Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Zelinsky Institute of Organic Chemistry RAS, Moscow, Russia
Lomonosov Moscow State University, Moscow, Russia

MCR 2016

X International Conference
"Mechanisms of Catalytic Reactions"

Svetlogorsk, Kaliningrad Region, Russia
October 2 - 6, 2016

ABSTRACTS

Novosibirsk-2016

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УДК 544.47+66.09
ББК Г544

М45 Mechanisms of Catalytic Reactions. X International Conference (MCR-X).
(October 2 - 6, 2016, Svetlogorsk, Kaliningrad Region, Russia) [Electronic resourse]: Book of abstracts / Boreskov Institute of Catalysis SB RAS ed.: prof. V.I. Bukhtiyarov, - Novosibirsk: BIC, 2016. p.328,
– 1 electronic optical disc (CD-R). ISBN 978-5-906376-15-2

В надзаг.:
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Zelinsky Institute of Organic Chemistry RAS, Moscow, Russia
Lomonosov Moscow State University, Moscow, Russia

Topics of book:
- First-principles approach, theory and simulation in catalysis;
- Advanced methods for studies of mechanisms of catalyzed reactions;
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- From mechanistic studies to design of advanced catalyst systems.

The Conference is accompanied by the School-Symposium of young scientists "Quantum-mechanical modeling of catalytic processes".

УДК 544.47+66.09
ББК Г544

ISBN 978-5-906376-15-2

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FINANCIAL SUPPORT

Russian Foundation for Basic Research

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PLENARY LECTURES

Catalysis and Energetics: Experience of the Boreskov Institute of Catalysis

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The presentation concerns the experience of the Boreskov Institute of Catalysis (BIC) in the development of catalysts and catalytic technologies for the production of high-quality fuel from the traditional raw hydrocarbons, as well as for processing of associated petroleum gas and application of catalytic processes for energetics of the future. Specifically, under discussion are BIC's proprietary ecologically sound coal-burning thermal power plants based on catalytic burning of different, including low-calorific, fuels; synthesis of high-quality fuel from renewable plant resources; application of reversible thermocatalytic processes for high-efficient direct conversion of nuclear and concentrated solar energy into chemical energy.

Under discussion are problems of quantum transformation of solar-to-chemical energy *via* creation of artificial photocatalytic systems mimicking the natural photosynthesis in plants and bacteria. The BIC experience of a considerable improvement in the utilization of motor fuel through its pre-conversion to synthesis gas using car-board catalytic processors is discussed, too. Another example under consideration is the possibility of efficient recuperation of low-potential heat through its accumulation by composite materials such as selective water sorbents.

PL-2

Electron Microscopy Advances in Catalysis

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In recent years, electron microscopy has made significant progress for the study of heterogeneous catalysts. With advancements in electron optics and data acquisition, electron microscopy has become capable of delivering images with atomic resolution and sensitivity [1,2]. Parallel developments of gas cells have made electron microscopy available for *in situ* observations of catalysts during exposure to reactive gas environments at pressures up to atmospheric levels and temperatures of up to several hundred centigrade [3-5]. It is desirable to take advantage of these technologies as they offer new insight into the dynamics and reactivity of catalysts at the atomic-scale and in chemical meaningful environment. Moreover, in combination with concurrent measurements of the catalytic functionality, electron microscopy opens up new possibilities for *"live"* observations of structure-sensitive functional behaviour in catalysis. In this contribution, I will present such recent advances in electron microscopy and illustrate their benefits for catalysis research by studies from our laboratories [2-10].

