-bed system were measured using a feed gas simulated diesel engine exhaust: 500 ppm NO, 600 ppm NH_3, 10 % O_2, 6 % H_2O balanced with N_2 (300 ml/min). Reaction products were analyzed by FTIR gas analyzer "Gasmet'' (Temet Instruments Dx-4000).

The performances of the {→FeBeta||[Mn-Ce/CeO_2-ZrO_2+FeBeta]} dual-bed system, FeBeta and [Mn-Ce/CeO_2-ZrO_2+FeBeta] in NH_3-SCR are compared in Fig. 1. It is evident, that when Fe-zeolite was placed as an upstream bed of the catalytic system favorable NO_x conversion within wide temperature (150–500 °C) is achieved. Presumably, at temperature below 250–300 °C NO_x was converted over [Mn-Ce/CeO_2-ZrO_2+FeBeta] combined catalyst (downstream bed) *via* bifunctional pathway (3), while at 300–500 °C NH_3-SCR (1) proceeds mainly over FeBeta (upstream bed).

$$2NO + O_2 \rightarrow 2NO_2 \text{ – NO oxidation on Mn-Ce/CeO}_2\text{-ZrO}_2 \qquad (3a)$$

$$NO + NO_2 + 2NH_3 \rightarrow 3H_2O + 2N_2 \text{ – Fast SCR on FeBeta} \qquad (3b)$$

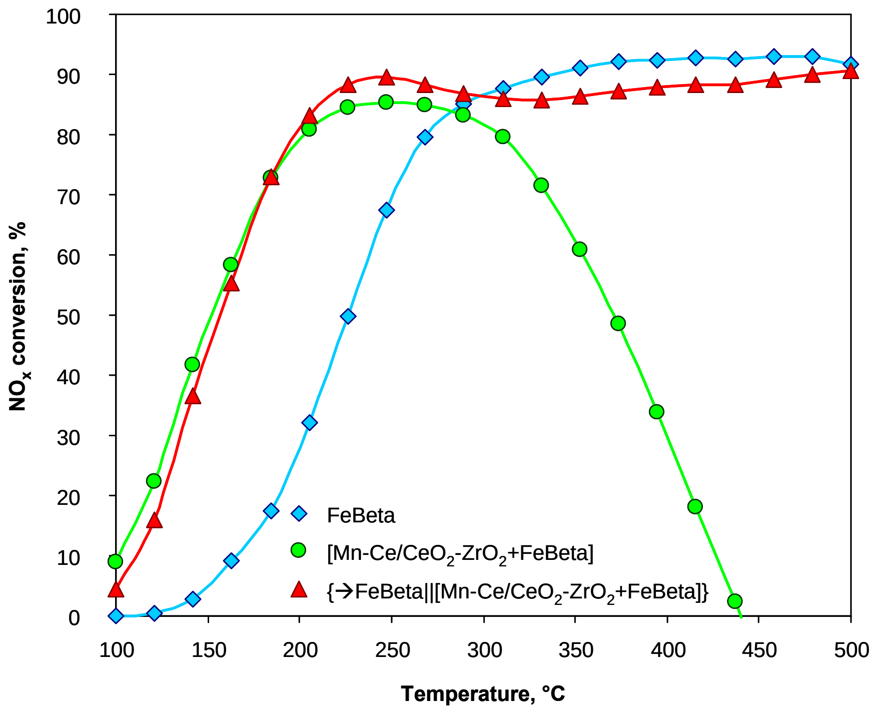

Figure 1. NH_3-SCR performance of dual-bed system as compared to FeBeta and [Mn-Ce/CeO_2-ZrO_2+FeBeta] combined catalyst.

The data obtained demonstrate that the {→FeBeta||[Mn-Ce/CeO_2-ZrO_2+FeBeta]} dual-bed system exhibits favorable performance in NH_3-SCR by exploiting the beneficial effects of both Fe-zeolite and combined catalyst.

Acknowledgement. This work was partially supported by the Russian Foundation for Basic Research (Grant 15-03-07802 A).

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PP-IV-7

Synthesis Dependent Ceria-Titania Interaction and Its Effect on the Performance of PtCeTi-SBA-15 Catalysts in Photodegradation of Phenol from Aqueous Solution

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Aromatic compounds such as phenol and its derivatives are among the most common organic pollutants from wastewaters released by various industries [1, 2]. Previous studies show a high interest on photodegradation of phenolic compounds [3]. A lot of them were related to the application of TiO_2 as photocatalyst [4]. Dispersion of TiO_2 on a support with high surface area and doping with lanthanide elements can increase photocatalytic performances due to extended light absorption range and a better charge separation. Cerium is an interesting candidate to TiO_2 doping. The electronic properties of the interface between Ti and Ce oxides are critical for their photocatalytic performances.

In this work we have investigated PtCeTi-modified SBA-15 mesoporous catalysts focusing on the synthesis parameters variation and their effects on support morphology, ceria-titania interaction, Pt oxidation state as well as photocatalytic activity of the obtained materials in degradation pf phenol from aqueous solution.

Ti-SBA-15 supports, with 5% TiO_2 content, were obtained by direct synthesis and hydrothermal treatment. The synthesis method, typically for SBA-15 mesoporous silica, was modified by using an alcohol as co-solvent (buthanol, propanol or ethanol). The obtained samples were named T5S, T5SB, T5SP and T5SE. Ce (2.5% CeO_2) and Pt (0.25 and 1%) were supported on Ti-SBA-15 mesoporous silicas by impregnation. The order of their immobilization was changed to obtain PCTS and CPTS samples. The obtained catalysts were characterized by XRD, SEM, TEM, EDX, TPR, XPS, UV-Vis. $HO^{\bullet}$ radicals from the surface were detected by fluorescence technique. The obtained results evidenced the ordered hexagonal mesoporous structure of the obtained Ti-SBA-15 supports (Fig. 1). Better reducibility was evidenced for ceria indicating stronger interaction of CeOx nanoparticles with well dispperesed TiO_2 on silica supports. XPS shown a high percent of Ce^{3+} on the surface for these samples. The presence of Pt also contributed to the stabilization of Ce^{3+}. The high dispersion of Pt (evidenced by H_2 chemisorption) facilitates the electron transfer between Pt and titania and influenced photocatalytic activity.

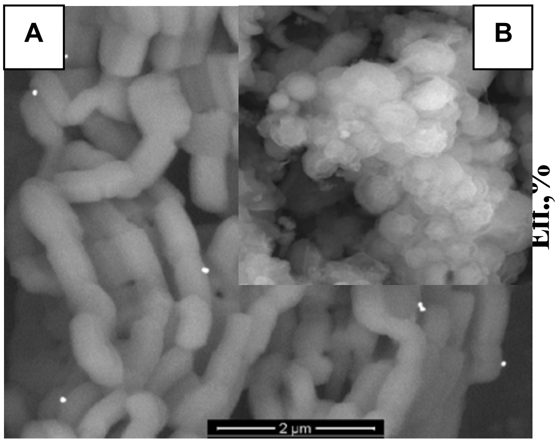

Fig. 1 SEM images of T5S (A) and T5SB (B) samples

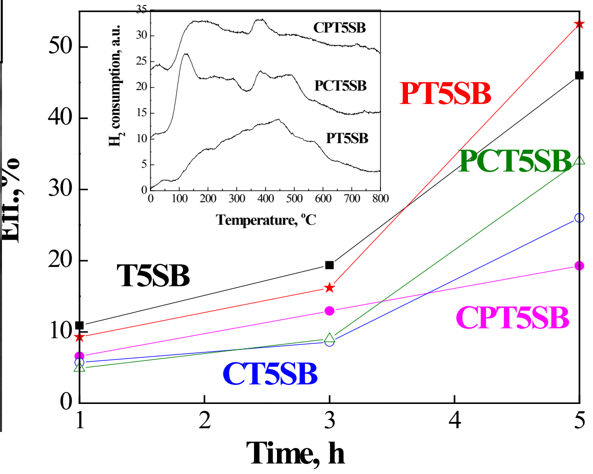

Fig. 2 TPR and photocatalytic results obtained for samples supported on T5SB

Comparing the results of the samples obtained with different alcohols, the best results were obtained by using of buthanol (Fig. 2). TPR show that the higher activity was obtained for samples with lower reduction picks. These results shown two Pt reducible species at lower and higher temperature as result of different interaction with support.

Under UV light the best results were obtained for samples with Ti and PtTi. Pt increase the activity of catalysts with Ce. The lower activity was obtained for samples in which Ce introduced in the last step. Under visible light the higher activity was obtained for samples with Ce after longher time of reaction (8-24 h).

Acknowledgement. The authors gratefully acknowledge the financial support from the Romanian National Authority for Scientific Research, CNCS-UEFISCDI, project number PN-III-P2-2.1-PED103/2017.

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PP-IV-8

Catalytic Decomposition of N-Acetylated Chitosan with Chitosanase Immobilized on Alumina

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Chitosan is one of the most abundant renewable polysaccharides prepared from chitin through chemical N-deacetylation. It is attracting more and more interest due to its potential application in medicine, industry and agriculture. Chitosan and its precursor chitin are the sources of industrial production of valuable substances such as glucosamine and chito-oligosaccharides. They possess distinctive biological activity and therefore are widely used for medical purposes. For instance, glucosamine is a chemical compound which is able to reactivate a decayed cartilaginous tissue, whereas chito-oligosaccharides show rather high antitumour, antifungal and antibacterial activity [1,2], immuno-enhancing effects, enhancement of protective effects against infection with some pathogens in mice. Enzymatic reaction can be favored over chemical catalysis under such circumstances where thermal degradation of labile compounds is minimized and use of chemicals with a potential for pollution can be avoided [3]. Chitosanase is a specific enzyme for chitosan degradation. There are a number of publications on the study of immobilization of chitosanase on different carriers using various methods and its catalytic activity [4]. Immobilization of chitosanase is preferable over the native ones owing to their multiply and repetitive use, the lack of reaction product contamination with the enzyme and its longer half-life and predictable decay rate. Therefore the purpose of this research work is to perform immobilization of chitosanase from *Streptomyces griseus* on alumina a powder carrier by both chemical adsorption and covalent binding with glutaric aldehyde, as well as to study the catalytic activity of immobilized enzyme in the hydrolytic decomposition of N-acetylated chitosan.

Commercial chitosan, average molecular weight 15 kDa, 18% N-acetylated was prepared and characterized in the department of nanomaterials of the Tomsk National Research Polytechnic University. γ-alumina powder samples (surface area 204 m^2/g, particle size 2.60 μm) were prepared by chemical deposition of alumina from 0.5 M solution of $Al_2(SO_4)\times 9H_2O$ with a subsequent heating it at T=70°C for 24 h. The separation of the product $Al(OH)_3$ from the solution was performed with 25% NH_4NO_3 solution. Then a gel-like residue was filtered, washed with water, dried up at T=60°C for 3 days, annealed at T=550°C for 4 h. The activity of free and immobilized chitosanase was assayed by a modified Elson-Morgan spectrophotometric method [5] by measuring a D-glucosamine concentration in a supernatant solution after enzymatic homogeneous and heterogeneous catalysis.

PP-IV-8

Chitosanase was immobilized on γ-alumina powder both by physical adsorption and with glutaraldehyde by cross-linking reaction. 0.4 g aluminum oxide powders were activated by dipping in 1 mL of 4% aqueous glutaraldehyde solution (optimized concentration) for 1 h at room temperature. The coupling of 1 ml diluted enzyme and glutaraldehyde-activated non-activated powders were allowed to occur at room temperature for 1.5 h. The powders were washed with distilled water at each step to remove the excess of glutaraldehyde and unbound enzyme. 1 ml of chitosan solution was mixed up with the aluminum oxide powders with immobilized enzyme, stood for 24 hours at 37 °C in an incubator. The reaction was stopped for 4 minutes by boiling a mixture in a water bath.

We found that the reaction time of hydrolytic decomposition of chitosan in the presence of chitosanase is significantly affected by the amount of substrate. Under these conditions, the immobilization of chitosanase on the alumina surface by adsorption was more effective (effectiveness of immobilization, E= 62.8 %) in comparison with immobilization with glutaraldehyde (E=36.6 %). Yield of glucosamine was 2 and 0.8%, respectively. The chitosanase immobilized by adsorption showed the better operational stability in a repeated use as compared to covalently bound one. This type of immobilization retained 66% of its activity after 2 precipitations (Figure).

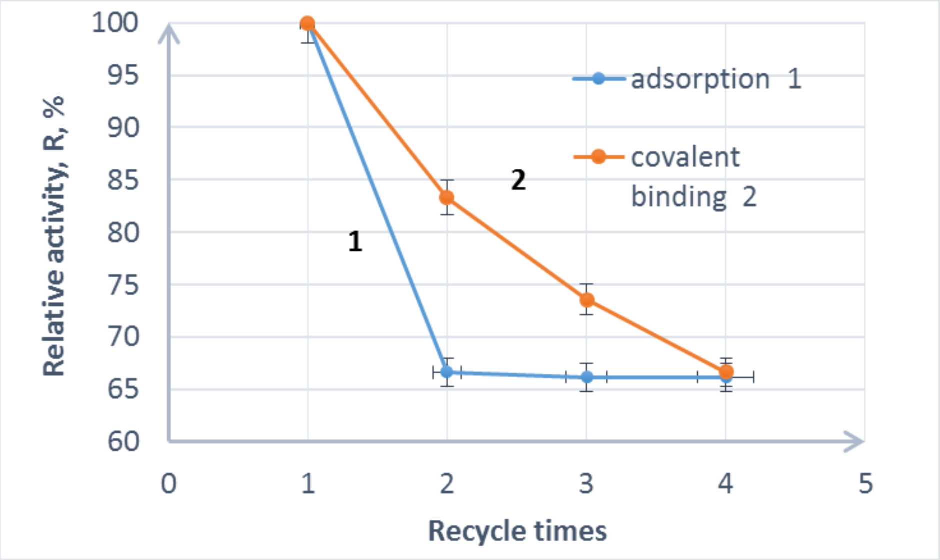

Figure. Operational stability of the immobilized chitosanase

Acknowledgement. This work was supported by the Russian Foundation for Basic Research (Grants 14-03-00898 and 17-03-00641.)

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PP-IV-9

Effect of Hydrodynamic Cavitation on Aerobic Oxidation of Sulfide Solutions

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Nowadays, industrial catalytic processes that produce essential commodities for everyday life demand of the reducing environmental footprints and enhancing sustainability. One of the approaches of the reduction and elimination of hazards is design of new devises for fine cleaning of gases and liquid effluents. Hydrogen sulfide (H_2S) and its associated hazards (high toxicity and corrosive activity) are well known in the oil and gas production and refining industries. Effective H_2S removal from waste solutions is possible by the selective liquid-phase catalytic oxidation with oxygen. Thus, aerobic oxidation of H_2S in the presence of cobalt sulfonated phthalocyanines allows transforming to non-toxic sulfur-containing products, such as sulfur and thiosulfate. Note that cobalt tetrasulfonated phthalocyanine ($CoPc(SO_3Na)_4$) is one of the most active catalytic systems for H_2S removal from neutral and alkalescent mediums (pH 7-9) [1].

In industry H_2S oxidation is carried out in a column-type devises with a continuous bubbling layer. Diffusion can affect the reaction rate, but increasing the turbulence of the fluid flow or initiating of the cavitation can diminish this effect.

Here, we demonstrated results of sulfide solutions oxidation with air oxygen in the presence $CoPc(SO_3Na)_4$ catalyst under high mass transfer and cavitation impact. The oxidation of 0.05M Na_2S solution was carried out at atmospheric pressure, temperature 25°C and a solution pH of 9.6 and 12.5 in the range of catalyst concentrations $5\cdot10^{-6}$-10^{-5} mol/l. Reaction was investigated in devises with high mass transfer coefficients and cavitation effect. Two type reactors were used:

- The shake-reactor with frequency of 360 shakes/min in which mixing of gas and liquid is occurred (regime of foam formation);
- The reactor with solution circulation and rotor generator of hydrodynamic oscillations. Latter is consisted from one movable disk (upper) and fixed disk (lower) to which perpendicularly located cavitators. The linear motion velocity of the movable cavitator relative to the fixed is 9 m/s. The cavitation number is 1.2. (regime of cavitation-foam formation).

It was found that cavitation impact leads to increasing the reaction rate in alkaline (pH 9.6) and strongly alkaline (pH 12.5) conditions (Fig. 1). Moreover, cavitation favors the rise of selectivity towards sulfur (Fig. 2).

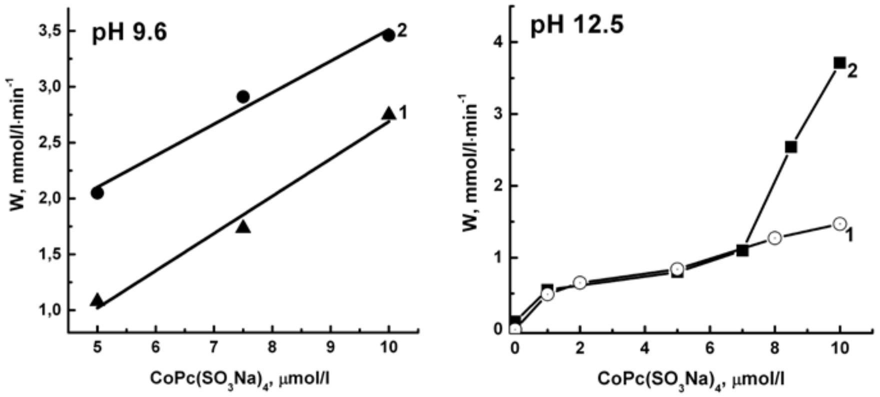

Figure 1 - The dependence of the reaction rate oxidation
of 0.05 M Na_2S solution (W) from catalyst concentration at 25°C.
1 - regime of foam formation, 2 - regime of cavitation-foam formation

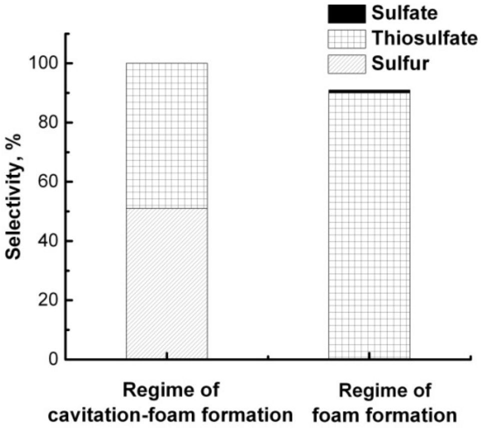

Figure 2 - The products composition of the H_2S oxidation with oxygen under
regime of cavitation-foam formation and regime of foam formation and
0,05M Na_2S, $7{,}5 \cdot 10^{-6}$ mol/l ($CoPc(SO_3Na)_4$) , T = 25°C, pH = 9.6

Analysis of experimental data points that H_2S oxidation under cavitation conditions leads to increasing the energy efficiency of the process and reduction of the amount of the catalyst up to two times in compared with reaction under regime of foam formation.

Acknowledgement

This study was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (state-guaranteed order for BIC, project number project 0303-2016-0014).

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PP-V-1

Mixed Cr-Zr Oxides as Promising Catalysts for Dehydrogenation of Alkanes

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Propylene is an important raw material of petrochemical industry for the production of various valuable chemicals and plastics. It is mainly produced as a by-product in steam and catalytic cracking of naphtha. Nevertheless, growing demand for propylene required new routes to obtain this commodity. One of the most promising pathways to produce high-purity propylene is a non-oxidative catalytic dehydrogenation of propane. Currently, different catalytic systems have been studied as catalysts for dehydrogenation and oxidative dehydrogenation of propane [1]. Catalysts with chromium oxide supported on zirconia show the highest activity in comparison with alumina–chromia, Pt–Sn and vanadium oxide catalysts. Co-precipitation and incipient wetness impregnation are the most frequently used preparation methods for chromia–zirconia catalysts [2, 3]. However, there were no systematic studies of correlation between the preparation conditions, structure of synthesised materials and nature of active sites for specific reactions. For example, in the case of alkane dehydrogenation, it was proposed that isolated Cr^{n+} species are active [4, 5], while other authors demonstrated high activity of “coordinatively unsaturated Zr cations” [3]. The present work is devoted to studying the influence of synthesis conditions and Cr/Zr ratio on the formation of active sites and catalytic activity of mixed Cr–Zr oxides in propane dehydrogenation into propylene.

A series of cromia–zirconia mixed catalysts with different Cr/Zr molar ratio was prepared by co-precipitation method. The required amounts of $ZrO(NO_3)_2\cdot 2H_2O$ and $Cr(NO_3)_3\cdot 9H_2O$ were dissolved in water. After that an aqueous solution of ammonia was added dropwise until pH=9. The as-prepared or overnight-aged precipitates were filtered and washed by distilled water. Then the catalysts obtained were dried at 100 ^oC overnight and calcined at 600 ^oC for 4 h. The structure and chemical properties of mixed chromium and zirconium oxides were studied by low-temperature adsorption of nitrogen, XRD and DRS. The method of temperature-programmed reduction (TPR) was used to evaluate the features of reduction of the catalysts. The catalytic properties of the samples were investigated in non-oxidative dehydrogenation of propane at 550 ^oC.

The results of low-temperature N_2 adsorption are presented in Table 1. The series of catalysts prepared without ageing was characterized by changing of the specific surface area value with increasing chromium content. One can see that the surface area values for these series varied from 24 m^2/g for pure ZrO_2 to 107 m^2/g for $Cr_{10}Zr_{90}O_x$. The increasing of chromium content up to 20 %mol led to a decrease of surface area (77 m^2/g for $Cr_{20}Zr_{80}O_x$). The catalysts prepared were characterized by mesoporous structure. Pore size distribution from 2 to 21 nm was observed for catalysts obtained without ageing, while thin pore size distribution from 2 to 6 nm was observed for aged catalysts. The surface area for mixed oxides synthesized with ageing changed in the range from 38 to 62 m^2/g.

Table 1. Values of specific surface area and H_2 consumption for binary oxides

Sample	S_{BET}, m^2/g	n(H_2), µmol/g	Sample	S_{BET}, m^2/g	n(H_2), µmol/g
ZrO_2	23	-	ZrO_2(aged)	5	78
$Cr_1Zr_{99}O_x$	24	241	$Cr_1Zr_{99}O_x$(aged)	54	334
$Cr_3Zr_{97}O_x$	76	541	$Cr_3Zr_{97}O_x$(aged)	59	496
$Cr_5Zr_{95}O_x$	65	677	$Cr_5Zr_{95}O_x$(aged)	37	682
$Cr_{10}Zr_{90}O_x$	107	981	$Cr_{10}Zr_{90}O_x$(aged)	62	956
$Cr_{20}Zr_{80}O_x$	77	942	$Cr_{20}Zr_{80}O_x$(aged)	42	893

According to the results of XRD data, the mixture of monoclinic and tetragonal ZrO_2 phases was found for pure ZrO_2 and ZrO_2(aged) samples. The increasing of chromium content led to stabilization of ZrO_2 mostly in the tetragonal phase. Tetragonal ZrO_2 phase in the aged samples dominated even in the binary oxide with low chromium content, while unaged $Cr_1Zr_{99}O_x$ - $Cr_5Zr_{90}O_x$ samples were presented mainly by monoclinic phase. Only reflexes of tetragonal ZrO_2 phase were observed for $Cr_{10}Zr_{90}O_x$ and $Cr_{10}Zr_{90}O_x$(aged). The reflexes of α-Cr_2O_3 were found only in the unaged $Cr_{20}Zr_{80}O_x$ catalyst. This indicates stabilization of chromia in a highly dispersed state. Reflexes of ZrO_2 phase were shifted to the high angle range for the samples with high chromium content due to incorporation of chromium in ZrO_2 structure.

It was shown by TPR-H_2 that two broad peaks of hydrogen consumption with temperature maximums of 351-383 and 488-535 ^oC were determined for all catalysts. The intensity of these peaks rose with increase of chromium content. Thus, these peaks may be attributed to reduction of Cr^{n+} from the high valence state ($Cr^{5+/6+}$). The amount of $Cr^{5+/6+}$ reduced to $Cr^{2+/3+}$ was close or larger than those for catalysts obtained without ageing. The calculated amount of H_2 consumption is presented in Table 1.

To summarize, the synthesized catalysts (both with and without ageing) had different structure and phase composition. The series of binary oxides prepared with ageing can be active in dehydrogenation reactions due to high content of tetragonal ZrO_2 phase. The materials without ageing contain more $Cr^{5+/6+}$, which may be reduced to active $Cr^{2+/3+}$ state. Activity measurement for $Cr_3Zr_{97}O_x$ and $Cr_3Zr_{97}O_x$(aged) catalysts shows the higher activity for unaged sample. Thus, the main role in catalytic activity is played by the content of reducible $Cr^{5+/6+}$.

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PP-V-2

Co-Based Fischer-Tropsch Catalysts Supported on Nitrogen-Doped Carbon Nanotubes: Effect of Content, Type, and Localization of Nitrogen Species

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Fischer-Tropsch synthesis (FTS) is an industrial process to obtain hydrocarbons from syngas [1]. This reaction is catalyzed by VIII group metals but only Co and Fe are simultaneously cheap, highly active and do not produce carbonyls. SiO_2, TiO_2, and Al_2O_3 oxides are the most commonly used supports for Co FTS catalysts. At the same time, these materials suffer from some disadvantages such as the formation of complex oxides with Co and low thermal conductivity.

Carbon nanomaterials, due to their inertness to metal and high thermal conductivity, have been widely proposed in the last decade as an alternative to oxide supports. They also reduce the probability of local overheating and metal sintering. Carbon nanotubes (CNTs) are distinguished among other carbon supports by their structuredness, chemical stability, rigidity, high porosity, and tunable surface properties [2]. Moreover, the overall production of CNTs has gradually increased while their price has reduced in the last years. At the same time, the surface of CNTs requires fictionalization to stabilize metal nanoparticles. In the present study CNTs were functionalized by doping with nitrogen atoms which are electron donors and facilitate the defect formation [3]. Thus, the aim of this work is to reveal the influence of nitrogen content and localization on the efficiency of Co-based CNT-supported catalysts in FTS.

Multi-walled N-CNTs were synthesized by CVD method using CH_3CN and CH_3CN/C_6H_{14} mixture as precursors. Post doping of oxidized undoped CNTs by NH_3 was also applied to obtain nitrogen species only on the surface of CNTs. Catalysts contained 15 wt.% of Co were obtained by the impregnation with Co nitrate ethanol solution and further calcination at 400°C in inert medium. TEM image of Co/N-CNT catalyst are given in Fig.1. Co particles in Co catalyst supported on oxidized N-CNTs were placed both on inner- and outer-channel surfaces.

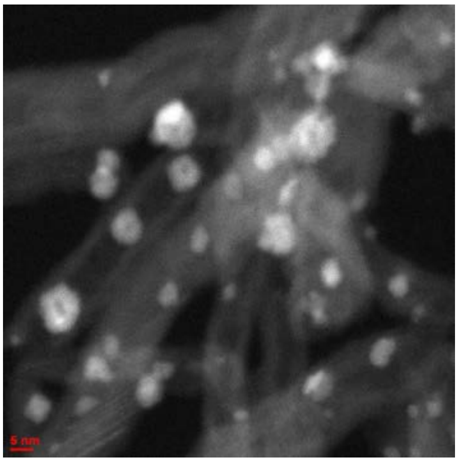

Fig.1. TEM image of Co/N-CNT catalyst.

Catalytic FTS experiments were performed in a stainless-steel fixed-bed reactor at T = 240°C and P = 20 bar. C5-C24 linear hydrocarbons were observed in the liquid fraction produced over Co/N-CNT catalyst (Fig.2). The most active catalyst was supported on oxidized N-CNTs and the most selective to C5+ was that supported on CVD-obtained non-oxidized N-CNTs.

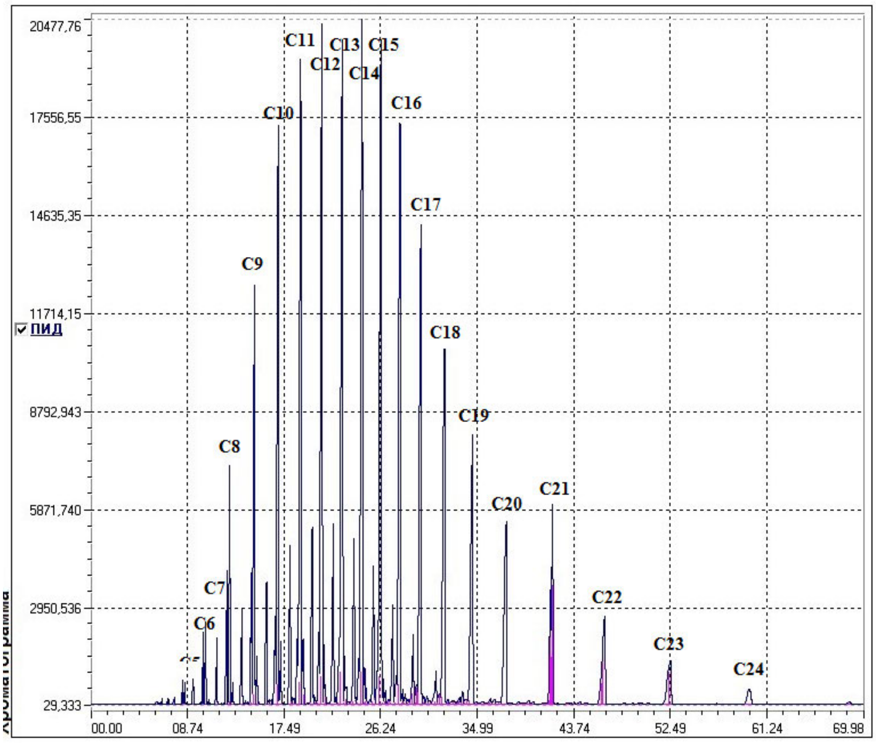

Fig.2. Chromatogram of the liquid fraction obtained during FTS test of Co/N-CNT catalyst.

Acknowledgement. The reported study was funded by RFBR according to the research project № 18-33-00390.

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PP-V-3

Condensation of Ketones and Glycols in the Presence of Polyoxometalates Containing Gd(III), Nd(III)

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Oxygen-containing heterocyclic compounds such as cyclic acetals have a plurality of properties, they are widely used as synthetic fragrances, solvents, cellulose ethers, biologically active agents in agricultural chemistry.

The present work is devoted to obtaining spiroacetals by condensation C_3-C_7 alkyl, dialkyl and cycloalkyl-substituted cyclopentanone and cyclohexanone with ethylene glycol in the presence of polyoxometallates catalysts containing rare earth elements (Gd, Pr, La).

The catalyst is prepared on the basis of a binary mixture containing equal weight amount of $(NH_4)_6Mo_7O_{24} \times 4H_2O$ and rare earth containing compound (nitrates of Gd(III), Nd(III)), followed by treatment with aqueous solutions of H_3PO_4 at 75-76 ºC . Prepared catalyst systems are investigated by EPR-, UV/VIS, FTIR – spectroscopy and TGA. It has been established that in all the studied cases in solution cations Nd^{3+}, coordinate to molybdenum-containing anions. Coordination realized through the phosphate groups. Typical IR bands assigned to Mo-O-Mo (798, 873 sm^{-1}), Mo-O (959 sm^{-1}) and P-O-Mo (1063 sm^{-1}).

The condensation is carried out in a thermostated glass reactor fitted with a condenser, thermometer, and Dean-Stark water separator at boiling temperature. The flask was placed a sample of the catalyst, and then added 0.1 moles ketone, 1 mole of ethylene glycol and toluene.. After azeotropic separation of required (estimated) water heating the reaction mixture was stopped, the organic layer was separated from the catalyst by atmospheric and vacuum distillation and the desired product was isolated. The duration of the reaction is 2-3 h., while in the presence of the traditional acid catalysts the reaction is completed for 10-13 h. Purity and composition of the product of condensation was determined by GLC method.

Identification of derived spiroacetal was performed by IR and ^1H NMR methods. Dioxane is obtained as a byproduct of self-condensation glycol. In the IR spectra of these compounds disappear absorption bands at 1750-1730 sm^{-1}, 3400-3500 sm^{-1} and 1100-1050 sm^{-1} characteristic of the stretching vibrations of the $> C = O$ groups and OH – groups. Accordingly, in the spectra of acetal appears new intense absorption bands at 1140-1170, 1200-1040, 950-860 sm^{-1}, corresponding to the stretching vibrations of oxirane communication, confirming the formation of the acetal structure.

5-Heptyl-1,4-dioxo-spiro [4.4] nonane was prepared similarly from 18.2g (I) of heptyl-cyclopenthanone and 12.4g of ethylene glycol (II). Yield 11.8 g (52%), bp.141-142ºC

(10 mmHg), d_4^{20}- 0.9524, n_d^{20}- 1.4584. IR spectrum, ν, sm^{-1}: 1150-1055, 660. ^1H NMR spectrum, δ, ppm.: 3.85-3.98 g ($4H^{2,3}$, $2CH_2O$), 2.13m ($1H^5$, CH), 1.22-1.84 m (18H, $3CH_2$ cycle and $6CH_2$ radical), 0.97t (3H, CH_3). % Found: C 74.86, H 11.62. $C_{14}H_{26}O_2$. Calculated%: C, 74.74; H 11.50.

5-cyclopentyl-1,4-dioxo-spiro [4.4] nonane was prepared similarly from 15.2g of 2-cyclopentyl-cyclopentanone and 12.4 g (VIII). Yield 15.6 g (79%), bp. 144-146ºc (3 mmHg.), d_4^{20}- 1.0474, n_d^{20}- 1.4884. IR spectrum, ν, sm^{-1}: 1200, 1200-1040. ^1H NMR spectrum, δ, ppm.: 3.86- 3.94 dd ($4H^{2.3}$,$2CH_2O$), 2.12t (5H, CH), 1.33-1.84m (14H, $3CH_2$ spiro and $4CH_2$ radical), 1.48d. (H, CH, radical). Found%: C 43.42; H 10.28. $C_{12}H_{20}O_2$ Calculated%: C, 73.47; H 10.2.

PP-V-4

Heteroatomic Compounds Removal from Distillates Using Catalysts Based on Meso-Macroporous Structures

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One of the most promising tasks of modern oil refinery is how to get rid of heteroatomic compounds containing in crude oil and its distillates. Some of them should be removed due to strict fuel requirements; others reduce catalyst activity during the process of refining. In order to provide maximum efficacy of hydrotreating units, catalyst activity should be constantly high. Metals like Ni, V, Na, and Fe are well-known catalytic poisons that are removed successfully. However, there are some non-obvious elements that also poison the catalyst. For example, As, Si, Cl cause serious damage to the catalytic system. Arsenic is a true catalyst poison as it chemically reacts with active catalytic sites (nickel and cobalt sulfide) transforming them into NiAs or CoAs [1]. Poisoned sites cannot be reactivated via regeneration, and even small amounts of arsenic on the catalyst will affect catalyst activity in a critical way. To prevent such undesirable effect, using of guard layer catalyst is needed. Guard layer catalyst can accumulate arsenic and other poisonous species to protect main catalyst.

Arsenic removal catalysts are known to be a composition of Ni-Mo supported on Al_2O_3 [2,3]. In present work we used meso-macroporous material as a support for such catalysts. This is explained by several factors. Firstly, meso-macroporous materials have considerable surface area which can help to trap more heteroatomic species than conventional support. Secondly, large pore size helps to overcome diffusional limitations for bulky molecules containing in middle and heavy distillates.

Acknowledgement. This work was supported by the federal target program "Research and Developments in Priority Fields of Science and Engineering in Russia for 2014-2020 yy," state contract no. RFMEFI57617X0087

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PP-V-5

A New Method For The Synthesis Of Fully Substituted 1,2,3-Triazoles: Comparative Study

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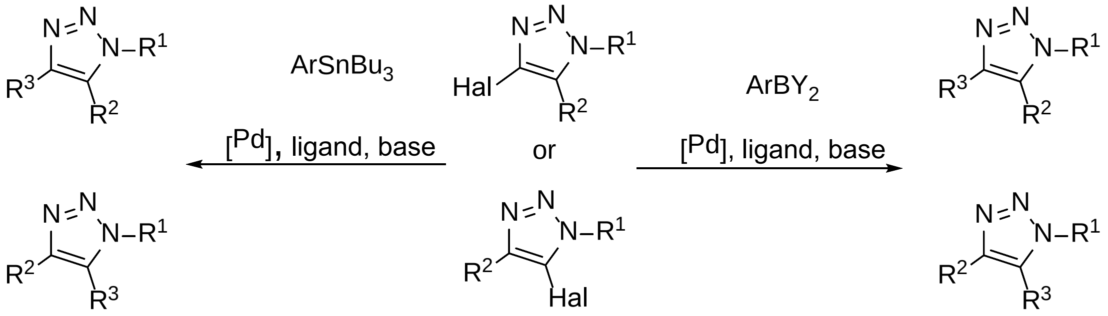
Copper(I)-catalyzed alkyne-azide cycloaddition reaction (CuAAC) is the most popular method for 1,4-disubstituted-1,2,3-triazoles synthesis. Besides many advantages of this approach such as high product yields, low sensitivity to air and moisture, high tolerance to different functional groups and preparative simplicity, there is an essential drawback which is low reactivity of internal alkynes and poor regioselectivity of CuAAC reaction with them. That's why synthesis of fully-substituted 1,2,3-triazoles is one of the unsolved problems of organic chemistry in general sense [1].

Recently some methods of the title compounds synthesis by using synthetically more affordable 4- or 5-halo-1,2,3-triazoles in cross-couplings with organoboron [1] (Suzuki-Miyaura reaction) or organotin [2] (Stille reaction) compounds were reported. Because of generally increasing tendency of searching for "green" chemistry consistent protocols an interesting and attractive next step in evolution of this synthetic approach is in avoiding utilization of toxic, flammable and relatively expensive organic solvents.



In continuation of our group research of 4- or 5-halo-1,2,3-triazoles cross-couplings with arylboronic acids in water[3] and also our group investigation of solvent-free conditions for Suzuki[4] and Stille[5] reactions of arylhalides, we decided to perform a comparative study of applicability of these methods to the fully-substituted 1,2,3-triazoles synthesis under conditions consistent with the concept of "green" chemistry.

PP-V-5

Acknowledgement. This publication was financially supported by the Ministry of Education and Science of the Russian Federation (the Agreement number 02.a03.21.0008).

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PP-V-6

The Preparation of Light Olefins over Perovskite-Type Systems

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Catalysts based on perovskite-type layered structures are alternative catalysts of noble metals in a variety of high temperature catalytic processes. Particularly, they are used for the industrial synthesis and the gas purification as these systems can maintain their catalytic and mechanical properties under the severe reaction medium. Currently, such compounds are intensively studied and find wide application [1-3].

The nanostructured perovskite-type oxides ABO_3 (A=Gd, Sm; B=Fe, Mn, V; n=1,2,…,∞) were investigated as catalysts for dry reforming of methane (DRM), CO hydrogenation and for propane cracking process. These complex oxides were synthesized by sol-gel technology, the high-temperature solid state reactions.

Compounds were characterized using different techniques: XRD, SEM+EDS, BET, TG to study structure and morphology. Oxidation state of Fe and Mn was determined by Mössbauer spectroscopy and XPS. The surface properties of the samples were measured via the low–temperature adsorption of nitrogen. The obtained adsorption–desorption isotherms were used to study the specific surfaces of the samples via BET method and the sizes of pores.

The catalytic activity were studied in a flow apparatus at atmospheric pressure in the temperature range of 773-1223 K for the DRM, 300-723 K for the CO hydrogenation and 298 – 1143 K for the propane cracking process and flow rates of 0.5-1.0 l/h. Analyses of the products were performed by chromatography (Crystal 2000M, Crystal 5000).

It was found that the samples of ferrites and manganites gadolinium obtained by sol-gel method are with higher catalytic activity than the ceramic samples. There is due to the state of nanocrystalline and a porous structure of the sol-gel sample. The hydrogen selectivity of the DRM reaction was increased in the row: $GdFeO_{3(ceramic)} < GdFeO_{3(sol\text{-}gel,\ glycine)} < GdFeO_{3(sol\text{-}gel,\ citric)}$. A similar dependence was observed in the CO hydrogenation.

Doping of manganese to ferrite gadolinium in the anion sublattice, like the surface modification with using manganese leads to an increase the olefins selectivity in the entire temperature range. The proportion of saturated and unsaturated hydrocarbons in the products of CO hydrogenation and a synergetic effect arising over $GdFe_{1-x}Mn_xO_3$ samples are mainly determined by the amount of hydrogen atoms that can migrate from one active center to another, and determined by the composition of these centers. Increasing the coordination unsaturation of metal atoms leads to a change in the binding energy of the metal not only with carbon, but also with hydrogen and leads to redistribution ratio H_I (loosely-coupled): H_{II} (hard-coupled) to the weakly bound hydrogen. The $GdFeO_3$, $GdFe_{0.95}Mn_{0.05}O_3$, 5%Mn/$GdFeO_3$ samples showed the highest stability, catalytic activity and selectivity of unsaturated hydrocarbons (ethylene and propylene) in the CO hydrogenation. Total selectivity of ethylene and propylene was 35% over $GdFe_{0.95}Mn_{0.05}O_3$ in the temperature range up to 723 K.

It was shown that the $SmVO_3$ catalyst is more effective for the propane cracking process of ethylene production, however dehydrogenation proceeds poorly in the presence of this oxide. Ethylene selectivity was increased to 72%. While the selectivity of propylene didn't exceed 8% in the entire investigated temperature range.

All the investigated oxides were shown a high stability. The catalytic properties were not changed after 50 hours of the DRM and CO hydrogenation and after 20 hours - of the propane cracking. Data SEM, XRD and Energy-dispersive X-ray spectroscopy (EDX) for the investigated samples after the catalytic reaction were shown the preservation of the perovskite structure and morphology of the samples, the carbon presence on the sample surface (estimated about 5%).

Acknowledgement. The reported study was supported by the Russian Foundation for Basic Research, research projects No. 16-33-00971 mol_a, 17-03-00647.

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Sulfur Reduction Additives for FCC Catalysts Based On Alumosilicates Al-SBA-15 and Al-SBA-16

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In the world, more stringent environmental legislation has stiffened requirements on reducing automotive exhaust emissions of sulfur oxides. It leads to a challenge for a petroleum refining industry to produce fuels with a concentration of sulfur less than 10 ppm [1]. Gasoline fraction of fluid catalytic cracking (FCC) contributes till 80 % of the total gasoline pool in some countries [2]. There are several options to decrease sulfur in FCC gasoline fraction: hydrotreatment of the feedstock, posttreatment of products, undercutting the FCC gasoline, adjust reactor and regenerator conditions. Using a sulfur reduction additive is a new approach, which could be attractive for refineries due to the lack of capital investments.

Ordered mesoporous silicas have attracted a lot of attention over the last several years [3,4]. These materials possess numerus attractive features, such as high specific surface area and the ability to modify surface. Ordered silicon oxides SBA-15 and SBA-16 have relatively thick walls compared to the other mesoporous materials. It is leads to a higher thermal and mechanical stability. High acidity that is achieved by insertion of metals in the structure of mesoporous oxide is one of the main properties that FCC additive should possess. The aim of this work was to test sulfur reduction additives for FCC catalysts, based on alumosilicates Al-SBA-15 and Al-SBA-16.

Materials Al-SBA-15/Al_2O_3 and Al-SBA-15/Al_2O_3 with different component ratios: 30/70, 40/60, 50/50 %wt. were synthesized. The samples were characterized by TEM, IR spectroscopy, TPD of ammonia, low-temperature adsorption/desorption of nitrogen, ^{27}Al NMR spectroscopy. According to the data obtained from adsorption/desorption of nitrogen all the materials have ordered pore system and exhibit type 4 isotherms, which are specific to mesoporous materials.

Catalytic cracking over a mixture of commercial microspherical cracking catalyst and sulfur reduction additive using vacuum gas oil (1.86 %wt. S) was carried out in a micro activity testing (MAT) laboratory system at 500 °C with a catalyst/feedstock ratio 3.4. The fractional composition of liquid cracking products was determined by a simulated distillation method on a Chromos GC-1000 chromatograph. The concentration of sulfur in the liquid products was determined on an energy-dispersive X-ray fluorescence analyzer. The coke content of the catalyst was determined by gravimetry. Additives made by impregnating lanthanum on carriers Al-SBA-16/Al_2O_3 and Al-SBA-15/Al_2O_3 are able to give a significant reduction on gasoline sulfur in MAT experiments. In the case of 5%La/Al-SBA-16/Al_2O_3 (Al-SBA-15/Al_2O_3 ratio=50/50 %wt.) and 5%La/Al-SBA-16/Al_2O_3 (Al-SBA-16/Al_2O_3 ratio=50/50 %wt.) the sulfur content in liquid cracking products decreased up to 35% and 33%, respectively, as compared with catalyst without additive. Additives based on alumosilicate Al-SBA-15 showed better sulfur reduction activity than based on Al-SBA-16, that can be explained by different pores structure. Compared to the situation using the pure FCC catalyst, additive can improve the yields of fraction with boiling range 200-350 ^{o}C with the same gasoline yield.

Acknowledgements. This work was supported by the Russian Science Foundation (Grant №17-79-10301). Authors thank Andrei Pahomov and group of companies «Chromos» for the equipment provided (Chromos GC-1000).

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PP-V-8

Nano-Sized K-Modified Transition Metal Sulphides as Promising Active Phase for Design of Bifunctional Catalysts for Syngas Conversion into Alcohols and Other Oxygenates

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The design of molybdenum sulfide based catalysts for alcohol production from syngas attracts interest both of academic and industrial research because of several reasons. Alcohols have extensive applications as precursors of surfactants, fragrance compounds, plasticizers, extragents, etc. in various industries. Alcohol containing fuels reduce the emission of greenhouse and toxic gases (CO and NOx) and generation of soot particles. Restriction of MTBE has initiated interest in alcohol-based additives. Synthesis gas is produced from coal, associated gas or biomass. After primary purification, it contains up to several dozen ppm of sulfuric compounds. Tradition oxide catalysts are deactivated by very small concentrations of sulphur compounds. Recent studies of the (Me)MoS2 systems have shown that they can be applied for syngas conversion [1, 2]. The advantage of the systems is their resistance to sulfur that strongly poisons traditional catalysts for synthesis gas conversion [3]. Modification of the catalysts by potassium shifts selectivity from hydrocarbons to alcohols. However, their commercial application needs significant improvement of selectivity towards alcohols [4].

The aim of this investigation is to understand the role of the second metal in mixed MeMoS active sites formed with participation of Nb, Fe, Co or Ni and to determine possible differences in catalytic behavior of these systems. Additionally, the role of electron donation from potassium to mixed MeMoS active sites was elucidated by computational methods with a view to predict catalytic properties of K(Me)MoS sites.

The catalyst samples were prepared by the incipient wetness impregnation of the alumina support. Samples with following composition was synthesized: (K)MoS2/Al2O3, (K)NbMoS2/Al2O3, (K)FeMoS2/Al2O3, (K)NiMoS2/Al2O3, (K)CoMoS2/Al2O3. Catalytic tests in syngas conversion were performed in a tubular fixed-bed flow reactor.