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Halogen Chemistry on Catalytic Surfaces

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Halogens play a central role in the manufacture of various important chemicals, pharmaceuticals, and polymers such as polyvinyl chloride, polyurethanes, and polycarbonates. Furthermore, halogens can be used to selectively functionalize C-H bonds in light alkanes under mild conditions, constituting an attractive route for upgrading the abundant reserves of natural gas to valuable chemicals and fuels. The attainment of sustainable halogen-mediated processes requires the development of closed-loop systems to secure an efficient halogen recycling released as hydrogen halides in the halogenation and/or in the elimination steps. This lecture reviews a decade of efforts towards the discovery, understanding, and implementation of heterogeneous catalysts for halogen recycling via oxidation/oxyhalogenation. Emphasis will be put on the derivation of synthesis-structure-function relationships associated with the complex halogen chemistry on solid surfaces to aid the design of superior catalytic processes.

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PL-4

Mechanisms and Kinetics in Complex Systems: Application to Biomass Processing

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In this talk, an overview of modern catalytic-based technologies for converting lignocellulosic biomass to renewable fuels and chemicals will be given. The main challenges in understanding the reaction mechanisms will be reviewed. We will discuss a multiscale overall approach toward revealing the mechanisms, the active sites, and the kinetics that combines experimental kinetics, isotopic tracing and kinetic isotope effects, spectroscopic studies, operando characterization and multiscale modelling. As a specific example, the mechanisms of Diels-Alders and dehydration chemistry will be outlined toward the production of renewable aromatics, such as para-xylene.[1-3] Special emphasis will be given in the kinetics of tandem reactions catalysed by different active sites. In addition, hydrodeoxygenation mechanisms for reducing furans into fuel additives and precursors for aromatics will also briefly be discussed.[4-6] We will show that metals are not very selective in this chemistry and metal/Lewis acids or oxides supported on metals can be superior catalysts.

Acknowledgement. We acknowledge support from the Catalysis Center for Energy Innovation, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award number DE-SC0001004.

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KEYNOTE LECTURES

How to Extend *In Situ* Photoelectron Spectroscopy Studies of Electrochemically Active Gas-Solid Interfaces to Liquid-Solid Interfaces?

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In this lecture I will describe approaches how to extend the in situ Photoelectron Spectroscopy of electrochemically active gas-solid interfaces to liquid-solid interfaces. The interface between a liquid and a solid can be studied by tender X-ray photons passing the liquid whereas the emitted photoelectrons have to pass the liquid before being detected. A second approach is related to the application of graphene membranes. Nanoparticles (NP) of the electrode material were deposited on the graphene which is exposed to water with the covered side. XPS measurements were performed through the graphene membrane. Advantages and drawbacks of the approaches are discussed.

KN-2

On the Mechanism of the Fischer-Tropsch Reaction

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Fischer-Tropsch (FT) synthesis is increasingly important technology to convert a wide range of carbon sources into liquid fuels. Despite its practical importance, many aspects about the exact nature of the elementary reaction steps underlying FT mechanism remain unclear. Modern insights into the relation between surface topology and reactivity dictate that direct CO dissociation occurs on step-edge sites of transition metals such as Co, Rh and Ru [1]. The alternative is hydrogen-assisted CO dissociation [2]. Another debate concerns chain growth paths via CHx species or direct CO insertion followed by C-O bond activation [3]. Recent theoretical studies emphasize strong binding of oxygen to Ru and Co. Then removal of water can be the rate-controlling step [4]. Here, we combine steady state isotopic transient kinetic analysis (SSITKA) and chemical transient kinetic analysis (CTKA) with first-principles based microkinetics simulations to better understand FT mechanism on Co catalysts.

The salient findings of the present transient kinetic study are as follows:

- First-principles calculations stress the importance of step-edge sites for facile CO dissociation and chain-growth on these sites [4].
- During methanation (260 ºC), the CO consumption rate is limited by C and O hydrogenation rather than CO dissociation.
- When C species are deposited on a Co nanoparticle surface followed by evacuation to remove all CO, chain growth proceeds upon hydrogenation. This shows that adsorbed CO is not a necessary prerequisite for chain growth.
- During FT synthesis (220 ºC), scrutinizing the labelled C content in higher hydrocarbons shows that the hydrocarbons formation rate is mainly limited by monomer formation rather than C-C coupling. Propagation is fast compared to CO dissociation.
- Under FT synthesis conditions, the CO consumption rate is not limited anymore by C and O hydrogenation; the reason is that, due to increased surface coverage, the lack of surface vacancies causes CO dissociation to become the rate-controlling step.
- Lack of surface vacancies is a necessary condition for high chain growth probability due to the reversibility of the fast chain-growth process.