MoS2 and NbMoS2 showed the highest syngas conversion in the overall temperature range. For catalysts promoted by Fe, Co or Ni, syngas conversion decreased in the following order: FeMoS2 > CoMoS2 > NiMoS2. The fact that the FeMoS2 catalyst demonstrated higher activity than CoMoS2 on a similar surface area could be explained by stronger adsorption of intermediates on the former catalyst. MoS2 and NbMoS2 catalysts showed the highest methane yield. Methane yield was lower than 5% for the FeMoS2, CoMoS2 and NiMoS2 samples. NbMoS2 had lower methane yield than MoS2. K MODIFIED

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PP-V-9

N-Methyl-D-Glucoseamine Synthesis over Ni-Impregnated Hypercrosslinked Polysterene

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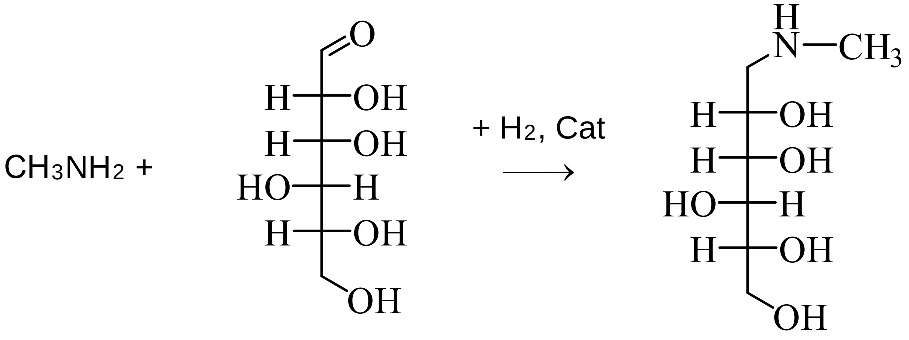
1. Introduction

D-glucose simultaneous catalytic hydrocondensation with methylamine can be considered a promising way of methylglucosamine synthesis [1,2]. Amines such as methyl amine are reacted with materials such as reducing sugars in hydroxy solvents such as methanol to prepare N-alkylpolyhydroxyamines. Accordingly, glucose is reacted with methyl amine and the resulting adduct is hydrogenated to yield N-methylglucamine. The production of N-methylglucamine as early as 1935 was patented by American scientists Robert B. Flint and Paul L. Salsberg, the rightful owner is the large chemical company E. I. du Pont de Nemours & Company [1,2]. The reaction for the production of N-methylglucamine by reductive amination proceeds in one step (1):



(1)

2. Methods

A sample of 100 grams of commercial glucose, 80 g of methanol and 30 grams of monomethylamine are placed in a pressure vessel with 9 g of reduced nickel catalyst containing 25% nickel of hypercrosslinked polysterene. Hydrogen is injected at a pressure of 50 bars with heating and vigorous stirring. The hydrogen absorption starts at 100 ° C and is completed within 15 minutes, after which the temperature is raised to 120 ° C. The product is separated from the catalytic material by filtration, and the filtrate is then evaporated. Methylglucamine can be isolated from this residue as a white solid, melting at 127 - 128 ° C.

3. Results and discussion

Catalysts initial activity of HPS-Ni was found to be 1.3 kg(Glu)/(kg(Cat)*h) at 99.3-99.6% D-glucose conversion. Process selectivity to N-methyl-d-glucoseamine was 97.6-97.8%. Sorbitol was found in traces during the analysis and can be considered the main side products. The investigation of the catalysts long term stability showed that after 10 reaction cycles of 2 hours hydrogenation the HPS-Ni catalyst was ground by a reactor mixer therefore catalysts particles diameter becomes smaller than 0.01-0.07 mm compare to initial (Table 1). Besides the catalysts mechanical losses were calculated to be 78%, the catalyst weight losses can be attributed to the catalysts particles grinding and losses during the centrifugation and separation. The catalysts activity after 10 cycles of D-glucose transformation showed a little slow down and was calculated to be for 1.1 kg(Glu)/(kg(Cat)*h) at 99.4-99.5% D-glucose conversion. Some losses of catalysts activity can be attributed to metal leaching. However some increase in Ni dispersion is noticed that can be also explained by the catalyst particles grinding and particles transformation during reaction. The oxidation state of an active metal according to XPS data remains +2 and Ni is mainly presented in the oxide form. It should be noted that D-glucose hydrogenation in the reactor equipped with impeller mixer results in high mechanical losses therefore the catalysts overall time on steam was only 20 h, that is insufficient for the study of metal leaching, poising and nanoparticles transformation.

Table 1 Catalysts characteristics used catalyst

Catalyst characteristics	Before synthesis	After synthesis
Surface area, m^2/g	240	187
Granulometric composition, mm	0.01-0.12	0.1-0.14
Nanoparticle size, nm	4-16	4-12
Ni oxidation state	+2	$+2^4$
Ni concentration, w %	2.3	2.4
Ni dispersion, %	25	27
Sample mass losses, %	27	12

Acknowledgement. This study was funded by RFBR project, grant number 17-08-00568.

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PP-V-10

The Prediction of Catalytic Activity of Synthetic Zeolites and Carbon Nanotubes in Prins Reaction by Theoretical Modeling of Interaction TS with Cavity

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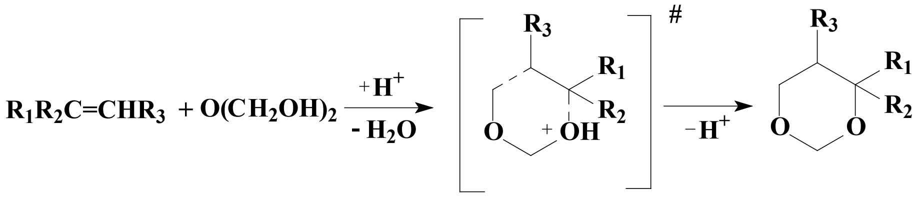
One of the important area of research the development a new catalysts is the using principles of molecular imprinting [1]. By this way the molecule should be chosen that have a shape with compliance geometric parameters to TS of investigated reaction. Then polymeric 3d structure with molecular fingerprint is formed and this material can be used as a catalyst. Our idea is that instead of formation material with fingerprint we offer its choosing from existing porous material (zeolites, nanotubes and etc). Quantum-chemical modeling allowed to use as a fingerprint the transition state itself. We believe that the sufficient criterion of choosing porous materials is degree of interaction in system TS – pore which depend from pore diameter. As result the catalytic activity of porous materials can be quantitatively described by TS-pore energy interaction and investigations of energy dependence on diameter of pores. We had tested our method on practical important Prins reaction, which mechanism is the object of our long time study [2-3].



We investigated interaction of frozen structures TS, which are forming during reaction from ethylene (**1**), propene (**2**), 2-methylpropene (**3**), 1-buthene (**4**) and trans-2-buthene (**5**) with formaldehyde oligomers, with some zeolites with various pore size (ANA, NAT, BEA, STI, GIS, YUG, PAR) and single-walled CNT. TS were found in MP2(fc)/6-31G(d,p) approximation [4], interaction with porous materials was modeled in Acc.Material Studio 5.5.

Table 1

The dependence of the adsorption energy of TS from the pores diameter of zeolites, KJ/mol

Zeolite A	d, Å	Ethene	Propene	1-Butene	2-Methyl-propene	trans-2-Butene
ANA	3.8	-49.5	-57.6	-59.2	-56.9	-63.8
NAT	4.0	-49.6	-60.2	-53.6	-52.1	-62.6
BEA	5.1	-107.3	-121.3	-140.3	-139.2	-140.1
STI	5.4	-90.6	-98.1	-134.6	-96.6	-137.3
GIS	5.8	-63.0	-72.6	-68.6	-77.9	-73.8
YUG	6.2	-52.6	-59.9	-65.3	-66.1	-70.2
PAR	6.6	-49.5	-57.6	-59.2	-56.9	-63.8

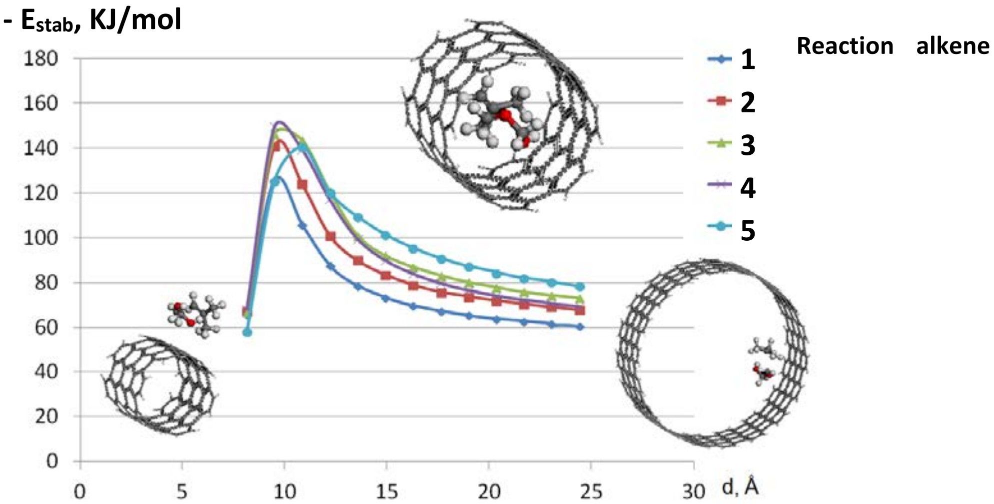


Fig. 2. The dependence of the adsorption energy of transition state from the diameter of CNT

In accordance with the data presented in table 1, zeolites with pores 5.1 – 5.4 Å are the preferred porous material for the stabilization of the investigated TS. Obviously that in this case transition state can fit into the pore of zeolite and stabilize due to the intermolecular interaction with inner surface of pore. If the pore diameter is less than 5 Å, then the transition state does not fit into of the pore and can be stabilized due to the outer surface of zeolite. In the case of zeolites with bigger size of pore the interaction is realized by part of inner or outer surface of pore.

The stabilization of TS of 1,3-dioxanes in CNT fig.2, is the best for CNT with diameter 9.4 – 10.9 Å. In this case TS also can fit into CNT and stabilize due to the intermolecular interaction with inner surface of tube. If the CNT diameter is less than 9 Å, then the TS does not fit into tube and can be stabilized only due to part of outer surface of CNT. A similar pattern is observed for tubes with diameter larger than 10,9 Å. Even in the formation such TS into nanotubes the intermolecular interactions can be realized only due to part of inner surface of CNT.

Results of theoretical modeling are in a good agreement with our investigations of formal kinetics of Prins reactions between *i*-butene and formaldehyde. So the kinetic constant of formaldehyde consumption in the presence of zeolites, which diameter is comparable to the predicted by theoretical modeling optimum diameter, was increased by 8.5 times - $(7,47 \pm 0,44)*10^5$ vs. $(0,88 \pm 0,03)*10^5$ s^{-1}. Kinetic constant of accumulation of 4,4-dimethyl-1,3-dioxane was increased by 7.4 times - $(4,60 \pm 0,27)*10^5$ vs. $(0,62 \pm 0,03)*10^5$ s^{-1}. Activation energy of reaction was decreased from 102 kJ/mol to 81 kJ/mol.

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PP-V-11

Model Sulfides Peroxide Oxidation in the Presence of Catalysts Based on Mesoporous Aluminosilicates

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Now the environmental requirements for motor fuels are constantly being tightened, particularly for the content of organosulfur compounds. This is due to the fact that sulfur compounds lead to atmospheric pollution, poison the catalysts of oil refining, cause corrosion of equipment during extraction, transportation and processing of oil. In connection with this, and also in connection with an increase in the content of sulfur compounds in extracted oils, the task of developing new methods for the desulfurization of oil and its distillates is very relevant [1].

The most common technology for the purification of petroleum fractions from sulfur - hydrotreatment - requires significant energy and capital investments that are unavailable for small refineries that is why such alternative non-hydrogen desulfurization methods as oxidative desulfurization, extraction, adsorption are being used with more frequency. An oxidative desulfurization method is based on the oxidation of sulfur-containing compounds to sulfoxides and sulfones with the subsequent extraction of oxidation products from petroleum fractions. This method is promising because of an opportunity to use released sulfoxides and sulfones it provides. The use of homogeneous catalysts for desulfurization of oil fractions is not always advantageous, because of the lack of catalyst regeneration possibility and an unavoidable loss of the catalyst.

Mesoporous aluminosilicates, whose pore size corresponds to the size of molecules of organosulfur compounds present in petroleum fractions, are interesting carriers for catalysts of the process of oxidative desulfurization [2]. In this paper, the catalysts based on mesoporous material (MCM-41) with applied oxides of transition metals (molybdenum, tungsten) were used to oxidize sulfur-organic compounds with hydrogen peroxide. It is known the carrier has a considerable impact on the properties of a catalyst, therefore, its perfection allows to improve the potential properties of a catalyst [3]. It was previously shown that the oxidation of sulfur compounds proceeds better in an acid medium [4]. In this regard, in order to increase the acidity of a carrier surface, the resulting MCM-41 was additionally coated with alumina and sulfo groups.

It is known that salts of transition metals, especially molybdenum and tungsten, are widely used as catalysts for oxidative desulfurization. Therefore, their oxides were applied by impregnation to the modified MCM-41 in various amounts.

The obtained catalysts were used to oxidize model mixtures, which were the solutions of methyl phenyl sulfide, benzothiophene and dibenzothiophene in a mixture of benzeneheptane (20:80 volume %) in the presence of hydrogen peroxide. As a result of the work, data on the effect of the nature of a carrier (the amount of aluminum, molybdenum and tungsten oxides applied) on the conversion of sulfur compounds and the selectivity of their oxidation were obtained. Proceeding from the data obtained, the catalyst composition and oxidation conditions, which allow to oxidize different classes of organosulfur compounds with high conversion and selectivity, including difficult-to-oxidize heteroaromatic sulfur compounds have been proposed.

Acknowledgement. The work was supported by the FTP "Research and development in the priority areas of development of the scientific and technological complex of Russia for 2014-2020." Activity 1.3, Agreement on granting the subsidy No. 14.607.21.0173 of 26.09.2017. Unique identifier of applied scientific research RFMEFI60717X0173.

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PP-V-12

A New Heterogeneous Approach for Selective Room-Temperature Transformations of Carbonyl- and Nitro-Compounds in the Presence of H_2

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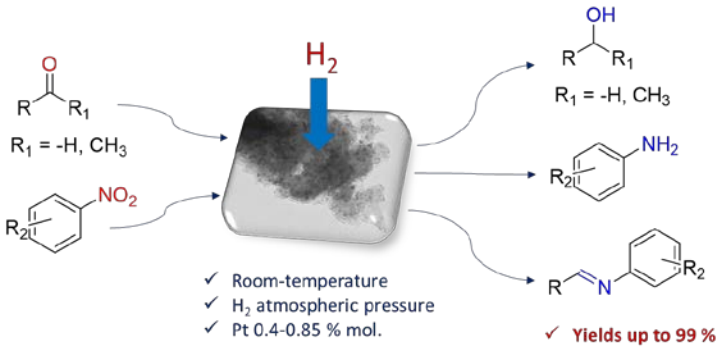
Hydrogenation reactions are one of the most important types of transformations in synthetic organic chemistry. Selective hydrogenation of carbonyl compounds makes it possible to obtain alcohols of various structures, including unsaturated ones. Hydrogenation of compounds containing nitro groups is used to produce amines, an important syntones for organic chemistry. Today we come to the era of “green chemistry”. There is a need in replacing the traditional methods for providing reduction reactions, which based on the use of stoichiometric reducing agents or homogeneous catalysts, with more convenient “atom-efficient” methods of heterogeneous catalysis with H_2 as benign reducing agent. However, to date, there are no heterogeneous-catalytic systems for performing *selective* hydrogenation reactions with high activity under ambient conditions.

Herein we report on Pt-based nanocatalysts supported on ceria-zirconia mixed oxides for room-temperature hydrogenation of aldehydes, ketones, nitro-aromatics to the corresponding alcohols and amines with quantitative yields in the presence of H_2 at atmospheric pressure. In addition, the catalysts show high activity in one-pot synthesis of imines from nitro-aromatic compounds and aldehydes. The catalysts were prepared by easy-to-use techniques allowed well-reproducible characteristics of the samples.



The exceptional low-temperature activity and selectivity of the obtained catalysts in the reactions with H_2 were attributed to the formation of active hydrogen species due to intense H_2 spillover on the surface of the catalysts. This effect was observed at temperatures -50-25°C for the first time in this work.

Acknowledgement. This work was supported by the Russian Science Foundation grant 17-73-20282.

PP-V-13

Hydrogenation of Furfural over Palladium-Containing Catalysts

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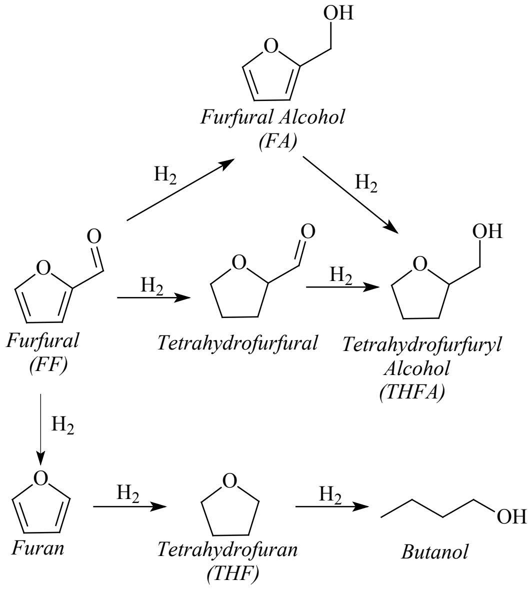
Catalytic hydrogenation has attracted much attention in recent years as a good-quality and practical method for the reduction of carbonyl compounds. Various catalyst systems were set especially for the reduction of ketones including chiral complexes. In contrast, only few protocols have been developed for the hydrogenation of aldehydes as it is more difficult to control the chemo selectivity of this transformation [1]. Furfural, having a high reactivity, readily forms a variety of derivatives, widely used as raw material for numerous syntheses of various organic compounds. In the gas-phase hydrogenation of furfural can be produce products, such as furfuryl alcohol, 2-methylfuran and tetrahydrofurfuryl alcohol. Resinous material and a ring-decomposed products are also found in the liquid phase hydrogenation reaction [2]. Scheme 1 shows the complexity of the process which could lead to multiple products.

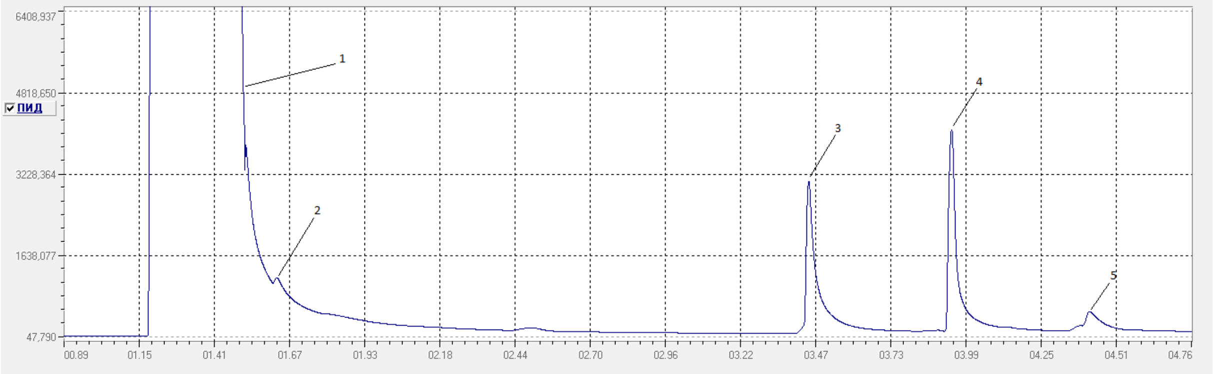


Scheme 1. The possible routes of Furfural hydrogenation.

Furfuryl alcohol (2-furanmethanol) is an important fine organic chemical for the polymer industry. It is used mainly for the production of dark thermostatic resins resistant to acids, bases and various solvents; liquid resins for galvanic bath-tube, and resins used for strengthening ceramics. It is also widely used as a solvent, e.g. for phenolic resins or pigments of low solubility [4].

In this work, palladium catalysts on different supports were studied: aluminium oxide (Al_2O_3) and hypercrosslinked polystyrene (MN270). As a precursor was used the palladium chloride synthesized catalytic systems with active metal content of 3% (3% Pd/Al_2O_3, 3% Pd/MN270). When using the catalyst Pd/Al_2O_3 the main product is furfuryl alcohol, in that case of 3% Pd/MN270 mainly tetrahydrofurfuryl alcohol was produced. Although the catalyst 3% Pd/Al_2O_3 in $PdCl_2$ is widely used as catalyst hydrogenation, and it is known because of its ability of selective hydrogenation for groups of aldehyde [3].

The palladium-containing catalysts were studied in the process of the hydrogenation of furfural using various solvents: hexane, water, toluene and 2-propanol. The highest yield of the product of the hydrogenation of furfural to furfuryl alcohol process was observed in the solvent 2-propanol (Fig. 1).



1 – 2-Propanol, 2 – Tetrahydrofuran, 3 – Furfural, 4 – Furfuryl alcohol,
5 – Tetrahydrofurfuryl alcohol

Fig. 1. Chromatogram of the reaction products of hydrogenation of furfural

The universal nature of palladium together with the mechanical properties predicts a wealth of research and infinite potential of this metal. 2-Propanol is an excellent solvent which easily enters into chemical reaction with the formation of the main products.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 15-08-00305.

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PP-V-14

Using a Band Nickel-Aluminum Catalyst in the Process of Obtaining Hydrogen

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Hydrogen is one of the most perspective sources of energy. Its reserves on our planet are practically inexhaustible. Unit of weight of hydrogen contain almost three times more thermal energy, than gasoline. It can be used as fuel in transport, in industry, and in everyday life. The widespread using of hydrogen as a fuel will help preserve the cleanliness of the environment [1-4].

One of the main problems of hydrogen energy is that hydrogen, as the main component of the process, practically does not occur in a free form in nature. Therefore, the main task of the development of hydrogen energy is searching of a method for efficiently producing hydrogen using the least expensive technology from compounds that are widely distributed in nature. The most promising method of obtaining hydrogen is the methane vapor conversion method [5]. However, this process is characterized by the presence of certain technical difficulties, namely: the process of separation of components is carried out using molecular membranes, which manufacture requires the use of nanotechnology. The hydrogen obtained in this case, depending on its method of use, is generally stored in compressed form in cylinders or is cooled with simultaneous compression to become a liquid (cryogenic storage method) [6].

Also, a major drawback of the technologies used at the moment is low conversion. Our work deals with the way to solve this problem by introducing new types of catalysts into the process. The reforming process was carried out in a steam reformer at a temperature of 700-800 °C on a block nickel-aluminum catalyst. A feature of this technology is the use as a carrier a ribbon from the alloy fekraloy. The basis of the catalyst is nickel, magnesium and aluminum oxide. The use of this carrier makes it possible to increase the conversion by 20 % relative to processes with known steam reforming catalysts.

The experiment showed that the degree of conversion with that catalyst at a temperature of 700-800 ^{o}C was 92-99 %, and the hydrogen yield per 1 kg of methane – 0.36 kg. Thus, in the course of the work, the efficiency of a tape catalyst based on nickel and aluminum with a carrier from a fecral alloy during the steam conversion of methane was established.

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PP-V-15

Nanostructured Heterogeneous Catalysts for the Selective Hydrogenation Reactions Containing no Noble Metals

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Hydrogenation of C-C multiple bonds, as well as –NO_2 functional groups are a key step in the synthesis of many important compounds. For example, the selective hydrogenation of phenylacetylene (PhA) is of great practical interest, since the major reaction product, styrene, is one of the most large-scale products in petrochemical industry [1]. Aromatic amines obtained via the catalytic reduction of corresponding nitrocompounds are widely used in the synthesis of different compounds for fine organic synthesis and pharmaceutical industry [2].The catalysts based on platinum-group metals are the most commonly used for the selective hydrogenation of nitro- and unsaturated compounds. The main drawbacks of this catalyst are the high loading of noble metal and their toxicity [3].

The development and study of the most efficient and environmentally safe catalytic systems are the topical problems of up-to-date catalysis. Therefore, the catalysts based on Fe nanoparticles attracted considerable interest in the recent years due to their availability in nature, low toxicity, and high selectivity in various processes (Fischer-Tropsch processes, catalytic dechlorination of chloroorganic compounds, hydrogenation of ketones and alkenes) [4-7]. The use of the catalysts based on Fe nanoparticles in the selective hydrogenation of acetylene compounds to ethylenes and hydrogenation of nitro-compounds to aromatic amines are especially interesting.

The first time we proposed a highly efficient supported monometallic FeOx/SiO_2 and bimetallic Fe-Cu/SiO_2 catalysts for the liquid phase hydrogenation of phenylacetylene to styrene and bimetallic Fe-Cu/SiO_2 catalysts for the selective hydrogenation of p-dinitrobenzene to p-phenylenediamine.

The 7%FeOx/SiO2 materials were prepared by incipient wetness impregnation of a silica carrier with a saturated aqueous solution of ammonium trioxalatoferrate. The impregnated samples were dried at 60 ºC in and then calcined at 250-500°C in air. The catalytic properties of FeOx/SiO2 samples were studied in the liquid phase hydrogenation of PhA in autoclave (0.13 M PhA solution in ethanol, pH2 6-20 bar, 100-150 °C, PhA:Fe = 15). The selectivity to styrene (St) depended on the PhA conversion, the variation being influenced by the calcination temperature of the samples and the reaction condition. The best selectivity reached 80% at 75% PhA conversion at 105°C and p(H2) = 13 bar for the sample calcined at 250 °C [8].

The catalytic properties of the supported bimetallic Fe-Cu catalysts depend on the method of synthesis and the conditions of thermal treatment. We studied the Fe–Cu/SiO_2

catalysts prepared by two novel procedures: deposition of Fe and Cu precursors by consecutive incipient wetness impregnation of porous silica beads with ammonium trioxalatoferrate and copper (II) nitrate solutions (CIm) and co-deposition of Fe (iron (III) nitrate) and Cu (copper (II) nitrate) precursors on the outer surface of the silica support powder using urea (CoD). The samples were dried at 80°C and then calcined at 300°C in air. The calcined samples were reduced in a H_2 flow at 300°C. The catalytic properties of Fe-Cu/SiO_2 samples were studied in the liquid phase hydrogenation of *p*-dinitrobenzene to *p*-phenylenediamine (0.08 M DNB solution in tetrahydrofuran, 0.2 g of catalyst, 150°C, pH_2 1.3 MPa). The catalysts obtained by co-deposition are more active and selective toward PhDA than catalysts obtained by impregnation. The catalysts reduced in hydrogen are less active. The best selectivity towards *p* -PhDA (89%) at complete conversion of *p*-DNB was obtained with the sample synthesized by co-deposition of metal precursors with urea, followed by calcination in air at 300 °C; the sample contains 7 wt % of iron and 3 wt % of copper [9].

The all samples were characterized by XRD, DRIFTS-CO, TEM, SEM-EDS, TPR-H_2.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-50-00126. A. Shesterkina is grateful to Haldor Topsøe A/S for financial support in the framework of Ph.D. student support programme.

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PP-V-16

Heterosubstituted Graphene Nanoflakes – Novel Supports for Co-Based Fischer-Tropsch Catalysts

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There is a growing demand for liquid hydrocarbons in the world. At the same time, the cost of oil production increases due to depletion of oil fields and the increase of cost of their exploration, development and subsequent purification of oil products. So, the alternative ways of hydrocarbon production are highly demanded. One of the main alternative approaches to the production of hydrocarbons is the Fischer-Tropsch synthesis (FTS). It is based on the catalytic hydrogenation of carbon monoxide obtained from coal, natural gas, and biomass. Iron and cobalt catalytic systems are widely used in industry in FTS. Cobalt is more expensive than iron, however, Co catalysts are more stable, less active in side reactions, and reduces the temperature of FTS. Usually Al_2O_3, SiO_2 and TiO_2 supports are used for cobalt FTS catalysts. At the same time, in last decades structured carbon supports such as carbon nanotubes, graphene, and carbon nanofibers have attracted interest from the research community. The advantages of these materials are their chemical inertness and high thermal conductivity [1].

In this work, a new type of carbon nanomaterial, graphene nanoflakes (GNFs), was studied as a support for cobalt FTS catalysts. This material contains rectangular particles with the size less than 100 nm which consist of several graphene layers [2]. The advantages of such support are its high surface area, mesoporosity and a large number of edge carbon atoms. At the same time, the surface of such carbon support requires additional functionalization for the stabilization of metal particles. In the present study, hetero-substitution of carbon atoms by nitrogen or boron ones is considered as a support surface modification method. The size of these atoms is close to that of carbon and their embedding in the graphene layers changes its electronic structure and produces defects. This leads to the better affinity of the surface to the metal particles [3].

GNFs were synthesized by pyrolysis of hexane and acetonitrile over a template consisting of nanosized magnesium oxide. The latter was prepared by dropping ammonium oxalate into magnesium nitrate. Nitrogen and boron-substituted GNFs were also produced by post-doping of oxidized unsubstituted GNFs by ammonia and boric acid. The fabricated supports were examined by SEM, TEM, and XPS. For further test in the FTS, supports were impregnated with Co nitrate solution and annealed at 400°C in an inert medium. SEM, TEM and XPS data for N-GNFs synthesized by pyrolysis technique are shown in Fig.1.

PP-V-16

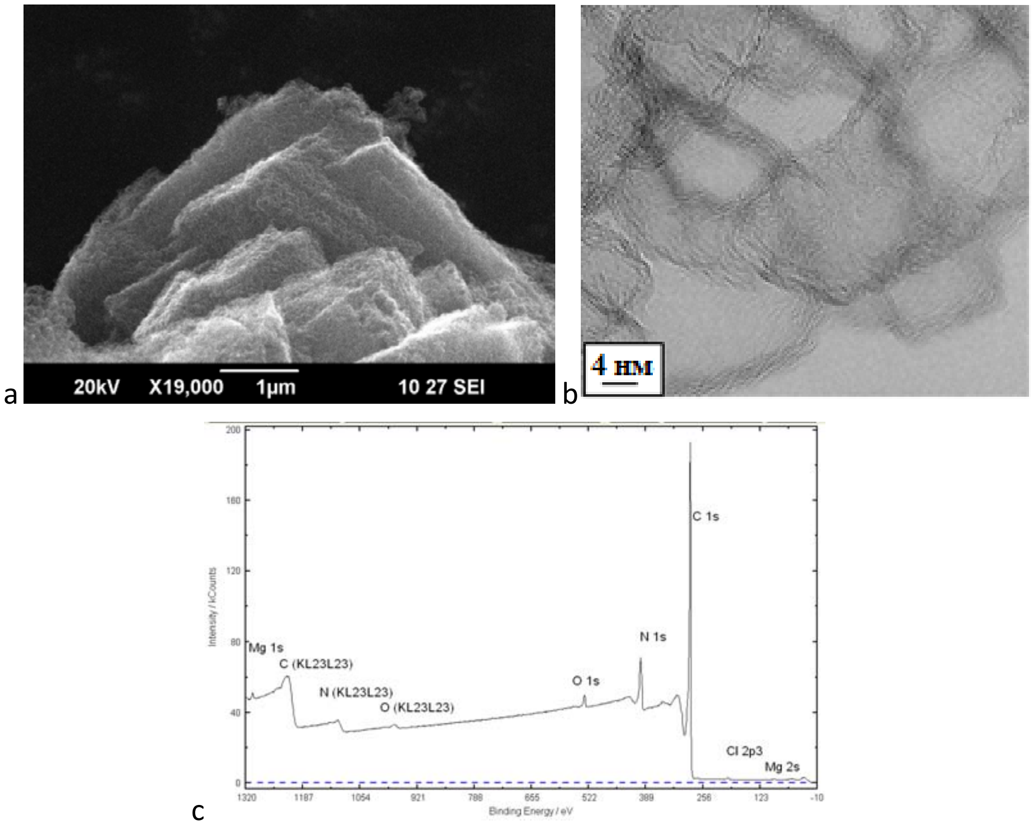

Fig. 1. SEM (a) and HRTEM (b) images and XPS survey spectrum (c) of N-doped GNFs synthesized by pyrolysis method.

Acknowledgement. The reported study was funded by RFBR according to the research project №16-29-06439.

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PP-V-17

Novel Catalysts Prepared by Pechini Technique for Low-Temperature Steam Reforming of Light Hydrocarbons

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Nowadays there is a problem of associated petroleum gas (APG) processing in Russia. APG are multicomponent gas mixtures consisting predominantly of methane and heavier hydrocarbons with smaller amounts of nitrogen and carbon dioxide. Since some oil fields are located far away from gas processing plants, an alternative way of APG utilization is necessary. Low temperature steam reforming (LTSR) of APG represents a promising method of APG conversion. Brutto-process consists of two reactions: steam reforming of C_{2+}-hydrocarbons with the formation of CO_2 and H_2 followed by CO_2 methanation:

1) $C_nH_{2n+2} + 2nH_2O \rightarrow (3n+1)H_2 + nCO_2$ (n > 1)

2) $CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O$

As a result of this process, methane content increases which leads to decrease in dew point temperature; also fuel characteristics of APG are improved which allows using the gas mixtures obtained in internal combustion engines for generating electricity directly on-site.

This work reports our new 30 wt.% NiO - 20 wt.% MO_x-Al_2O_3 (M = Mg, Cr, Ce) catalysts prepared by Pechini technique for the LTSR of model propane-methane mixture. Fig. 1 shows temperature dependencies of propane outlet concentrations (on the dry basis) in the LTSR of propane-methane mixture over catalysts prepared by Pechini technique and industrial catalysts.

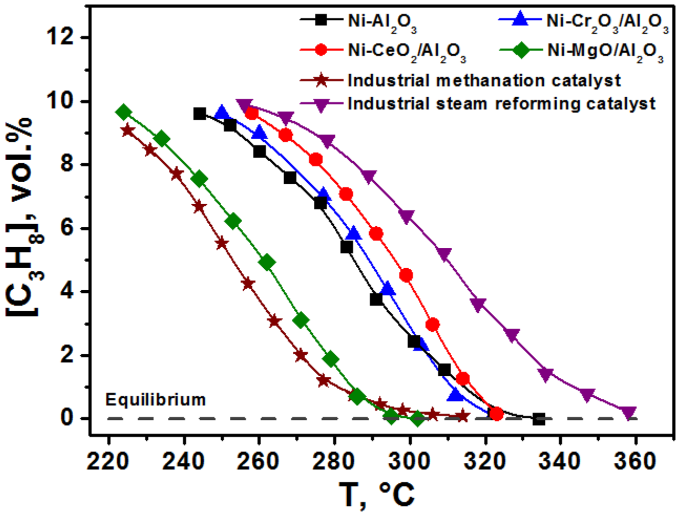

Fig. 1 Reactions conditions: 6.4 % of C_3H_8, 54.3 % of CH_4, 39.3 of H_2O. P = 1 bar, WHSV = 1500 h^{-1}.

Ni-Ce/Al_2O_3, Ni-Cr/Al_2O_3, Ni/Al_2O_3 catalysts showed similar performance being more active than the industrial reforming catalyst, but less active than Ni-Mg/Al_2O_3 and the industrial methanation catalyst. The Ni-Mg sample showed activity close to that of methanation catalyst, but contained lower amount of Ni and had higher thermal stability (reduction temperature 600 instead of 430 °C). The effect was attributed to Ni-MgO epitaxial interaction that results in higher Ni dispersity.

Acknowledgement. The reported study was funded by RFBR and Government of the Novosibirsk region according to the research project № 17-43-543136 r_mol_a (S.I. Uskov)

PP-V-18

Catalytic Selective Carbonyl Compounds Hydrogenation at Ambient Conditions

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The reactions of carbonyl compounds hydrogenation are of great interest for organic synthesis because they allow obtaining alcohols of different structures. Alcohols are used in the pharmaceutical and food industries, as well as in the chemical industry for the production of synthetic polymers, rubbers, plasticizers, solvents and substrates for organic synthesis.

Oxides such as ceria and zirconia, and ceria-zirconia mixed oxides are well known as a supports used to impart metal-support interactions to enhance catalytic performances by generation of active centres at the interface between metal and support [1].

At the present work, we have designed catalysts with a low Pt content and tested it at the hydrogenation reactions of such carbonyl compounds as cinnamaldehyde and benzaldehyde at mild conditions.

The carriers were prepared by co-precipitation method of ammonium cerium (IV) nitrate with different zirconia precursors: $ZrO(NO_3)_2$, $ZrOCl_2$ and a mix of $ZrO(NO_3)_2$ and $ZrOCl_2$; all the carriers were characterized by BET method (table 1). Pt-contained catalysts were prepared by pH-controlled precipitation method to obtain a uniform distribution of metal on the surface of the carrier.

Table 1.

Sample	CZ-N Precursor $ZrO(NO_3)_2$	CZ-Cl Precursor $ZrOCl_2$	CZ-N+Cl Precursor $ZrO(NO_3)_2 + ZrOCl_2$
S_{BET} , m^2/g	103	107	118

The obtained catalysts were tested in hydrogenation of cinnamaldehyde and benzaldehyde to cinnamyl and benzyl alcohols respectively. Selective hydrogenation of carbonyl compounds was carried out at room temperature and atmosphere pressure in a glass flask as a reactor.

In cinnamaldehyde hydrogenation the best performance showed the Pt catalyst supported on CeO2-ZrO2 mixed oxides prepared from $(NH_4)_2Ce(NO_3)_6$ and $ZrOCl_2$.

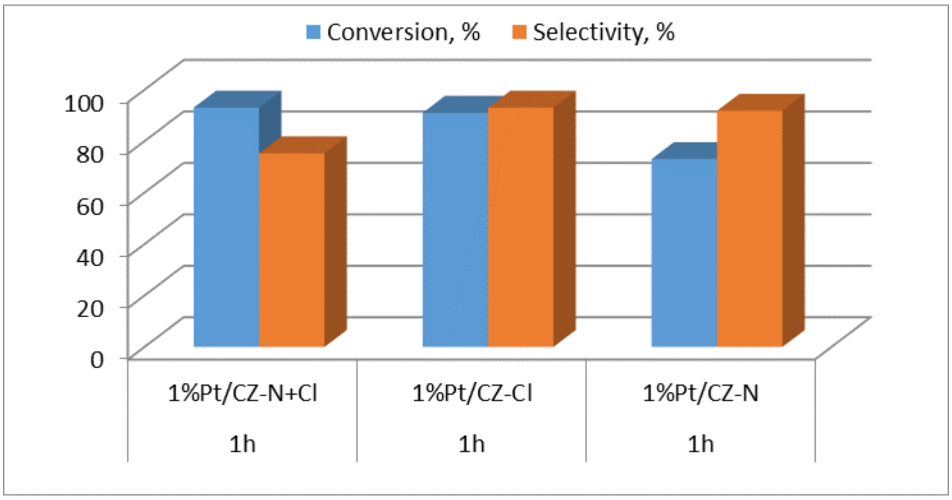

Figure 1. Cinnamaldehyde hydrogenation. Reaction conditions:
$V_{mixture}$ – 1,5 ml, C – 0.2 M, time – 1 h, m_{ct} – 50 mg, $P(H_2)$ – 1 atm, solvent – EtOH.

Catalysts with a different Pt loading were tested at hydrogenation reaction of benzaldehyde.

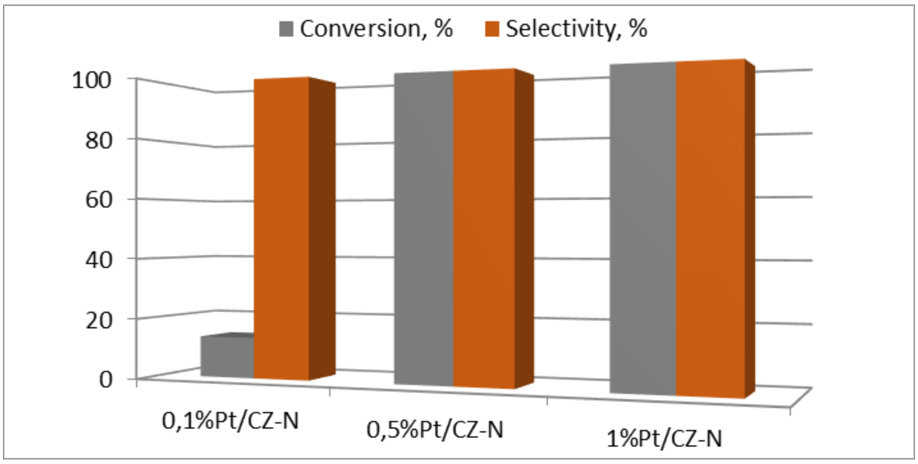

Figure 2. Benzaldehyde hydrogenation. Reaction conditions:
$V_{mixture}$ – 1,5 ml, C – 0.2 M, time – 2 h, m_{ct} – 50 mg, $P(H_2)$ – 1 atm, solvent – EtOH.

While on the catalysts with Pt content 1 and 0.5% wt. the yield of benzyl alcohol is almost quantitative, decreasing the amount of Pt to 0.1% wt. led to drop in benzaldehyde conversion.

Pt catalysts supported on ceria-zirconia mixed oxides prepared in this work showed exceptional high activity and selectivity in hydrogenation of cinnamaldehyde to the corresponding unsaturated alcohol and benzaldehyde hydrogenation to benzyl alcohol.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 17-73-20282

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PP-V-19

Thermoregulated Synthesis of Nanostructured Nickel Phosphide with a High Catalytic Activity in Hydroprocessing

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Nowadays quality of oil feedstocks decreases as well as environmental requirements to fuels become stricter. Also a tendency to use non-traditional sources of crude oil as a feedstock exists. Traditional hydroprocessing catalysts have certain disadvantages so the search for new catalysts always becomes an actual goal.

Widely used noble metal catalysts of hydrogenation processes are characterized by high price and inapplicability for feedstocks with high-sulfur content. At the same time, the activity of another class of hydrogenation catalysts, transition metal sulfides, decreases over time in low-sulfur feedstocks.

An alternative class of hydroprocessing catalysts is a number of transition metal phosphides. These catalysts are explored insufficiently and deserve more attention. It is known that metal-rich phosphides demonstrate high activity in hydrogenation and hydrotreating processes [1, 2].

Organic derivatives of phosphine and metal phosphates are often used as phosphorous source for transition metal phosphides. It is well known that organic derivatives of phosphine can be oxidized to phosphoxides by air oxygen. In order to obtain phosphides from phosphates it needs applying high temperature (600-800°C), which is difficult to carry out in a laboratory. Rarely hypophosphites of sodium and ammonium are used as phosphorous source. They are easily transformed to phosphides at low temperatures under inert or reduction conditions [2].

Nickel phosphide is one of the most active phosphides in hydroprocessing. Different types of nickel phosphide exist. The most active type is Ni_2P. It has higher activity than phosphides of other transition metals like W, Mo, Co, Fe [1, 3].

It is interesting to synthesize easily an active catalyst with good physico-chemical characteristics. In present work, thermoregulated synthesis of nickel phosphide in autoclave system has been studied. Hypophosphorous acid and sodium hypophosphite were taken as phosphorous sources. Different inorganic salts of nickel and nickel hydroxide were taken as nickel sources. The ratios of P/Ni were 2-4. One part of the process was carried out down to 100°C, another part of the process – at 350-400°C. The best yields of phosphide are obtained at pH = 7. Synthesized nickel phosphides were analyzed by a set of physico-chemical methods.

PP-V-19

Catalytic activity tests were carried out in autoclave system at 350-400°C and at initial pressure of hydrogen of 40-60 atm. Guaiacol, component of bio-oil, which obtained from biomass by fast pyrolysis, was taken as a substrate. Cyclohexane, benzene and phenol were obtained as main products. The qualitative and quantitative composition was determined by GC-FID and GC-MS analyses.

Acknowledgement: This work was supported by the Russian Foundation for Basic Research, grant 18-03-01186 A.

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PP-V-20

The Conversion of Associated Petroleum Gases in the Synthetic Fuels

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Currently, very urgent problem of rational and profitable use of natural and associated petroleum gases (APG) [1,2]. The solving of this problem is conversion of the gases into products with the high added value. The most attractive option of the APG salvaging is conversion it in liquid hydrocarbons (GTL technology). That allows to obtain the wide range of products: gasoline and diesel fuels, lubricants, olefins, solid paraffins, ceresins and other raw materials for petrochemistry.

In the Research Institute "Nanotechnology and New Materials" SRSPU (NPI) was created the monocycle, test complex of conversion of natural and associated petroleum gases (APG) into synthetic hydrocarbons by the Fischer - Tropsch method (pic. 1). The complex include stages: gas cleaning from sulfur compounds, pre-reforming, primary reforming, cooling and syngas drying, Fischer-Tropsch synthesis, separation of gases, liquid and solid products.

The complex is designed to provide monocycle extended researches and obtaining of products, working out of technological modes and researches of main interferences of process stage. Obtain the baseline data to design industrial plant. The tests of pilot batches of catalysts. The pilot complex allows modeling a gases composition, different types of conversion (steam, steam and carbon dioxide, partial oxidation). Convert it into syngas and in the synthetic hydrocarbons.

The unique reactor of gas convection reforming was developed. In it carried the heat transfer by the convection of flue gases, which is allow significantly reduce the size of the reforming stage.

Pic. 1 – The monocycle, test complex of conversion of natural and associated petroleum gases (APG) into synthetic hydrocarbons by the Fischer - Tropsch method

PP-V-20

On stage of the Fischer-Tropsch synthesis is used the monotube reactors, in which heat of reaction is removed by phase transition of water into vapor in annulus of reactor by analogy with the industrial. Size of the catalyst reactor zones varies from 10 mm to 2000 mm. To intensify the heat and increase performance FT catalyst used gas circulation, which allows the FT synthesis process is quasi-isothermal mode at high gas space velocities (> 3000 h^{-1}).

Maximum performance of pilot complex for synthetic liquid hydrocarbons is 1.5 L\day, allowable operating pressure - 6,0 MPa.

Acknowledgement. The results were obtained in association with RF ministry of education in the boundaries of state assignment for RAD. Application code №10.2980.2017/4.6, with equipment using of CUC "Nanothecnologies" SRSPU (NPI).

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PP-V-21

Catalytic System for the Oxidation of Cyclooctene to Epoxide by Molecular Oxygen

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The use of catalysts in chemical technology, as is known, contributes not only to the increase in the speed of the process, but also directs its for the formation of target products, substantially increasing their yield. The regulating function of the catalyst becomes more and more attractive in the implementation of catalytic processes in practice. The use of catalysts with a very pronounced regulating function simplifies the schemes for isolating the desired products from the reaction mixture and provides a high degree of purity, which is especially important in subsequent use, for example in pharmaceutical, polymer chemistry.

In the literature it is indicated [1,2] that as a result of direct liquid-phase initiated oxidation of cyclooctene by molecular oxygen, proceeding in the absence of a catalyst by a radical chain mechanism, in contrast to other cycloolefins and straight chain carbon olefins, an epoxide with an output up to 65 -70%.

In the present work, we used catalytic systems, which are adducts or complexes formed as a result of the interaction of a number of functionally substituted nitrogen-containing heterocycles (substituted pyridines and phthalimides) and organic compounds of d-metals (molybdenum, vanadium) for the selective oxidation of cyclooctene to epoxide and to increase the yield of the epoxide.