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Combinations of Catalytic and Kinetic Tools for Small Molecule Synthesis

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A great need exists for new reactions, reaction sequences and synthetic methods to permit any substance or material of any complexity to be synthesized with the highest possible efficiency, in the smallest number of steps, and with minimal cogeneration of waste, preferably from renewable starting materials. Currently, a shift is taking place in chemical synthesis technology with unprecedented opportunities to combine organic synthesis, biocatalytic methods, as well as homogeneous and heterogeneous catalysis, mediated by both metals and organocatalysts, for rapid and selective generation of complex molecular building blocks and materials. In our ongoing work [1-5], this catalytic toolbox is often complemented by detailed kinetic investigations, providing better insights into reaction mechanisms and for aiding in development of new reactions and new catalysts. Recent progress is discussed.

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KN-4

Size Effects in Adsorption Properties of Metal Nanoparticles: an Insight from the DFT Computational Modeling

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Metal nanoparticles, dispersed on a solid support of high surface area, form the active component of many modern catalysts. The size of such metal species varies from particles of several thousand to clusters of a few atoms. The properties of (large) nanoparticles are size-dependent, hence tunable. Understanding how the reactivity of such nanoparticles scales with size is crucial for the rational design of new catalysts. The modeling strategy based on three-dimensional symmetric Pd clusters terminated by low-index surfaces allows calculations of catalytic reactions on particles with a diameter of 1-2 nm at an efficient DFT level [1,2]. Moreover, the results obtained for particles of about 100 atoms can be used to predict the adsorption and catalytic properties of larger particles using the scaling relations [3]. Employing this modelling technique we were able to study structural and size effects in CO adsorption on Pd nanoparticles [4]. Calculated CO adsorption energies on Pd_n nanoparticles were found to exhibit two trends regarding the particle size n. (*i*) When the surface structure is dominated by extended close-packed facets, then adsorption of CO molecules becomes weaker with decreasing particle size. This trend results from a contraction of the lattice caused by the surface stress. (*ii*) At some critical size below $n \sim 50$, the concomitant upward shift of the metal d-levels induces a higher activity for CO adsorption and significant increase of activity is found for Pd clusters of about 20 atoms [4].

In the present contribution we extend the study of size effects to the case of CO adsorption on the surface of Pt nanoclusters and discuss the effect of lattice contraction on absorption of hydrogen in Pd and Pt nanoparticles.

Acknowledgement. This work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (Basic Budget Funding Project V.44.2.2).

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KN-5

High-Valent Diiron Oxo Species: Key Intermediates in Challenging Oxidations

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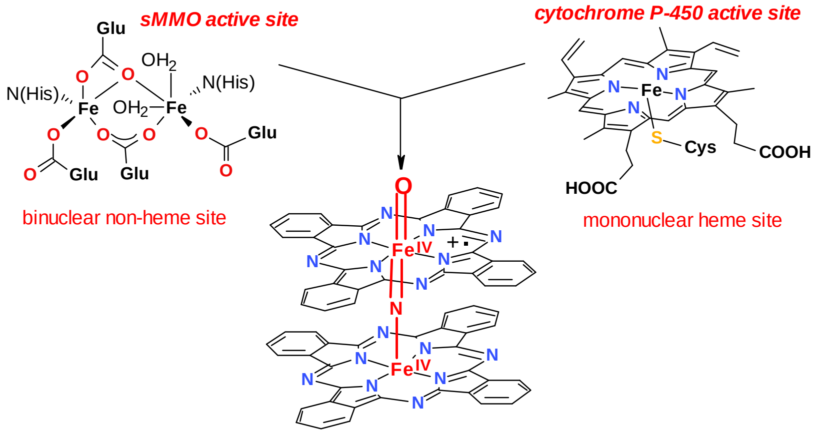
Bioinspired approach is a promising strategy to design powerful oxidizing catalysts. Cytochrome P-450 and methane monooxygenase (MMO) efficiently catalyze challenging reactions, *e.g.* oxidation of strong C-H bonds, using mononuclear iron porphyrin and non-heme diiron sites, respectively. We have proposed a novel concept: to use diiron catalytic site like in soluble MMO but in macrocyclic ligand environment like in cytochrome P-450 [1].