In order to create these catalytic systems, the influence of the nature of the used components, their molar ratio on the efficiency of subsequent use, namely, the kinetic and quantitative indices of the oxidation of cyclooctene in epoxide, was studied. As a result of detailed studies, a catalytic system was proposed, the use of which excludes the formation of a number of by-products of oxidation such as hydroperoxides and acids. As a result, the yield of the desired epoxide in the oxidation process is increased to 88%.

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PP-V-22

Ethanol Conversion over Binary Ti-W-O Catalysts

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We have previously shown that various compounds such as acetic acid, hydrogen, acetone, etc. can be produced from ethanol. The present work is devoted to the study of the effect of the composition of titanium-tungsten oxide catalysts on their activity in the reaction of the conversion of ethanol to such compounds as diethyl ether, acetic aldehyde and ethylene.

Mixed titanium-tungsten oxide catalysts of various compositions were prepared by coprecipitation from aqueous solutions of titanium chloride and ammonium tungstate. Nine catalysts were synthesized with an atomic ratio of the elements from Ti:W=1:9 to Ti:W=9:1.

The activity of synthesized catalysts was studied in a flow-through system with a tubular reactor in the temperature range 100-500°C. Etylene, acetic aldehyde and diethyl ether were the products of the conversion of ethanol over titanium-tungsten oxide catalysts. The yield and distribution of ethanol conversion products depends strongly on the atomic ratio of titanium to tungsten in the composition of the catalyst.

Provided studies have shown that the yield of acetic aldehyde with an increase in the amount of titanium in the binary titanium-tungsten oxide catalyst first increases and on the sample Ti:W=3:7 reaches its highest value equal to 49.8%. With a further increase in the titanium content of the catalyst, the yield of acetic aldehyde decreases, while on the sample Ti:W=7:3 its yield is zero and on catalysts with a higher titanium content the reaction of formation of acetic aldehyde does not proceed. The yield of ethylene with increasing titanium content in the binary catalyst composition increases. Thus, on the catalysts with rich of titanium, the formation of ethylene proceeds, while on the samples rich with tungsten the reaction of formation of acetic aldehyde proceeds. It can also be said that, at 200°C, the maximum conversion of ethanol on the samples studied reaches up to 70%.

Thus, based on the studies carried out, it can be said that titanium-tungsten oxide catalysts at low temperatures are dominated by the dehydrogenation of ethanol with the formation of diethyl ether and acetic aldehyde, while at higher temperatures the dehydration reaction predominates to form ethylene. It should also be noted that catalysts rich in titanium are active in the ethylene formation reaction, while samples rich in tungsten are active in the formation of acetic aldehyde.

PP-V-23

Ring-Opening Metathesis Polymerization of Norbornene Monomers Linked to Fullerene and 1-Phenyltetrazol-5-Ylsulfanylmethyl Fragments

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Polymers containing fullerene units offer a uniquepotential for technological applications, primarily as n-type conducting materials in bulk heterojunction (BHJ) optoelectronic devices [1, 2]. They should besufficiently stable under operating conditions andreadily soluble in organic solvents, which is importantfor the preparation of thin films.

We described the synthesis of norborene monomers containing a methanofullerene 1 and 1-phenyltetrazol-5-ylsulfanylmethyl 2 fragments (Fig. 1) [3, 4].

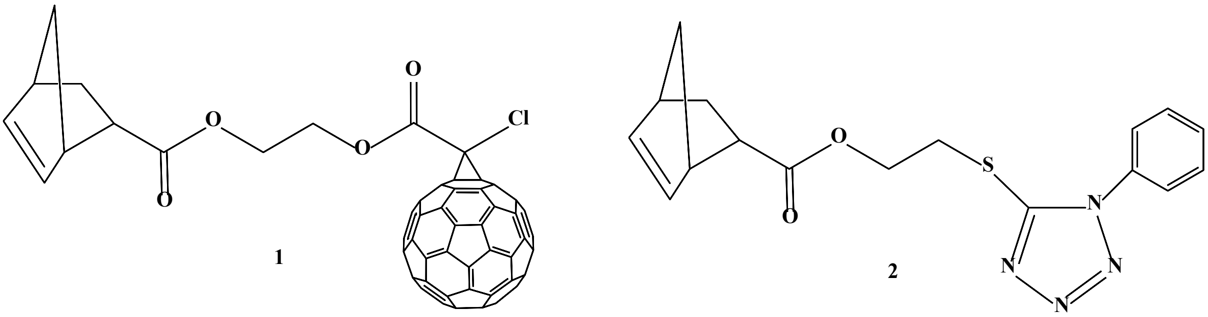
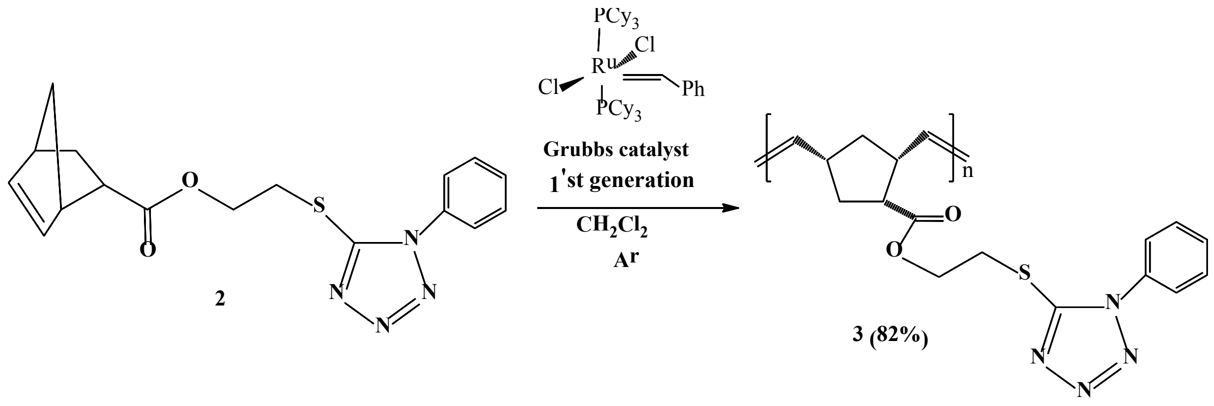


Fig. 1. Structures of norborene monomers

However, the polymer obtained from {1-chlor-1-[(2-bicyclo[2.2.1]hept-5-ene-2-yl)ethoxycarbonyl]-1,2-methano}-1,2-dihydro-C_{60}-fullerene **1** by ring-opening metathesis polymerization in the presence of first-generation Grubbs catalyst was insoluble in organic solvents (PhMe, $CHCl_3$,MeCN, etc.). A possible way of obtaining soluble polymers of the given series implied preparation of copolymers of **1** with other readily soluble monomers. For this purpose we have synthesized analogous monomer 2-[(1-phenyl-1*H*-tetrazol-5-yl)sulfanyl]ethyl(2*R**)-bicyclo[2.2.1]hept-5-ene-2-carboxylate **2**.

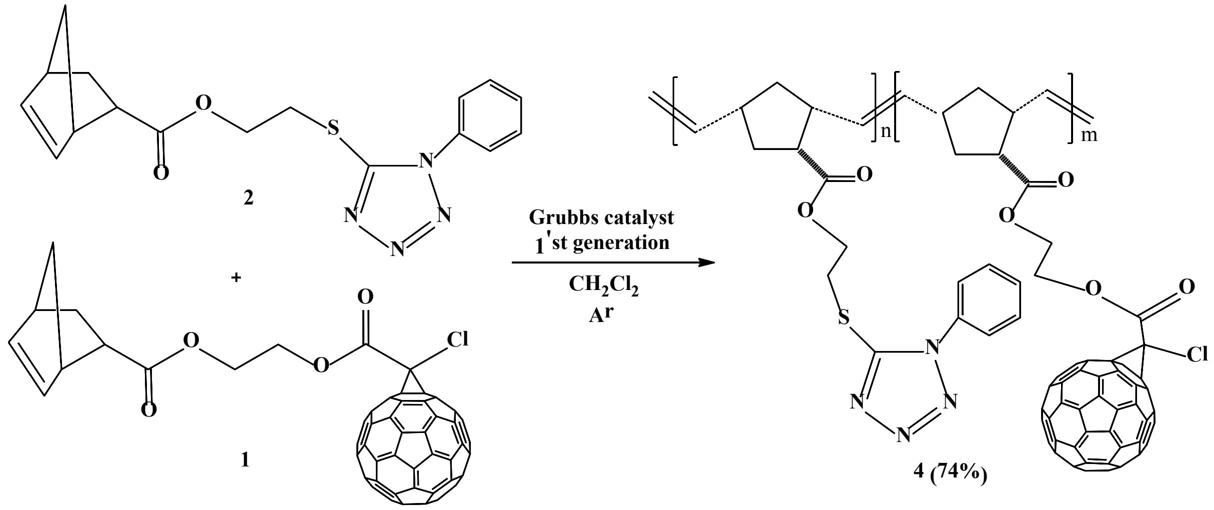
The product of gomopolymerization of **2** (polymer **3**) was a light green powder readily soluble in PhMe, *o*-dichlorobenzene and $CHCl_3$ (Scheme 1).

PP-V-23



Scheme 1

In the next step, equimolar amounts of monomers **1** and **2** were brought into copolymerization under thesame conditions as in the polymerization of **2**. We thus obtained copolymer **8** (Scheme 2) soluble in a numberof organic solvents (chloroform, methylene chloride).



Scheme 2

The number of fullerene units in **4** was determined from the intensity ratio of the SCH_2 and OCH_2 proton signals in the ^1H NMR spectrum. The fraction of monomer **1** units in polymer **4** is 30 %.

Copolymer **4** containing fullerene and phenyltetrazolylsulfanyl fragments attracts interest due to possible π-stacking interactions which could affect morphology of films prepared therefrom. Furthermore, both these fragment are capable of taking up an electron or radical species, so that copolymer **4** may berecommended as a component of *n*-type BHJ systems, inhibitors of radical oxidation processes inpolymeric materials, etc.

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PP-V-24

Studies of Pyrophosphate Catalysts for the Dehydration of Methyl Lactate

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Introduction

The growing demand for acrylic acid (AA) and its derivatives requires the development of new efficient and environmentally friendly methods for producing acrylic acid and acrylates. One of the most promising and environmentally friendly ways of their synthesis is the dehydration of lactic acid and its esters derived from renewable feedstocks. The main problem for this task area is the lack of efficient catalyst systems. At present the best results demonstrate salt catalysts, particularly phosphates of alkaline earth metals. The most stable form of catalysts phosphate is pyrophosphate, structured by silica.

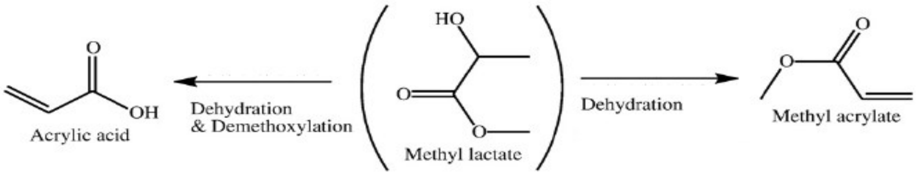
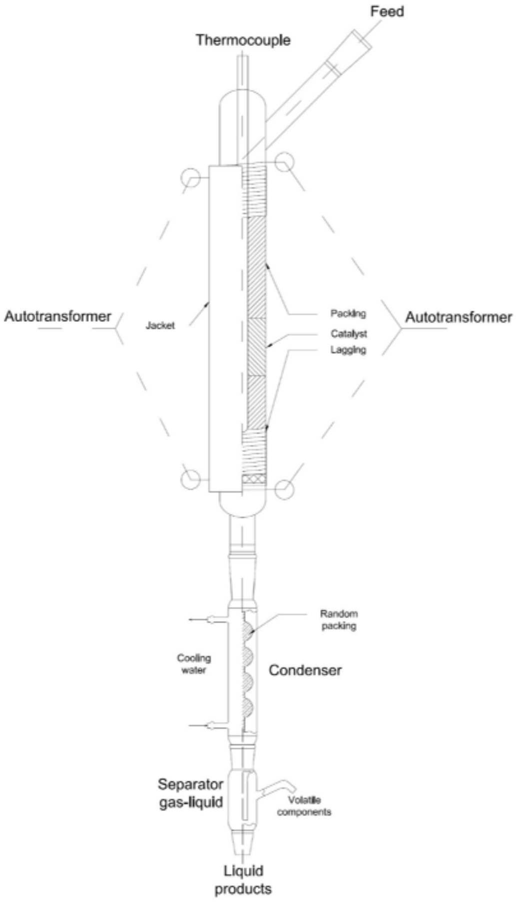


Fig. 1, The main reaction pathways and simplified reactor drawing



The aim of this work is the development of catalytic systems for the effectively process of the methyl lactate (ML) dehydration. The catalytic activity of these samples was investigated: $Ca_2P_2O_7/Mg_2P_2O_7/SiO_2$(1/1/1mol.),$Ba_2P_2O_7/Mg_2P_2O_7/SiO_2$(1/1/1mol.), $Ca_2P_2O_7/Ba_2P_2O_7/SiO_2$ (1/1/1mol.) and $Ca_2P_2O_7/ Mg_2P_2O_7/Ba_2P_2O_7/SiO_2$ (1/1/1/1mol.).

Experimental part

Investigation of the catalyst systems were carried out in a vertical tubular fixed catalyst bed reactor (5 ml volume) at atmospheric pressure in a nitrogen stream, at temperatures ranging 350-390^{0}C and with a residense time 0.5 – 1 sec, ML mixture was fed to the reactor with water in a weight ratio of 20/80. Experiment proceeds 4 hours, every hour an analysis of the reaction mixture. The product composition was determined by GC and HPLC analysis. Activity of catalysts were evaluated by ML conversion (X_{ML}, wt.%) and the selectivity to AA (S_{AA}, wt.%), which was determined by the amount of acrylic acid formed by the dehydration reaction.

After each experiment, the catalyst was regenerated by air at 480^0C for 40 min. During regeneration, all samples recovery their initial catalytic properties. This statement was confirmed by series of experiments on 1 sample on convergence of conversion and selectivity.

Results

The following table shows the best results achieved for each of the investigated catalyst system.

Sample number	Catalyst	X_{ML}, wt.%	S_{AA}, wt.%
1	**$Ba_2P_2O_7/Mg_2P_2O_7/SiO_2$**	**98.6**	**50.4**
2	$Ca_2P_2O_7/Ba_2P_2O_7/SiO_2$	24.1	25.7
3	$Ca_2P_2O_7/Mg_2P_2O_7/SiO_2$	74.5	47.9
4	$Ca_2P_2O_7/ Mg_2P_2O_7/Ba_2P_2O_7/SiO_2$	99.0	29.4

Also there is a comparison the stability of the catalyst systems at 370^oC and residense time 1 sec.

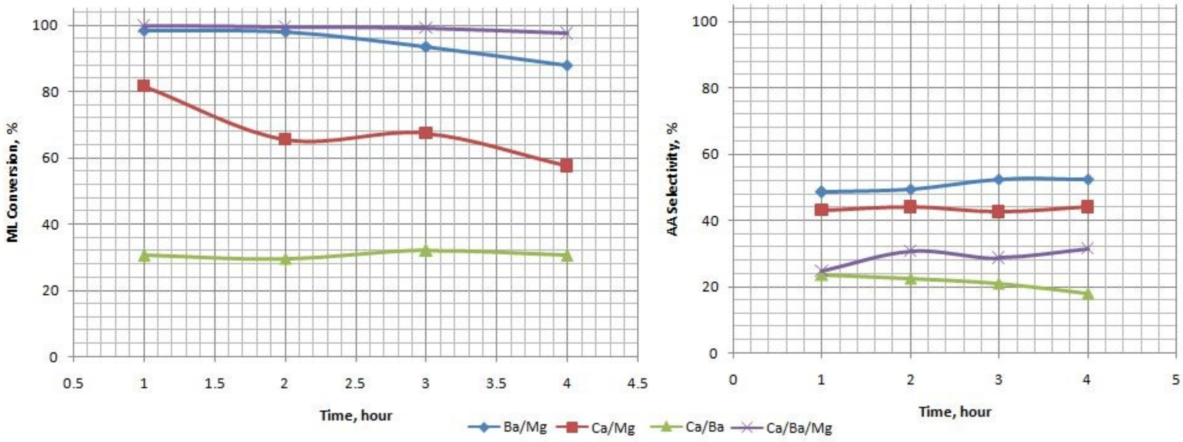


Fig. 2, The trends line of catalysts activity (1 - $Ba_2P_2O_7/Mg_2P_2O_7/SiO_2$,
1 - $Ca_2P_2O_7/Ba_2P_2O_7/SiO_2$, 2 - $Ca_2P_2O_7/Mg_2P_2O_7/SiO_2$,
4 - $Mg_2P_2O_7/Ca_2P_2O_7/Ba_2P_2O_7/SiO_2$)

The above data show that the most active, selective and stable catalyst system is Ba2P2O7/$Mg_2P_2O_7/SiO_2$ (1/1/1 mol.). Our new sample with all three types of pyrophosphates showed the same conversion but in twice lower selectivity.

Conclusions

Catalyst systems based on pyrophosphates Ca, Ba, Mg supplemented with SiO_2 were investigated. Activity of each catalyst was tested in the optimal conditions for the process of methyl lactate dehydration to acrylic acid.

PP-V-25

Morphology of Carbon Formed on the Metal Iron Subgroup from High Hydrocarbons

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In connection with the depletion of light oil reserves, the share of heavy oil coming into the processing is constantly increasing, so the volume of oil residues obtained after standard refining is growing. Improving existing and developing new technologies aimed at increasing the depth of processing of heavy oils and oil residues is a very urgent task [1].

One of the traditional methods of processing particularly heavy fractions of petroleum is carbonization. One of the directions for improving the technology of deep processing of heavy hydrocarbon oil residues by the carbonization method is the use of catalytic additives that can significantly affect the yield of light distillate fractions.

Thus, the influence of initiating additives (ferrosphere of flue ash from heat electropower station) and coal / fuel oil ratio in the feedstock on the yield of distillate fractions during the joint cracking of brown coal and fuel oil was studied in [2].

The use of catalytic additives in the thermolysis of heavy oil fractions significantly affects not only the yield of light distillate fractions, but also the quality of the resulting solid carbon materials. As is known, during the catalytic pyrolysis of light hydrocarbons, the formation of carbon nanofibers or nanotubes is possible depending on the nature of the catalysts used and the conditions for pyrolysis [3, 4].

The nature of the carbon material formed during the catalytic process should also influence the subsequent crystallization and graphitization of the resulting coke.

However, the regularities of the formation of catalytic carbon from high-molecular hydrocarbons have been studied little [5, 6]. At the same time, it can be expected that heterogeneous catalysts based on metals of the iron subgroup, which actively influence the pyrolysis of light hydrocarbons, should also be active in the pyrolysis of heavy hydrocarbons, and thereby be an instrument for controlling coking processes.

In this work, the effect of metals of the iron subgroup (Fe, Co, Ni) deposited on the mesoporous synthetic carbon support "Sibunit" on the catalytic pyrolysis of high molecular weight (hexane, undecane) hydrocarbons was studied to produce carbon nanomaterials.

The impregnation method was used to prepare NiO / Sibunit, CoO / Sibunit, Fe_2O_3 / Sibunit catalysts with different content of deposited oxides. The prepared catalysts were studied in the pyrolysis reaction of C_6-C_{11} (hexane, undecane) alkanes resulting in the formation of carbon nanofibers. It was found that the activity of catalysts in the formation of carbon from high molecular weight hydrocarbons varies in the following order: 10% NiO / Sibunit> 10% CoO / Sibunit> 10% Fe_2O_3 / Sibunit

It is established that carbon nanofibers with a diameter of 10-80 nm are deposited on the NiO / Sibunit catalysts from the vapors of high-molecular paraffin hydrocarbons. The morphology of carbon deposited on a 10% CoO / Sibunit catalyst from hexane and undecane was studied. It is established that carbon on cobalt is deposited in the form of two morphological forms: 1 - carbon nanotubes, 2 - carbon nanofibers with a stacked structure. The decisive effect on the morphology of the carbon formed is the size of the metallic cobalt particles.

It was established that carbon on the catalyst 10% Fe_2O_3 / Sibunit from hexane and undecane is deposited in the form of carbon nanotubes or nanofibers. At the same time, the diameter of carbon nanofibers exceeds the diameter of nanotubes. Particles of iron carbide are responsible for the formation of carbon nanofibers with a large diameter, and metallic iron is responsible for thinner carbon nanotubes.

Thus, it can be expected that the introduction of highly dispersed metal catalysts in the composition of heavy oil residues during the delayed coking process will make it possible to influence the formation of highly structured carbon materials. This will allow obtaining petroleum coke with new physical and chemical properties.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 17-73-30032.

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PP-V-26

Using Superacid Catalysts for Obtaining Olefins

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The goal of research was to study the superacid zeolite-containing catalyst of the pentasil structure by the example of a process for converting methanol to lower olefins over a wide range of temperatures.

Methanol, as an intermediate product, is formed in the processes of carbon dioxide, steam and oxygen conversion of methane during chemical processing of natural gas to produce C2 + hydrocarbons.

Subsequently, from methanol, olefins or a high-octane component of gasoline are produced. Depending on the conditions of the reactions, it is possible to regulate the ratio of products. The advantage of this process is that methanol production is one of the most widely known and used technologies in modern petrochemistry [1].

In the MTO process (methanol to olephins), it is advisable to use the zeolite of the SAPO structure, since it promotes high selectivity in the formation of light olefins and almost complete methanol conversion [2-4].

Due to its pore diameter 5.5 - 6 Å, zeolites of the pentasil typ ZSM-5 have increased stability to coke formation, but low selectivity in the direction of C2-C4 olefins [5, 6]. That’s why ZSM-5 is mainly used in the production of heavier hydrocarbons.

In carrying out the study, a zeolite of the pentasil ZSM-5 type structure was used as a catalyst. The experiments were carried out at a pressure in the reactor of 2,0 MPa, in the temperature range 230-270 °C, the volumetric flow rate was 1 h^{-1}.

It was found that, in the temperature range 230-250 °C, methanol conversion reaches a maximum at 250 °C, a further increase in temperature reduces the conversion from 25,14 to 20,63 % by weight at 250 and 270 °C, respectively.

At the same time, as the temperature rises, the content of C3-C5 hydrocarbons increases due to the intensification of cracking reactions and compaction products. At temperatures above 250 °C, the probability of obtaining propoxy, butoxy, pentoxy groups formed by methylation of the next lower term increases. At reaction temperatures of 230 – 240 °C, the gas composition is unstable. This is due to the low activity of the acid sites of the catalyst under the given conditions.

The maximum yield of ethylene was observed after 12 hours of the experiment at a temperature of 250 °C. With an increase in the experiment time, the ethylene yield decreased, which is due to the partial deactivation of the catalyst due to the blocking of active sites by the products of compaction (coke).

As result of researches it was proved that the use of zeolite of the pentasil type ZSM-5 structure in the process of conversion of methanol to lower olefins is effective. Besides, optimal parameters for the process were found: temperatures of 250-260 °C and a pressure of 20 atm. The maximum conversion values of methanol, ethylene content and yield at these parameters were 25,15; 85,10 and 17,85 % by weight, respectively.

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PP-V-27

New Heterogeneous Catalyst for Tandem Processes Based on Hydroformylation Reaction

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Some reactions of organic synthesis can be coupled in tandem processes based on hydroformylation reaction. Advantage of these processes is the possibility for obtaining compounds of different classes bypassing stages of isolation and purification of intermediates. In our work we have synthesized a new heterogeneous Rh-containing catalyst and investigated it in tandem hydroformylation-acetalization (HA) and hydroaminomethylation (HAM) processes. We used the silica polyamine composite **BP-1** as a solid support for catalyst designing [1,2]. It is a hybrid material containing inorganic and organic structures, where poly(allylamine) chains were anchored on an amorphous silica gel surface. This material combines high density of functional groups and rigidity of silica gel matrix. In the first step NH_2-groups of **BP-1** were treated with **4-DPPBA** (4-diphenylphosphinebenzoic acid) in the presence of diisopropylcarbodiimide (DIC) as activator in CH_2Cl_2, yielding the modified support **P-1**. Next, Rh(acac)$(CO)_2$ was added and after washing and drying catalyst **K-1** was produced (fig. 1).

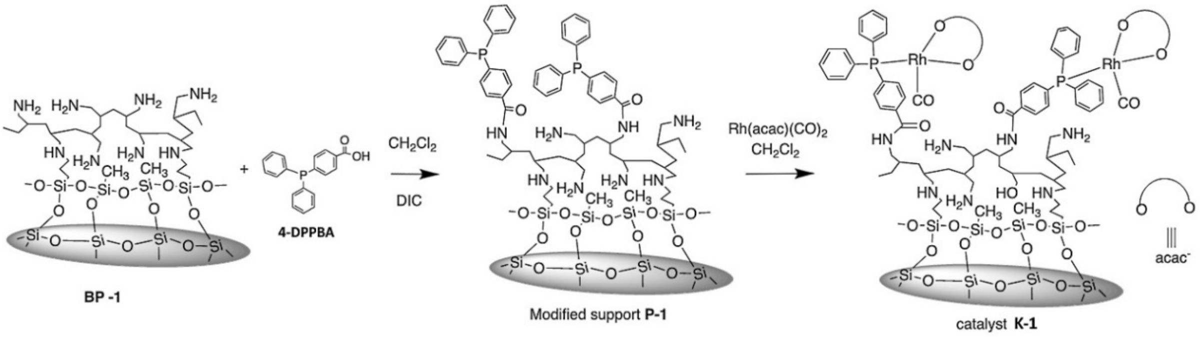


Figure 1. Synthesis of **K-1**

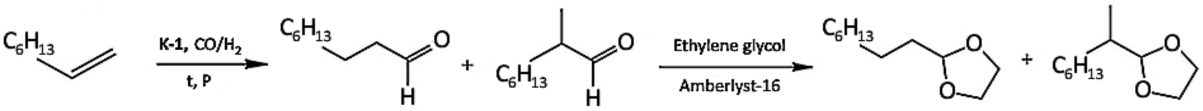
Catalyst was characterized by solid-state NMR spectroscopy, IR spectroscopy, XPS, TEM, and elemental analysis. Rhodium has been determined in state of Rh^{+1}, included in phosphine complex and rounded with CO and acetylacetonate ligands.

In catalytic experiments we used octene-1 as a long-chained substrate. Firstly, we showed activity and stability of **K-1** in hydroformylation reaction under different conditions, applicable for HA and HAM reactions. Results are presented in table 1.

Table 1. Octene-1 hydroformylation on **K-1**

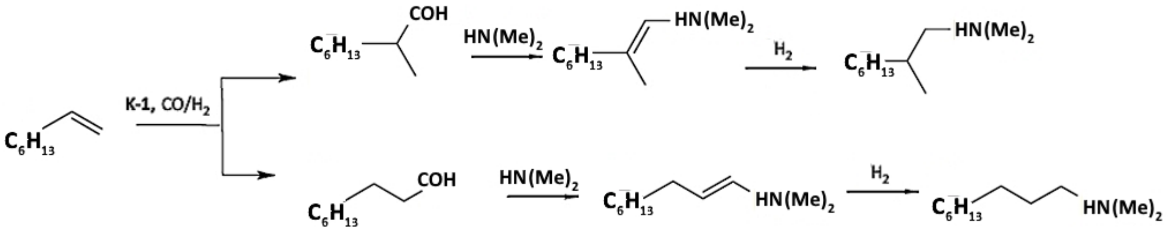
Run	Solvent	T,°C	$P_{syngas\ (1:1)}$, MPa	Time, h	Octene conversion, %	Aldehydes yield, %	n/iso
1	Toluene	80	4	5	99	99	2
2					99	65	2
3					98	64	2
1	DMFA	120	4	5	84	65	2,5

Tandem hydroformylation-acetalization reaction is a perspective route for cyclic acetals obtaining. Acetals can be applied as motor fuels components, surfactants, smelling compounds, as synthons for alcoxyalcohols producing, in agrochemisty, ect.



Acid co-catalysts for the second stage proceeding are required. We tested solid acid Amberlyst-16 as an acid component in catalytic system together with **K-1**, so, we proposed completely heterogeneous catalytic system, which has shown high activity in tandem reaction, using octene-1 and ethylene glycol as substrates. Total acetals yield was 95% in the first run and 65% in others, reaction time was 5 hours and it occurred at 80°C and under 4.0 MPa syngas (1:1) pressure. Catalytic system can be easily separated from products and used in 5 re-runs without loss of activity.

HAM reaction can be also catalyzed by **K-1**. Octene-1 was converted into amines with 57% total yield, when as a source of amines 25% DMA/DMFA solution has been used. The reaction proceeded at 120°C under 4.0 MPa syngas (1:1) pressure.



Thus, Rh-containing heterogeneous catalyst **K-1** performed ability to be applicable in oxo-processes in different variants.

Acknowledgement. This work was supported by the Russian Federation Basic Research Agency (RFBR), research project No. 17-03-00464 a.

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PP-V-28

Epoxidation of Fatty Acid Methyl Esters with Hydrogen Peroxide in the Presence of TS-1 Catalyst

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Epoxidized vegetable oils (EVOs) have drawn much attention in recent years in the chemical industry, since they are environmentally friendly, biodegradable, renewable, highly available and non-toxic. Nowadays, the largest proportion of EVOs in the industrial sector is used for producing polyvinyl chloride (PVC) stabilizers. EVOs are currently produced in industry by a homogeneous catalytic conventional epoxidation process, in which the unsaturated oils are converted with percarboxylic acids. In our opinion, epoxidized fatty acid methyl esters can be a promising substitute for EVOs because the starting materials for their production have a lower viscosity and higher reactivity [1]. Moreover, the use of green hydrogen peroxide (H_2O_2) as an oxidant in combination with heterogeneous catalysts is one of the most promising routes to eliminate the percarboxylic acids drawbacks [2].

Nowadays, Ti-based catalysts are the most effective systems for the liquid-phase oxidation of various organic substrates with H_2O_2. Among these catalytic systems, a special place is occupied by TS-1 catalyst, which is considered to be the best oxidation catalyst [1].

We investigated the heterogeneous liquid-phase epoxidation of fatty acid methyl esters (FAMEs) with H_2O_2 over TS-1 catalyst. The FAMEs obtained by transesterification of rapeseed oil were used as a substrate. The main unsaturated compounds in FAMEs are methyl oleate (57.3 wt%), methyl linoleate (24.6 wt%) and methyl linolenate (7.9 wt%). In this work, the solvent nature, temperature, FAMEs/H_2O_2 molar ratio and catalyst concentration influencing on the FAMEs conversion and epoxide selectivity were considered. All experimental results are listed in Table 1. Conversion and selectivity values are given after 6 h.

The solvent nature has a significant effect on the epoxidation of organic substrates with H_2O_2 over TS-1 catalyst. So, it has been reported that the protic solvents (*e.g.* methanol) have a positive effect on the reactivity of TS-1 in the epoxidation of propylene [3]. In contrast, the activity of TS-1 in the epoxidation of FAMEs is lower in protic solvents than aprotic-polar solvents (Table 1). This might be an indication that the reaction does not occur inside the micropores of the TS-1 catalyst, but at the external surface where the solvent effect might be different [4].The FAMEs conversion in aprotic-polar solvents falls in the following order: acetone > ethyl acetate > acetonitrile. However, the epoxide selectivity in ethyl acetate and acetone was significantly lower than in acetonitrile due to acid catalyzed hydrolysis of reaction product [4].

The conversion of FAMEs increases with increasing the temperature. The epoxide selectivity is only slightly affected by temperature up to 333 K, but is lower at 343 K. This phenomenon can be explained by formation of cleavage products at higher temperature. For further investigations, the temperature was kept at 323 K.

The conversion of FAMEs increases linearly with increasing the catalyst concentration in the reaction mixture. Moreover, by increasing the concentration of TS-1 in the reaction mixture from 7.8 to 31.0 g·L^{-1}, it was possible to slightly increase the epoxide selectivity. However, the use of a large amount of TS-1 catalyst can lead to an increase in the cost of FAMEs production. Therefore, the most appropriate catalyst concentration is 15.5 g·L^{-1}.

As can be seen from Table 1, the FAMEs conversion increases with increasing the FAMEs/H_2O_2 molar ratio. However, the FAMEs/H_2O_2 molar ratio does not significantly affect on the epoxide selectivity. In our opinion, the use of a large excess of H_2O_2 is impractical, since this leads to its inefficient decomposition into O_2 and H_2O. Therefore, the optimum FAMEs/H_2O_2 molar ratio is 1/2.

Thus, the epoxidation of FAMEs with H_2O_2 over TS-1 catalyst provides an attractive route to produce PVC stabilizers. This method allows to obtain epoxidized FAMEs with a high yield.

Table 1. Influence of various factors on the FAMEs epoxidation of with H_2O_2 over TS-1

T, K	Solvent	Concentration of catalyst, g·L^{-1}	FAMEs/H_2O_2 molar ratio	FAMEs conversion, %	Epoxide selectivity, %
323	Methanol	15.5	1/8	20.22	19.03
323	Ethanol	15.5	1/8	17.57	39.27
323	1-Pentanol	15.5	1/8	11.22	40.89
323	Acetone	15.5	1/8	85.12	30.37
323	Ethyl acetate	15.5	1/8	77.84	44.69
323	Acetonitrile	15.5	1/8	76.70	61.35
313	Acetonitrile	15.5	1/8	55.39	56.22
333	Acetonitrile	15.5	1/8	93.05	54.66
323	Acetonitrile	3.9	1/8	46.92	49.57
323	Acetonitrile	7.8	1/8	58.39	61.75
323	Acetonitrile	31.0	1/8	96.22	63.30
343	Acetonitrile	15.5	1/8	98.33	46.36
323	Acetonitrile	15.5	1/4	74.16	65.58
323	Acetonitrile	15.5	1/2	64.28	64.50

Acknowledgement. This work was supported within the framework of the Program of development of Flagship University of Russia for Nizhny Novgorod State Technical University n.a. R.E. Alekseev.

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PP-V-29

Catalytic Method for the Synthesis of 2,7-*bis*-Aryl-Substituted 4,9-Dimethyl-2,3a,5a,7,8a,10a-Hexaazaperhydropyrenes

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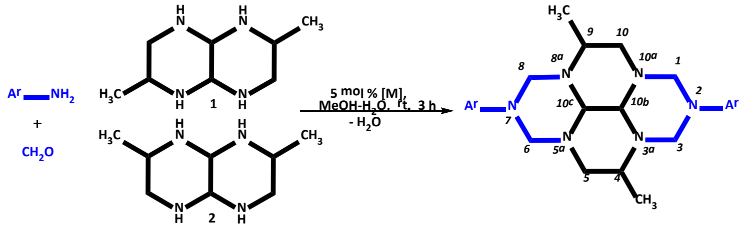
Interest in the synthesis of annelated polyazapolycycles is generated by the possibility of their use as candidate compounds for the development of drugs with antimicrobial, analgesic and cytostatic properties. In continuation of our investigations [1] into the catalytic synthesis of different polycyclic compounds, and also with the aim of developing an effective method for the synthesis of hexaazapolycycles with pharmacologically significant substituents that are previously undescribed and promising for practical application, we have studied the possibility of the one-pot preparation of 2,7-*bis*-aryl-substituted 4,9(10)-dimethyl-2,3a,5a,7,8a,10a-hexaazaperhydropyrenes by multicomponent condensation of aromatic amines with formaldehyde and isomeric mixture of 2,6(7)-dimethyl-1,4,5,8-tetraazadecalins (**1**, **2**). It has been shown that under the optimized reaction conditions (5 mol% [M], MeOH-H_2O, 20 °C, 3 h), pharmacologically significant aromatic amines (2- and 4-aminophenols, 2- and 4-aminobenzoic acids, 4- and 5-aminosalicylic acids) reacted with formaldehyde and 2,6(7)-dimethyl-1,4,5,8-tetraazadecalins to selectively produce 2,7-*bis*-aryl-substituted 4,9-dimethyl-2,3a,5a,7,8a,10a-hexaazaperhydropyrenes **3** in 82-95% yield. Among the catalysts tested, the catalytic activity of $YbCl_3{\cdot}6H_2O$ proved to be the highest. In the absence of a catalyst the yield of heterocycles did not exceed 25%.



3, 82–95 %

The assignment of the signals in the spectra of novel 2,7-*bis*-aryl-substituted 4,9-dimethyl-2,3a,5a,7,8a,10a-hexaazaperhydropyrenes **3** was carried out based on two-dimensional homo- (COSY, NOESY) and heteronuclear (HSQC, HMBC) NMR experiments. Molecular peaks in the positive ion mode MALDI TOF/TOF mass spectra confirm the proposed structures.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 16-29-10687.

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PP-V-30

Bifunctional Pd-Catalyst Based on Mesoporous Aromatic Frameworks for Guerbet Reaction

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In the recent twenty years, new catalysts based on transition metal nanoparticles seem to be the most promising for many important processes in organic synthesis and petrochemistry due to their outstanding properties. Their incredibly high specific surface area allows to compare them with homogeneous catalysts, but at the same time, nanoparticles are much more stable and also can be easily regenerated and reused.

Unfortunately, nanoparticles are prone to aggregation, which leads to the growth of particles and, consequently, to the decrease of the total surface area and to the reduction of catalytic activity. The main paths to solve this problem are the stabilization of particles by organic ligands or ionic liquids and their immobilization in pores of heterogeneous supports or organic polymers, for example, porous aromatic frameworks (PAFs).

PAFs are the organic analogues of molecular sieves. Their main advantages are high surface area, thermal and chemical stability, simple functionalization and regular rigid structure. Moreover, the structure of PAF can influence the shapes and sizes of nanoparticles formed in its pores, the selectivity of process and catalytic behavior of active centers. [1]

Originally, the Guerbet reaction is a condensation reaction of two alcohols to the final "Guerbet" alcohol, but nowadays this reaction seems to be a powerful tool for catalytic upgrading of ethanol and other alcohols to provide higher molecular weight molecules. By using acetaldehyde alcohol dehydrogenation and aldol condensation can be separated to provide a more selective process. [2]

In this work, we studied three catalytic systems for the Guerbet reaction: Pd–PAF-20-SO_3H PAF-20-SO_3H, and Pd–PAF-20 + PAF-20-SO_3H. The last two systems did not show any catalytic activity in this reaction, that is why we concentrated our efforts on the first one. Pd – PAF-20-SO_3H is a catalyst based on nanoparticles of Pd, immobilized in pores of PAF, modified with sulfonic groups. We examined its activity in the reaction of acetaldehyde and ethanol and in the conversion of acetaldehyde in different solvents under different pressures. The results are presented below in the Table 1.

PP-V-30

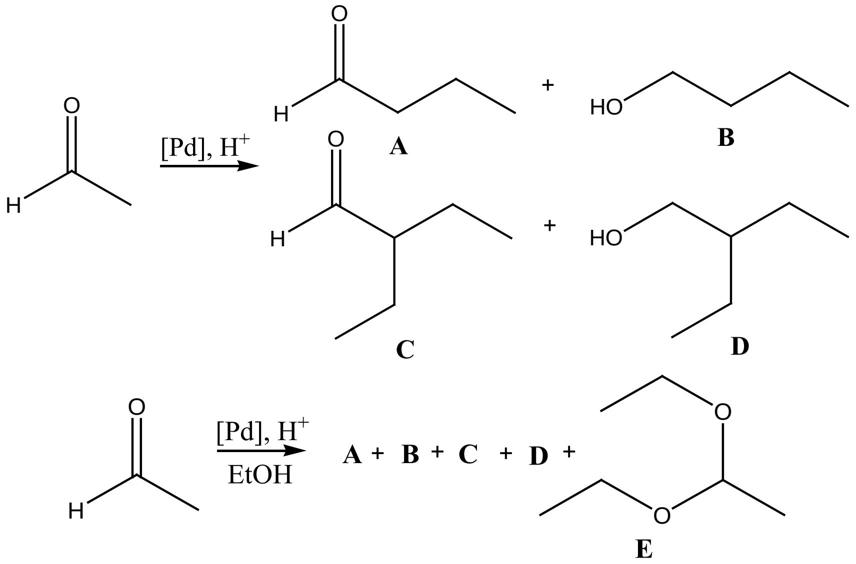

Table 1. Catalytic conversion of acetaldehyde over PAF-based Pd catalyst

№	*Solvent*	*P (MPa)*	*Products*	*Yield, %*	
				C_4	*C_6*
1	Hexane	2, H_2	A - D	5	8
2	Ethanol	2, H_2	A - E	9	13
3	Nonane	2, H_2	A - D	2	6
4	Dioxane	2, H_2	None	–	–
5	Hexadecane	2, H_2	None	–	–
6	Tetralin	None	None	–	–
7	Hexane	0.2, H_2	A - D	4	11
8	Ethanol	0.2, H_2	A - E	16	21
9	Hexane	None	None	–	–
10	Ethanol	None	A - E	26	17

Reaction conditions: acetaldehyde (0.1 ml, 1.8 mmol), solvent (1.6 ml), catalyst (10 mg, 5% mass. Pd), substrate:Pd = 360:1, 80 °C, 2h.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 18- 33-00556

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PP-V-31

Hydrogenation of Model Compounds via Water Gas Shift Using Dispersed Unsupported Ni/Mo Sulfide Catalysts

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Nowadays, the poor-quality petroleum feedstocks characterized by high viscosity and heteroatomic compounds content are involved in refining processes. Thus, in order to satisfy environmental restrictions, the deeper hydrotreatment is necessary. For this purpose, more active and efficient catalysts should be developed[1].

Conventional catalysts used in hydrotreating processes are Mo- or W-based catalysts promoted by Ni or Co supported on γ-Al_2O_3, amorphous aluminosilicates or zeolites. In refinery process involving heavy oil feedstocks dispersed unsupported catalysts are more perspective, than supported ones. Compared with lasts, highly dispersed unsupported catalysts suspended in heavy oil are more resistance to deactivation. The main advantages of these catalysts are excluding of pore blocking process and exception of diffusion limitations. Besides, unsupported catalysts have a high content of highly dispersed active sites, provided by large size reactant molecules. Thus, using of dispersed unsupported sulfide catalysts formed in situ by decomposition of oil/water soluble metal precursors allows obtaining a good interfacial contact with substrates. While unsupported Ni(Co)Mo(W) sulfide catalysts have been often used as model catalysts for hydrotreating reactions, their high activities could become more attractive for commercial applications[2]. At the same time Ni(Co)Mo-based catalysts are active in water gas shift reaction over a wide temperature range. Thus, the H_2O/CO system could be an alternative source of hydrogen for hydrotreating processes[3].

In this work the activity of dispersed unsupported Ni/Mo sulfide catalysts formed in situ by decomposition of oil soluble metal precursors in hydrogenation of aromatic (2-methylnaphthalene, tetralin, anthracene), sulfur (dibenzothiophene) compounds and their mixtures was investigated.

The experiments were performed at the temperature range of 340-380°C using in situ H_2, formed through a WGS in CO/H_2O system.

It was shown, that unsupported Ni/Mo sulfide catalysts are active in WGS and provide hydrogenation of aromatic compounds under in situ generated H_2.

The influence of CO pressure, CO/H_2O ratio, weighted water content on activity and selectivity of the catalysts were established.

The reported study was funded by RFBR according to the research project № 18-38-00593.

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PP-V-32

Heterogeneous Catalytic Synthesis of Biological Active Molecules Based on Cycloacetals and Gem-Dichlorocyclopropane

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We combined cycloacetal and gem-dichlorocyclopropane fragments in different molecules and measured their biological activity. For this reason we used haloid methyl-, oxymethyl-, aminomethyl- and vinyl-, carbo- and heterocycles that mention above.

We obtained ethers and esters, amines, amides, urethanes and ureas and other polyfunctional molecules, which contain each or both carbo- and heterocycles, by well-known synthetic methods.

We widely used heterogeneous catalysts mainly zeolites, distinct from each other with pore size and acidity, for the transformation and functionalization of cyclic acetals and gem-dichlorocyclopropanes. In particular, low-temperature catalytic isomerization of vinyl-gem-dichlorocyclopropanes to gem-dichlorocyclopentenes was carried out.

The cleavage of substituted cyclic acetals to the corresponding diols is successfully realized. The catalytic condensation of alcohols containing carbo- and heterocyclic groups with unsaturated compounds in high yields leads to the corresponding ethers.

In advance it was shown that cycloacetal fragment facilitates combination with polar biopolymers whereas gem-dichlorocyclopropane fragment function force toxic characteristic.

The different group of compounds were obtained and tested both in vitro and in vivo. So we found among them the high effective substances with antioxidant, antibacterial, antiviral properties.

These results substantiate good perspectives for obtaining of new pharmaceuticals by use this way.

Acknowledgement. This work was supported by the Russian Science Foundation (grant no. 15–13–10034).

PP-V-33

Investigation of Decationization, Dealumination and Ional Exchange Methods in Modification of Zeolite Y

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The structure of the zeolite catalyst is formed from internal cavities, which determine the diffusion of organic compounds in the volume of the catalyst. Particularly important are the size and shape of the catalyst particles, the lattice part of the zeolite and the cationic composition. These factors depend on a large extent on the methods of forming the catalyst.

A zeolite lattice module is of great importance when using a zeolite-based catalyst. Ultrastabilization, or enhancement of the lattice modulus, is achieved by dealumination of the zeolite, which can occur under the influence of certain technological methods: isomorphic substitution of aluminum atoms by silicon atoms or, for example, thermocouple dealumination [1].

According to existing studies, it is known that catalysts based on zeolite Y, modified with calcium cations, rare earth elements (RE^{3+}) and ammonium, have the best activity, selectivity, productivity and stability in the alkylation process [2].

Synthetic and post-synthetic methods of modification include:

- Decationization - gradual replacement of Na + cations on the H + zeolite by ion exchange with ammonium ions and subsequent calcination;
- dealumination - removal of aluminum atoms from the zeolite lattice under the influence of water vapor at high temperatures;
- ion exchange - replacement of a part of acid sites by metal cations [3,4].

In this study, experiments have been conducted on the modification of Y zeolites by decationation, dealumination, ion exchange for calcium, lanthanum and ammonium cations, and the properties of the resulting catalysts have been studied.

As initial product were used:

- sodium form of zeolite Y with the ratio SiO_2/Al_2O_3 = 5.0 – 5.2, Na_2O content 13.1 – 13.3 %;

- low alkaline high-silica zeolite Y with a ratio of SiO_2/Al_2O_3 = 9.1, a Na_2O content of 1.99 % by weight.

Analysis of the obtained samples showed that calcination of zeolites negatively affects the degree of crystallinity of the samples, which decreases from 100 % to 70 %. The number of aluminum atoms in the lattice decreases from 55 to 35 – 36, which leads to an increase in SiO_2/Al_2O_3 from 4.5 to 8.4 – 8.8.

Thermocouple processing of the samples leads to an even greater dealumination of the zeolite structure.

Ion exchange for lanthanum cations allows the introduction of more than 10 % by weight of La_2O_3 into zeolites.

The obtained samples have a high crystallinity. Significant dealumination of the zeolite structure as a result of the exchange for lanthanum cations is not observed, as evidenced by approximately equal values of the unit cell parameter. There is no escape of aluminum atoms from the structure, even despite numerous intermediate heat treatments of the samples. This result is due to the stabilization of the zeolite framework as a result of the entry of lanthanum cations into the cells and the cavity of the aluminosilicate structure.

The decrease in crystallinity and the growth of the silicate modulus of the samples as a result of the modification are due to the insufficient stabilization of the zeolite structure by the lanthanum cations due to their low concentration (La_2O_3 content - 3.8 % by weight). Further modification of lanthanum cations does not affect the degree of crystallinity and the unit cell parameter of the zeolite, which is due to the stabilization of the structure by lanthanum cations.

Ion exchanges for calcium and lanthanum cations, conducted at 80 and 180 ^oC, do not lead to significant changes in the phase composition of the zeolite products. In all cases, the degree of crystallinity decreases insignificantly - from 100 to 70-95 %, and the value of SiO_2/Al_2O_3 takes values in the range from 4.1 to 5.0.

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Catalytic Hydrotreatment of Lignin Using 5%Pd/C with Biofuel Components Obtaining

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Introduction

Due to the rapid consumption of available oil reserves, one of the main priorities of the 21st century is to find new resources to obtain fuel and chemicals. In this context the most appropriate choice is biomass - an abundant and renewable resource. Lignin is the second most abundant natural polymer after cellulose. [1] Approximately 70 million tons of kraft lignin (KL) is formed annually as a byproduct of the paper industry as a "black liquor." Lignin is considered as a low energy fuel, as it has a high oxygen content. KL comprising sulfur from cellulose pulping process, is more unsuitable as a fuel. One purpose of hydrotreating is to reduce the content of oxygen and sulfur in lignin and further to process it into the fuel. The catalysts used in the process for the depolymerization of lignin in order to obtain high conversion and to suppress side condensation reactions. In many cases, catalysts are involved in the selective cleavage of bonds, thereby increasing the yield of the specific compounds or types of compounds [2]. Application of the hydrotreating catalysts of lignin increases product yield and promotes hydrodeoxygenation [3]. Typically studied hydrogenation catalysts are usually composed of transition metals (e.g., cobalt, nickel and molybdenum) or noble metals (eg palladium) [4].

Materials and Methods

This paper presents the results of the study of Kraft lignin hydrotreating process, (alkali lignin, Sigma-Aldrich, USA) using 5%Pd/C. The process was conducted in a six-cell reactor Parr Series 5000 Multiple Reactor System for 4 hours in a hydrogen atmosphere under the following conditions: substrate weight - 1.0 g catalyst weight - 0.1 g, the temperature range of 200 - 300 ° C, a hydrogen partial pressure - 1 MPa , the volume of solvent - 30 ml. Also polar solvents were used: 2-propanol, water and ethanol [5]. Substrate conversion was calculated at the end of the reaction, based on the difference between the initial mass and the mass of the substrate dryness. Sampling in all experiments was performed every 30 minutes. Analysis of samples was carried out using GC-2010 chromatograph and mass spectrometer GCMS-QP2010S (Shimadzu, Japan). The catalyst was investigated using the following physico-chemical methods: X-ray photoelectron spectroscopy, infrared spectroscopy, infrared spectroscopy of diffuse reflection of the adsorption of CO (DRIEFT), transmission electron microscopy, thermal gravimetric analysis, differential scanning calorimetry, the low-temperature nitrogen adsorption.

Results and Discussion

The mathematical modeling of 3d sublevel of palladium shown that the palladium is contained in the sample mostly in the form of Pd (0). Also the catalyst has a mesoporous structure with an average pore diameter of about 4.5 nm. The palladium content on the surface is 1.6% (at.). The calculated data on the surface of palladium suggest that the samples palladium concentrated not on the surface but in the volume of the catalyst.

Among the products obtained during hydrotreating of lignin the most promising for fuels are aromatic hydrocarbons (benzene, toluene, cyclohexane), and also phenolic compounds which can be used as additives to conventional fuels and fuels derived from biomass. Furthermore, a number of cyclic and aromatic hydrocarbons, can also be used in various fields of fine chemicals as solvents and reagents. Maximum feedstock conversion was achieved at 300 °C (98%). Maximum selectivity to phenol was achieved at 250 °C (68% selectivity at 90% conversion). The optimal solvent is 2-propanol.

Significance

Pd/C catalyst demonstrate high conversion of substrate and also high selectivity to aromatic hydrocarbons, and phenolic compounds. So it can be considered as promising in hydrotreatment of kraft lignin with obtaining of biofuels components.

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PP-V-35

Catalyst Based on Mesoporous Aromatic Frameworks in Knoevenagel Condensation Reaction

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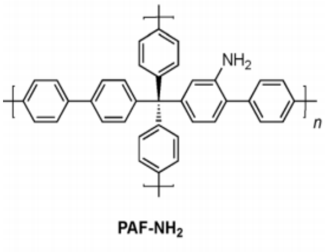
Knoevenagel condensation (reaction between an aldehyde or ketone and an active methylene-containing compound, commonly catalyzed by weak bases) is a carbon-carbon bond formation reaction, widely used in fine chemistry and in pharmaceutical industry as one of the basic processes to get valuable α,β-unsaturated carbonyl compounds.



Porous aromatic frameworks (PAF) are comparatively new class of polymeric carbon materials with a system of regular pores. The advantages of these materials are their chemical and thermal stability, high surface area, and the possibility to control the average pore size during the synthesis [1]. In our work, we have synthesized heterogeneous solid base catalyst - amino-functionalized porous aromatic frawework (**PAF-NH$_2$**) and examined its catalytic activity in model reaction between benzaldehyde and malononitrile taken as activated methylene substance in different polar and non-polar solvents. Results are shown in **table 1**. Catalyst was characterized by method of adsorption-desorption N_2, IR spectroscopy and elemental analysis.

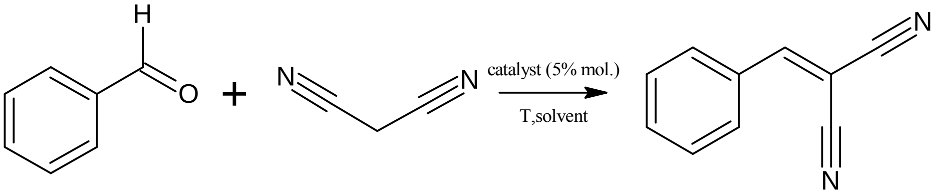


Table1. Knoevenagel condensation between benzaldehyde and malononitrile catalyzed by PAF-NH$_2$ catalyst

Entry	Solvent	T (˚C)	Time (h)	Conv.(%)
1	benzene	80	4	91
2	acetonitrile	80	4	76
3	ethyl acetate	77	4	51
4	ethyl alcohol	78	4	100
5	toluene	80	4	98
6	THF	66	4	83

The main product - 2-benzylidenemalononitrile- was obtained with quantitative yield over 4 hours at the boiling temperature of solvents. Conversion in similar conditions in all solvents without catalyst amounted to 5% - 15%. Catalyst was reused at least five times in benzene without any substantial loss of its catalytic capacity. PAF-NH_2 can be perspective heterogeneous catalyst for other type of condensation reaction.

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PP-V-36

Ni-Mo Sulfide Catalysts Based on Mesoporous Aluminosilicates in Hydrogenation of Model Compounds via WGSR

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Nowadays, strong ecological restrictions require production and use of more eco-friendly transportation fuels with lower sulfur and aromatic content. Therefore clean fuels researches including hydrogenation of aromatic compounds and sulfur removal have become an important direction of catalysis studies worldwide. It is well known that hydroprocesses require a large consumption of hydrogen affected on petroleum products cost. Thus, it would be highly beneficial for industry to develop refinery processes involving alternative hydrogen sources, namely, in situ hydrogen generation via water gas shift reaction (WGSR) [1].

Hydroprocessing catalysts consist of Ni(Co)-Mo(W)-sulfides supported on γ-Al_2O_3, SiO_2-Al_2O_3 and zeolites. It is important, that these catalysts are also active in WGSR [2]. Thanks to large pores and high specific surface area, mesoporous aluminosilicates are promising supports for hydroprocessing catalysts. The most attractive supports are aluminosilicates Al-MCM and Al-HMS types, which are ideally suited thanks to their high surface area, wide ordered pores structure and thermal stability [3].

In this study, Ni-Mo sulfide catalysts based on mesoporous aluminosilicates Al-MCM and Al-HMS types were investigated in hydrogenation and hydrodesulfurization reactions. The H_2O/CO system was chosen as a hydrogen source in situ formed through the WGSR.

The activity of Ni-Mo sulfide catalysts in hydrogenation/hydrodesulfurization of model compounds (dibenzothiophene (DBT) and 1-methylnaphthalene (1-MN)) was investigated at the temperature range of 340-380 °C and the CO pressure of 3-5 MPa. The influence of mesoporous material's type and Si/Al ratio on catalytic activity was established.

It was shown, that supported Ni-Mo catalysts are active in WGSR and provide hydrogen generation in H_2O/CO system resulted in hydrogenation of aromatics and sulfur-containing substrates.

It is found, that Mo-containing catalysts promoted by Ni, are the most active at the temperature of 380 °C and CO pressure 3 MPa.

Also, the influence of H_2O/CO molar ratio and CO pressure on substrates conversion was studied. It was found, that optimal H_2O/CO ratio is at the range of 1.5-2.0. CO pressure does not significantly affect on substrate conversion.

The reported study was funded by RFBR according to the research project № 18-38-00593.

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PP-VI-1

Synthesis of M-TiO_2 (M = Er, Pt, Au, U) Photocatalytic Porous Nanoparticles

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Recently, the nanostructured materials have received wide attention. Special focus was given on materials exhibiting photocatalytic properties such as ZnO [1], CeO_2 [2], Cu_2O [3] or TiO_2. Due to high availability and low cost, many research works on the synthesis of TiO_2 with various particle shapes have been published [4, 5, 6].

As semiconductor with high band gap, TiO_2 can be activated only under the UV light [7]. Notwithstanding the enhancement of the photocatalytic activity the lowering of conduction band (CB) or raising of valence band is desired [8, 9, 10]. In order to improve its photocatalytic properties the noble metal modified TiO_2 was used. The lower Fermi level of noble metal results in better separation of charge carriers which increases its photocatalytic activity [11]. Furthermore, researches have tried different dopants such as Mo [12], Ag [13], Fe [14], N [15], S [16] etc.

In this work we would like to report the synthesis of M-doped TiO_2 (M = Er, Pt, Au, U) and the effect of the dopant on photocatalytic properties. Crystalline structure of prepared mesoporous NP was determined using XRD, catalytic activity was measured using degradation of organic dyes such as rhodamines under VIS irradiation and the types or reactive oxygen species (ROS) were investigated.

Acknowledgement: Special thanks belong to Sigma-Aldrich Slovakia for providing support after university fire and to Dr. Girman and Dr. Kalavsky for providing irreplaceable lab equipment.

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PP-VI-2

Improved Mixed Catalytic Packing for Hydrogen - Water Isotopic Exchange

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Single or associated with other processes, the isotopic exchange between hydrogen and liquid water (LPCE) is one of the most efficient process for tritium removal from nuclear effluents, produced in fission and fusion reactors. In order to increase the efficiency of isotopic exchange process, the chemical exchange is usually associated with conventional distillation process so that, the tritium is transferred from tritiated water to the hydrogen gas, through the following consecutive steps:

$$HTO_{(L)} + H_2O_{(V)} \rightarrow HTO_{(V)} + H_2O_{(L)} \quad (1)$$

$$\underline{HTO_{(V)} + H_{2(G)} \rightarrow HT_{(G)} + H_2O_{(V)} \quad (2)}$$

$$HTO_{(L)} + H_{2(G)} \rightarrow HT_{(G)} + H_2O_{(L)} \quad (3)$$

The chemical exchange (reaction 2) becomes effective only in presence of hydrophobic catalyst which repels the liquid water but allows to water vapor and hydrogen gas to reach the active catalytic center and to accelerate the isotopic transfer process. On the other hand, the process (1) is a conventional water distillation process and need an efficient contact element (hydrophilic packing) in order to increase the contact area between water vapor and liquid water. The mixture consisting of catalyst and hydrophilic packing it's called ***"catalytic mixed packing"*** and play the key role in LPCE process.

Over one hundred types of hydrophobic catalysts and also many types of mixed catalytic packing have been prepared and tested on the world but the characteristics and operation parameters are different from author to author. This paper presents the most significant aspects concerning the manufacture and improvements of various types of mixed catalytic packing, manufactured at tested by authors at ICSI Rm-Valcea. The main improvements have been focused on the improvement of the main characteristics of selected Pt/C/ PTFE catalyst (surface area; pores volume; metallic area; platinum particle size etc), the wettability of stainless steel hydrophilic packing and catalyst: hydrophilic packing ratio. The influence and interdependence of these parameters is presented and discussed, too.

A new improved of mixed catalytic packing , having new geometry, new inner structure and higher performances has been selected and proposed to be used in the future Industrial Tritium Removal Facility for detritiation of heavy water from Cernavoda Nuclear Power Plant. The improved mixed catalytic packing, can be also an option for similar detritiation processes from ITER reactor (Water Detritiation System and Isotope Separation System).

PP-VI-3

Methanol Production from Gas of Pyrolitic Processing Organic Waste Materials

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Existing methods of gasification and pyrolisis were established over100 years ago, they provide receiving the energy of the gas with a certain content of the liquid phase. This gas is then purified from the liquid phase and used in piston and gas turbine installations for electricity production. Recently, new methods of conversion of biomass with the yield of dry energy content of combustible gas (hydrogen and carbon monoxide). The ratio of H2:CO is equal to (1.6 – 2.0). In our developed process are recycled carbon materials: wood and agricultural waste, coal, peat, waste products. The resulting composition of gas is promising for the production of methanol and further processing it into motor fuel.

The volume of synthesis gas -2240 Nm3/h

- Pressure process is 50 ATA
- Temperature in the reactor 205 - 240°C
- The amount of the synthesis gas 100кмole/h (1246 kg/h)
- The stoichiometric ratio in the synthesis reaction fo = 1.61

The ratio of H2:CO = 1.64

- Synthesis gas composition, %vol. :

H_2 – 59,80
CO_2 - 0,40
CO - 36.40
N_2 – 2,80
CH_4 – 0.60

- The carbon efficiency must be ≥70 %.

In the work of Rozovskii [2, 3] it is shown that in the synthesis of methanol on CuO-ZnO/Al2O3 catalyst reaction at a temperature of 200-280°C and a pressure of 40-80 ATA proceeds through two routes:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad Kp_1 \qquad (I)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad Kp_2 \qquad (II)$$

It was shown that methanol is formed from CO_2. If the original mixture no CO_2 and H_2O, the synthesis of methanol will not going to happen under these conditions. For a more complete conversion, the stoichiometric ratio fo should be equal to 2.0. The optimum CO_2 content is 3-5%vol. Small quantities of carbon dioxide reduce the rate of methanol formation. Shown above the composition of the gas has fo < 2.0 (lack of hydrogen). In this case, the reaction after separation of methanol in the reactor will accumulate (CO and CO_2).

In this paper the mathematical modeling of the technological flow scheme without recycling of the three reactors, three separators, heat exchangers and tanks. The mathematical description of the isothermal process in the equilibrium reactor of methanol synthesis is:

$$\begin{cases} \mathbf{A} \cdot \mathbf{N} = \mathbf{A} \cdot \mathbf{N_0} \\ \mathbf{S} \cdot \ln\mathbf{N} = \ln\mathbf{K_P} \end{cases} \qquad (1)$$

where A is the atomic-molecular matrix of the reaction (6x4); S – stoichiometric matrix (6x2); lnКp – a column vector of logarithms of the equilibrium constants; N, N0 – vectors – columns of the molar amounts of components in the equilibrium and initial mixture. The indices 1, 2, ..., 6 are respectively CO_2, CO, CH_3OH, H_2O, H_2, N_2. A system of six nonlinear algebraic equations (1) were solved by Newton's method.

A mathematical description of vapor - liquid separator has the form:

$$k_i = \frac{P_{oi}\gamma_i}{Pf_i}; \qquad (1)$$

$$\sum \frac{(k_i - 1)z_i}{1 + e(k_i - 1)} = 0; \qquad (2)$$

$$x_i = \frac{z_i}{1+e*(k_i-1)} \qquad (3)$$

$$y_i = k_i * x_i \qquad (4)$$

z_i is the mole fraction of component i in gross composition (liquid + vapor);k_i-coefficient of phase equilibrium; x_i -mole fraction of component in liquid phase y_i-mole fraction of component in vapor phase; e is the proportion of the vapour phase; P is the pressure in the system; P_{oi} is the saturated vapor pressure i component; γ_i is the activity coefficient of a component in liquid phase; f_i is the fugacity coefficient of a component in vapor phase on the equation of state Redlich – Kwong - Soave [1].

The addition of water in the absence of CO_2 and an excess of CO in the synthesis gas improves the performance of the installation. The carbon efficiency η = 72.4%. From 2240 Nm3/h calculation of the technological scheme gives 886 kg/h of methanol CH3OH with a content of 95-99% by weight. The obtained results were confirmed experimentally in a laboratory flow-through reactor.

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PP-VI-4

Cerium Modified Mesoporous Titania with Photocatalytic and Photoelectrochemical Properties

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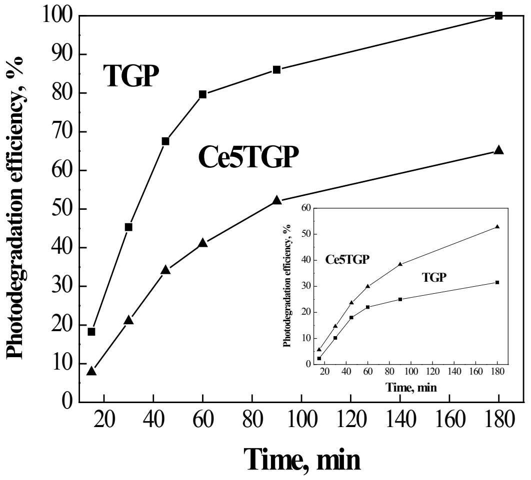
Photocatalysts attracts great interest because their applications in degradation of various pollutants and conversion of the light energy into chemical energy, domains of great interest. Nanostructured assemblies or composites based on titania have drawn significant attention in recent years due to their relevance in photocatalytic and solar cell applications [1-3]. The mesoporous structure of TiO_2 is of particular interest because the mesoporous channels offer a large surface area. Ceria is chosen in this study to be the small bandgap component [4] for the construction of TiO_2–CeO_2 mesoporous composites.

Mesoporous TiO_2 has been synthesized through triblock copolymer templated sol-gel method via an evaporation-induced self-assembly (EISA) process. The sol-gel was carried out in the presence of Pluronic P123 as the structure directing agent and propanol as solvent and co-surfactant. TiO_2 was modified with CeO_2 (2.5 and 5 wt. %) by direct synthesis or impregnation. The gels were calcined in air at 400 °C. The CeTGP thin films were obtained from the gels supported on ITO glass support by spinning method.

The obtained powder oxides were characterized by thermal analysis, nitrogen adsorption-desorption, X-ray diffraction, SEM electron microscopy and UV-Vis diffuse reflectance spectroscopy. Photocatalytic properties were tested in photocatalytic oxidation of dyes (methyl orange) and phenol from aqueous solution under UV and visible light. The supported layers were characterized by SEM microscopy with EDX and EIS spectroscopy. The current-potential curves were investigated in dark and under visible light irradiation in 0.2 M Na2SO4 aqueous solution.

The obtained results evidenced the mesoporous structure of materials with spherical morphology and ordered particle arrangement. Mesoporous TiO_2 sample, named TGP, shows strong absorption in UV (250-350 nm) region. Cerium leads to the enlargement of the absorption band to visible (400-500 nm). The red-shift in CeTGP samples was attributed to the important Ce 4f role in generation of the electron-hole pairs under visible light illumination. Comparing the band gap energy of CeTGP samples with the energy of pure titania TGP sample were evidenced lower values.



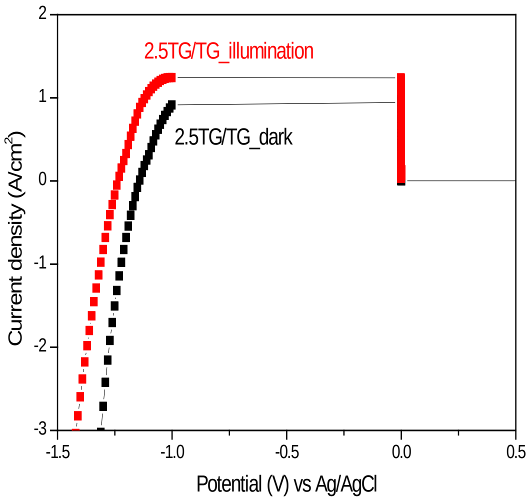


Fig. 1 Photocatalytic results obtained under UV and visible light (small Fig.)

Fig. 2 Photoelectrochemical properties

The modification of TiO_2 with cerium decreased its photocatalytic performances under UV light and increased the photocatalytic efficiency in visible light. The best photocatalytic and photoelectrochemical properties (Fig. 2) were obtained for samples with 2.5 % CeO_2. The smaller circular radius for TGP 2.5%Ce sample sustains a lower transfer resistence and a higher separation efficiency of the photogenerated electrons and holes that is beneficial for a faster photoelectrochemical reaction.

Acknowledgement. The authors gratefully acknowledge the financial support from the Romanian National Authority for Scientific Research, CNCS-UEFISCDI, project number PN-III-P2-2.1-PED103/2017.

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Noble Metal-Based Catalysts for Steam and Autothermal Reforming of n-Hexadecane and Diesel Fuel to Synthesis Gas

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In last decades, the development of new technologies for on-site power generation attracts considerable attention [1,2]. Among commercially available auxiliary power units of 1-kW scale, solid oxide fuel cell (SOFC) based systems are considered as the most effective in electricity generation.

Diesel fuel is one of the most promising liquid hydrocarbons that can be converted into hydrogen-rich gas for SOFC feeding due to readily available infrastructure and wide application scope. Autothermal reforming (ATR) and steam reforming (SR) are considered as the most promising methods for diesel fuel conversion to produce synthesis gas. However, there is a limited number of works which use real diesel in the studies because of unpredictable effects of the diesel constituents on the reforming process. Model mixtures or diesel surrogates (such as n-hexadecane) are used instead. The development of efficient coke-resistant and sulfur-tolerant diesel ATR and SR catalysts for SOFC applications is very challenging, especially considering the complex and ill-defined nature of the fuel.

In this work we studied noble metal (Rh, Pt, Ru) based catalysts for ATR and SR of n-hexadecane and Euro-5 diesel fuel. The catalysts of composition 0.1 mmol/ Rh-, Pt-, Ru/$Ce_{0.75}Zr_{0.25}O_{2-\delta}$, prepared by sorption-hydrolytic deposition technique, demonstrated high dispersity with a particle size of 1-2 nm [3]. Among the catalysts tested in n-hexadecane SR under the the following operating conditions: $H_2O/C = 3$, GHSV = 23,000 h^{-1}, T = 550 °C, the Rh-based sample showed the best activity - it provided complete conversion of the fuel during 8 h on stream and the outlet concentrations of H_2, CO_2, CO and CH_4 close to the equilibrium values (54, 18, 5 and 6 vol.%, respectively). In ATR of diesel fuel under the following operating conditions: $H_2O/C = 2.5$, $O_2/C= 0.5$ at GHSV = 30,000 h^{-1}, T = 650 °C, this catalyst demonstrated stable operation during 9 h, then the conversion decreased to 86% during the next 6 h. The results obtained were used to develop a structured Rh/$Ce_{0.75}Zr_{0.25}O_{2-\delta}$ catalyst comprised of an active component supported on FeCrAl grid pre-coated with η - Al_2O_3 [4]. The obtained 0.24 wt.% Rh/$Ce_{0.75}Zr_{0.25}O_{2-\delta}$/η-$Al_2O_3$/FeCrAl catalyst provided a 100% conversion of n-hexadecane in ATR during 12 h, and hydrogen productivity of H_2 ~ 2.5 $\mathrm{kg_{H_2}\,kg_{cat}^{-1}\,h^{-1}}$ [5].

Acknowledgement. The authors appreciate the financial support from the Ministry of Education and Science of the Russian Federation, project No 14.607.21.0149, Unique Identification Number RFMEFI60716X0149.

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PP-VI-6

Halloysite as a Carrier for Metal Sulfides Nanostructures and Its Application in Photocatalysis

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Now there are no industrially applicable nanostructured photocatalysts due to the high cost of their production, since carriers for such systems are usually carbon nanomaterials: graphene, carbon nanotubes, and other synthetic materials that are difficult to obtain. We propose to use cheap natural nanomaterial produced in tons, and not synthesized in grams, which will significantly reduce the cost of production and will easily expand it to industrial scale. The halloysite mineral is the promising carrier for photocatalysts also due to its eco-friendly properties, low toxicity.

Here we report nanostructured halloysite photocatalyst with CdS, CdxZnyS nanoparticles on the outer surface and inside halloysite nanotubes. Different synthesize techniques and conditions like (pH, time and precursor's concertation) were investigated. It was found that ligand assisted method [1] is more efficient than vacuum sulphur precursor loading method. The structure and physico-chemical properties of catalysts were analysed using TEM, EDX, XRD, elemental analysis and UV-Vis spectroscopy. The proposed materials showed good catalytic activity and high stability in the release of hydrogen under the action of visible radiation.

Acknowledgement. This work was supported by the Ministry of Education and Science of the Russian Federation (Grant № 14.Z50.31.0035)

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PP-VI-7

Photocatalytic Activity of Sc-Doped TiO_2 *In Situ* Synthesized by Sol-Gel Method

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TiO_2 is a type of wide bandgap semiconductor, used in areas ranging from photovoltaics and photocatalysis to photo-/electrochromics and sensors.[1] These applications can be roughly divided into "energy" and "environmental" categories, many of which depend not only on the properties of the TiO_2 material itself but also on the modifications of the TiO_2 material host.[2] One of the most effective method to reduce the band gap of TiO_2 is implementation of metal ions into the oxide host. The doping of titania provides appearance of new states within the band gap for photoexcitation with lower energy. Using scandium as doping ion based essentially on two reasons:
(*i*) the close size of Sc^{3+} to size of Ti^{4+}, what is to favor the formation of a solid solution;
(*ii*) The substitution of Sc^{3+} in the site of Ti^{4+} generates holes in the valence band.[3]

In this work *in situ* doping of TiO_2 by Sc was carried out by the direct hydrolysis route. Specifically, a weighed amount of titanium (IV) n-butoxide was dissolved in the aqueous colloid solution of $Sc_2(SO_4)_3$ where concentration of scandium salt was 1, 2.5 and 5 mol. %. Solutions was heated up to the boiling point under continuous stirring and aged at this temperature for 2 hours. All of the solvent, i.e. water, was evaporated, and obtained powder was dryed at 150 °C during 4 hours. After drying shade of powder turned to beige. X-ray diffraction (XRD) patterns of all composites were obtained using a Shimadzu MAXima-X XRD-7000 automatic diffractometer (λ=1.5406 Å for Cu$K\alpha$ radiation) in the angle interval 2ϑ of 5-80° with step 0.03° and an exposure time of 30 sec. The UV-Vis spectra in the wavelength range of 190–800 nm of samples were recorded on Shimadzu UV-3600 spectrophotometer using $BaSO_4$ as a standard. The chemical composition of the samples was determined by the energy-dispersive X-ray analysis (EDX) using a JED 2300 analyzer.

According to XRD data all samples have crystal structure of anatase, crystal size is nearby 9 nm (Fig. 1). Content of Sc determined by EDX was 3.3, 4.4 and 6.9 at.% for samples synthesized with 1, 2.5 and 5 mol. % of Sc salt, respectively. The main abruption of optical absorbance spectrum indicated on the titania. Long tail in range of visible spectrum correlates with Sc-content, and the sample with the highest Sc content has the most intensity of tail.

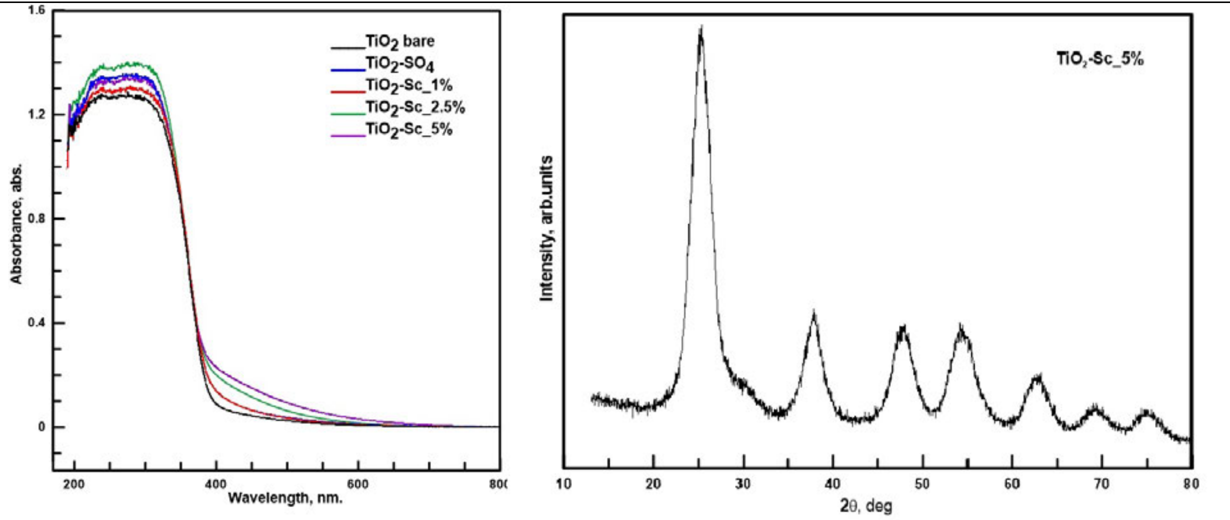

Fig. 1. Optical absorbance of samples TiO_2 with different content of Sc (left part) and X-ray diffraction pattern for TiO_2, doped Sc_ 5% (right part)

To confirm the photocatalytic effect of doping TiO_2 by Sc the composites were studied as photocatalyst in the oxidation of cyclic aromatic organic compounds under visible light irradiation. Hydroquinone $C_6H_4(OH)_2$ (HQ) dye was chosen as a model compound. Photooxidation of HQ in the presence of TiO_2-Sc showed the almost complete degradation of HQ during 14 hours.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 17-79-20165 and was performed in Institute of Solid State Chemistry UrB RAS.

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PP-VI-8

Effect of Crystallinity of Ni-Mg-O Catalysts on Their Activity in the Reaction of Steam Reforming of Glycerol into Hydrogen

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It is known that one of the properties of solid catalysts affecting its activity is the degree of its crystallinity. The degree of crystallinity of binary solid oxide systems depends on the initial oxides used in the preparation, formed new chemical compounds and the conditions for their preparation. Naturally, the crystallinity of the prepared solids affects in some way ещ their catalytic activity. In this connection, we studied the effect of the degree of crystallinity of Ni-Mg-O catalysts on their activity in the reaction of steam reforming of glycerol into hydrogen.

For the studies, nickel-magnesium oxide catalysts were prepared by precipitation from aqueous solutions of nickel and magnesium nitric acid. Thus, nine catalysts were synthesized with an atomic ratio of the elements from Ni: Mg = 9: 1 to Ni: Mg = 1: 9. The X-ray analysis shows that in all samples the percentage of Mg/Ni components is maintained so that the fluctuations of the reflex intensity in the diffraction pattern prove that. Based on the X-ray diffraction studies, the degree of crystallinity of all the catalysts studied was calculated.

The study of the activity of synthesized samples in the reaction of the glycerol steam reforming of glycerol showed that at reaction temperatures up to 500°C different glycerol decomposition products are formed, while at higher temperatures the direction of the reaction shifts towards hydrogen formation and also carbon monoxide as a by-product.

Effect of catalysts crystallinity on its activity in steam reforming of glycerol into hydrogen it is shown in fig.1.

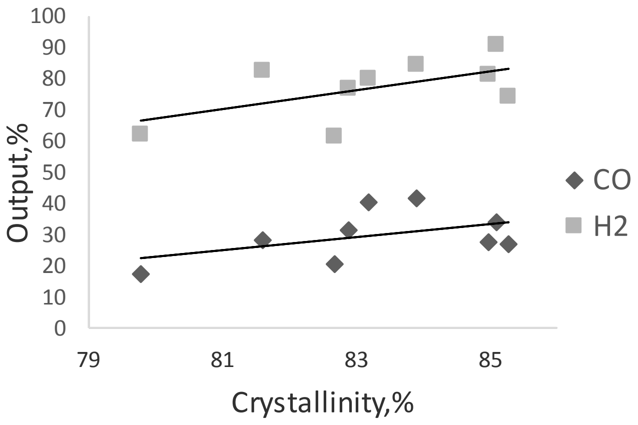

Fig.1 Dependents of hydrogen and carbon monoxide yields on catalysts crystallinity.

As can be seen from the figure over Ni-Mg-O catalysts increasing of the degree of crystallinity leads to rising of the yields of hydrogen as well as by-product carbon monoxide.

PP-VI-9

Electrocatalytic Activity of Pd/C Composite Material Obtained by Pulse Alternating Current Synthesis

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The current interest in fuel cell technologies continues to grow because of their potential to eliminate unwanted pollution of the environment. And although the most developed fuel cells, in which H_2 are used as fuel, more attention is paid to fuel cells with direct oxidation of liquid fuel [1]. One of the promising fuels is ethanol, as it has unique physicochemical properties and is renewable. As a catalyst in fuel cells, it is customary to use platinum, but the oxidation of ethanol proceeds rather hard both on platinum and its alloys. In this case, the most promising replacement for Pt is Pd. Palladium is more common in nature and less expensive than platinum, it is also more active in the reaction of ethanol oxidation in an alkaline medium.

In this work for the preparation of Pd/C catalytic systems we were used a new original synthesis method - pulse alternating current (PAC) technique. Earlier we have successfully used a PAC for synthesis of metal-carbon, metal oxide-carbon nanostructured materials based on Pt nanoparticles [2], nickel oxide [3] and tin dioxide [4], which demonstrated good electrochemical properties in corresponding applications.

We investigated the effect of an alternating pulse current on palladium in various electrolytes, in this work we settled on chlorides K, Na, Ba, Sr, Li. The electrochemical cell has two Pd foil electrodes 0.25 mm thick immersed in an aqueous solution of electrolytes. The electrodes are connected to ac source operating at 50 Hz. Pd loading in the catalyst was controlled by the current amplitude and duration of the synthesis process. Finally, the freshly prepared catalyst was rinsed with H_2O and dried at 80 °C for 1 h.

X-ray diffraction studies of the synthesized composite material showed the presence of peaks in the range from 15 to 60 degrees typical for metallic palladium, the palladium nanoparticles have a narrow size distribution 3-7 nm. Transmission electron microscopy of the obtained catalysts showed a uniform distribution of palladium over the surface of the carbon carrier and its average particle size of 2-4 nm. The smallest particle size was in the catalyst synthesized in a solution of lithium chloride.

The catalytic properties of the resulting Pd/C composite material were investigated in the electrochemical oxidation of ethanol in an alkaline medium. All samples showed a high electrocatalytic activity in this reaction. The best properties demonstrated a sample synthesized in lithium chloride and it was compared with the Pt/C catalyst. It was shown that the overall rate of oxidation of ethanol on a Pd/C catalyst is higher than on a Pt/C catalyst synthesized in a similar method.

Thus, nanoscale Pd/C composite materials were preparation by pulse alternating current technique. The influence of the electrolyte solution during the synthesis on the particle size is shown. The materials are characterized by a higher electrocatalytic activity in the electrooxidation of alcohols in an alkaline medium than the Pt/C catalysts obtained by the similar method.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-23-00078.

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PP-VI-10

Hydrogen Production from Ammonia Borane under Light Using Titanium-Based Nanocatalyst

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Because of increasing of environmental pollution and usage of fossil fuels it is necessary to develop the new energy concepts. As a type of alternative fuel, hydrogen (H_2) is a leader in terms of energy capacity (per unit of weight). Note that water is the only product of H_2 combustion (oxidation). H_2 may be obtained using renewable energy (such as solar, wind energy etc.). But using H_2 as an energy carrier requires solving the problem of development of effective system of its storage and generation.

To achieve this goal it is perspective to use ammonia borane (NH_3BH_3, AB). This compound is a leader in the mass and volume content of hydrogen among hydrides and stable on air and in the aqueous solution. There are lots of studies dedicated to catalytic hydrolysis of AB. However, such way requires a purification of the gas from ammonia impurity and a method to control H_2 generation. These problems may be solved by using a photocatalytic hydrolysis of AB. It was firstly reported in literature in 2013. Hydrolysis of NH_3BH_3 under the visible and UV light in the presence of catalysts such as MoO_{3-x}, WO_{3-x}, CuO/TiO_2, $Cu/TiO_2/C$, $Cu^0/S/TiO_2$, CdS/TiO_2, $CdS/CdTiO_3$, Pt/TiO_2, Ag/SBA-15, Ag-TiO_2/SBA-15, $Pd/H_2Ti_3O_7$, AgPd, PdAu, PtAg etc. has already been investigated. Unfortunately, it is impossible to compare these studies because most of them don’t contain the data about content of ammonia impurity in the gas product and incident radiation power (there is no rationing to incident photons quantity (photon efficiency)). Thereby it may be claimed that systematic approach in these investigations is absent.

The aim of this study is to systematically investigate a number of photocatalysts (TiO_2 (anatase), polytitanates of K and Na, Ag/TiO_2-catalysts) in the photocatalytic hydrolysis/hydrothermolysis of AB under the action of UV ($\lambda = 365$ nm) and visible light ($\lambda = 450$ nm). Nanotubes and nanorods of polytitanates of K and Na were obtained from TiO_2 (Hombifine N) and $TiOSO_4$ by recrystallization in 10 M alkali solution. The temperature of recrystallization, the duration of process and other parameters were varied. Photocatalysts have been characterized by ICP-AES, ATR-FTIR, TEM HR, XRD, BET, UV-Vis DRS.

TiO_2 nanostructures are more active in the process of photocatalytic hydrolysis of AB under UV light comparing with initial TiO_2. It may be caused by the contact of the nanosized polytitanates’ phase with the phase of anatase resulting increasing of H_2 generation rate.

The surface of TiO_2 was modified by a small (<0.1 wt.%) quantity of colloidal Ag (particle size 4-5 nm) with the aim to improve an activity under the visible (λ=450 nm) and UV (λ=365 nm) light and to decrease the concentration of ammonia in the obtained hydrogen [1]. Optimization of composition of Ag/TiO_2 catalyst with a small content of metal was carried out. It was established that hydrolysis of AB does not occur without light if the content of Ag is less than <0.06 wt.% in the catalyst. It is highly important for creation the H_2-generating systems having ability to regulate the gas generation by the light. In this study, a possibility to control the process of AB hydrolysis by using 0.04 wt.%Ag/TiO_2 catalyst under UV light in the turning on/off regime was demonstrated. The photon efficiency calculation data are presented at the first time. According to these calculations, it is possible to activate AB hydrolysis process by light on the surface of photocatalyst.

Authors for the first time implemented a process of photocatalytic hydrothermolysis of NH_3BH_3. It is the most perspective process for solving problems of hydrogen energy and H_2 storage systems. A significant increasing of H_2 generation rate under the action of light (UV and visible) in the presence of TiO_2 and Ag/TiO_2 catalysts compared with bare AB was demonstrated. Ag/TiO_2 catalyst facilitates increasing of H_2 yield under UV and visible light. These results are consistent with the DRS spectra of this catalyst. The gravimetric capacity of 7.0 wt.% H_2 has been achieved for 15 min at 90 °C.

Acknowledgement. This work was conducted within the framework of budget project No. 0303-2016-0015 for Boreskov Institute of Catalysis.

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PP-VI-11

Design and Photocatalytic Activity of Nano-Zinc Oxide Obtained by Pulse Alternating Current Synthesis

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Zinc oxide is a semiconductor with specific physicochemical properties. Over the past years ZnO sparked interest with the ability to be used in the ecology as a photocatalyst for purification of water from organic pollutants [1].

The photocatalytic activity of nano-ZnO depends on particles size distribution, specific surface area and presence of different oxygen- and zinc-related defects [2].

It is well known that zinc oxide microstructure is strongly influenced by the preparation conditions. Thereby, it is necessary to develop a simple, large-scale and low-cost way to obtain nano-ZnO with desirable properties for photocatalytic application.

In this work the novel approach to nano-ZnO synthesis was successfully developed. This method is based on the electrochemical oxidation of zinc electrode in electrolyte solution with ZnO formation. It was shown that the Zn oxidation rate strongly depends on the ratio of anodic and cathodic current density (j_a:j_k). Moreover, a type of electrolyte is found to have a great influence on ZnO microstructure. Flower-like architecture of ZnO nanoparticles (ZnO-NPs) and nanorods (ZnO-NRs) with different dimensions and mesoporous structure are formed during pulse alternating current synthesis.

It was shown that NPs obtained in 2M KCl have a better photocatalytic activity in methylene blue degradation under UV light than NRs obtained in 2M NaCl. It is connected to a larger surface area and pore volume, and more defective structure of ZnO-NPs.

Thereby, pulse alternating current synthesis provides a possibility to prepare nano-ZnO materials with control of their microstructure depending on synthesis conditions.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-23-00078.

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PP-VI-12

Studies on the Kinetics of Polyethylenfuranoate Formation

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One of the most significant problems in modern world is scarcity of natural resources. The main source of renewable carbon-contain raw materials is biomass. In conditions of global warming and diminishing petroleum oil reserves also recent climb in oil prices and consumer demand for environmentally friendly products, idea about substitutes fossil fuel for biomass in chemical industry is becoming urgent [1,2]. Around the world, the increased attention of researchers is attracted by the different ways to move from today's fossil-based economy to a more sustainable economy based on biomass [3]. The chemical industry is the most energy intensive sector, with organic chemicals and polymers being its most important products.

The most promising way to develop the alternative routes of environmentally friendly bio-based materials is the production of polyethylenfuranoate (PEF). The main idea is using furan-2,5-dicarboxylic acid (FDCA) as an alternative monomer to the ubiquitous terephthalic acid which is one of the fossil-based monomers of polyethylene terephthalate (PET) and the fifth largest bulk plastics worldwide. FDCA can be obtained across HMF by cyclodehydration of poly-sugars [4,5] with its following catalytic oxidation [6].

FDCA can be used as a monomer in polycondensation reaction. However, it is more preferably to use its dimethyl ester- dimethyl-2,5-furandicarboxylate (DMF), since the acid is difficult to be purified. This polymer is obtained in a two-step process involving the transesterification of dimethyl furanoate with a ethylene glycol, and a second step involving polycondensation of bis(2-hydroxyeythyl) furanoate.

The kinetics of catalyzed transesterification of DMF with diethylene glycol was studied. A number of the experiments have been carried out using ~~at~~ five different reaction temperatures from 110 to 180 and different catalysts such as zinc acetate tetrabutyl titanate and antimony oxide (III). Apparent rate constants and activation energy were calculated using to ref from literature and Arrhenius equation. The optimal synthesis conditions were also selected (time, pressure, temperature) to achieve a high rate of DMF conversion (more than 98%).

Acknowledgement. This work was supported by the Russian Science Foundation,
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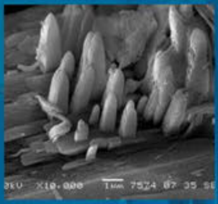

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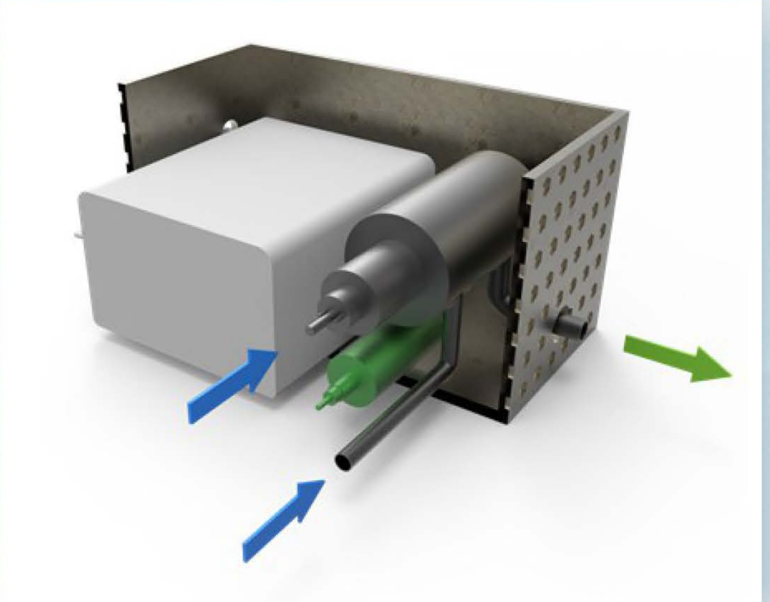
Самыми быстро развивающимися в настоящее время являются технологии ПОМТЭ (топливные элементы с протонно-обменной мембраной) и ТОТЭ (твердооксидные топливные элементы). Технологические тренды направления топливных элементов: переход к доступным органическим и неорганическим топливам, повышение ресурса работы.

Институт катализа СО РАН совместно с дочерним малым инновационным предприятием ООО «УНИКАТ» ведет разработку топливных процессоров, позволяющих из различного топлива получать «по требованию» водородсодержащий газ необходимого качества для питания ПОМТЭ и ТОТЭ, а индустриальный партнер ЗАО «Нижегородские сорбенты» вместе с АО «ГК ИнЭнерджи» проводят консолидацию имеющегося научно-технологического задела в России для разработки наиболее перспективных вариантов конечных энергоустановок, обеспечение последующего производства высокотехнологичных продуктов с высокой добавленной стоимостью, в том числе, комплексных энергетических установок и систем.



В настоящее время совместные работы проводятся в рамках проекта по теме «Разработка макета энергоустановки на основе электрохимического генератора с риформером дизельного топлива» (УИН RFMEFI60716X0149), финансируемого Минобрнауки Российской Федерации.

Scientific edition

5th International School-Conference on Catalysis for Young Scientists Catalyst Design: From Molecular to Industrial Level

May 20-23, 2018, Moscow, Russia

Abstracts

Editors: Prof. V.I. Bukhtiyarov, prof. O.N. Martyanov

Научное издание

V Международная школа-конференция по катализу для молодых ученых Каталитический дизайн: от исследований на молекулярном уровне к практической реализации

20-23 мая 2018 г., Москва, Россия

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Компьютерная обработка: Ю.В. Климова, А.А. Спиридонов
Обложка: А.А. Смирнов

Издатель:
Федеральное государственное бюджетное учреждение науки
Институт катализа им. Г.К. Борескова
Сибирского отделения Российской академии наук
630099, Новосибирск, пр-т Академика Лаврентьева, 5, ИК СО РАН
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: 158 МБ. 1 CD-R. Подписано в тираж: 08.05.2018. Тираж: 170 экз.
Системные требования: i486; Adobe Reader (чтение формата PDF).

ISBN 978-5-906376-21-3

QR
droid

QR code:
http://www.catalysis.ru/resources/institute/Publishing/Report/2018/ABSTRACTS_CATALYST_DESIGN-V-2018.pdf