Binuclear porphyrin-like complexes forming highly reactive oxidizing species with unprecedented properties

Although metal phthalocyanine and porphyrin complexes are widely used in many catalytic applications and their catalytic chemistry is well-documented [2], their dimeric counterparts, in particular, μ-nitrido diiron complexes have not been considered as catalysts until recently.

Quite unexpectedly, some single-atom bridged diiron complexes are capable of reacting with oxidants retaining their dimeric structure to form ultra high-valent diiron species. These short-living species were detected and characterized by UV-vis, EPR, ESI-MS, Fe K edge EXAFS, XANES and Mössbauer techniques [1]. Of particular interest are the unusual catalytic properties of these highly electrophilic species which are able to oxidize methane [3,4] and to perform oxidative transformation of the aromatic C-F bonds [5] under very mild condions.

Acknowledgement. Research support was provided by Agence Nationale de Recherche (ANR-08-Blanc-0183-01; ANR-14-CE07-0018-02), CNRS (PICS project 6295) and Région Rhône-Alpes.

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KN-6

Signal Enhancement with Parahydrogen for Operando NMR in Catalysis

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NMR spectroscopy is a powerful analytical technique with a very broad scope of applications in modern catalysis. It can, inter alia, provide valuable mechanistic information when used in the in situ and operando studies of model catalysts and catalytic processes. However, a relatively low sensitivity of NMR-based techniques is a major obstacle for such studies, which is particularly severe if one attempts to characterize low-concentrated species such as functional groups and active catalytic centers on the surfaces of materials, short-lived reaction intermediates, etc. A major boost in sensitivity required for such studies can be provided by the family of the so-called hyperpolarization techniques. They can enhance NMR signals by 2-4 orders of magnitude, making much lower concentrations detectable and/or dramatically reducing the required signal accumulation time.

One of the hyperpolarization techniques uniquely suited for catalytic research is based on the use of parahydrogen in reactions that involve H_2. Activation of H_2 and hydrogenation of unsaturated substrates catalyzed by transition metal complexes and clusters in solution have been successfully addressed in the past using this approach termed parahydrogen-induced polarization (PHIP). Useful kinetic and mechanistic information was obtained, and direct detection of short-lived intermediates not observable with conventional NMR has been demonstrated. We have extended this approach to hydrogenations catalyzed by heterogeneous catalysts, including immobilized metal complexes, supported and unsupported metals, and metal oxides, paving the way to developing a novel hypersensitive mechanistic tool for heterogeneous catalysis [1,2]. Several examples of PHIP studies of heterogeneous hydrogenations will be presented.

Further potential extensions of the PHIP technique will be demonstrated, including activation of H_2 by metal-free systems such as frustrated Lewis pairs. Furthermore, efforts to extend the technique toward other types of major industrial catalytic processes are under way. In addition to parahydrogen, they can be based on the use of nuclear spin isomers of other symmetric molecules. Recent progress with the catalytic synthesis and use of nuclear spin isomers of ethylene will be described. In addition to providing useful mechanistic and kinetic information, PHIP is extremely useful for boosting sensitivity in MRI studies of operating reactors. Applications that have been demonstrated recently include MR imaging of fluid dynamics in microfluidic chips and of a catalytic reaction in an operating model microreactor.

Acknowledgment. The research was supported by RSF (#14-13-00445) and RFBR (##14-03-93183, 16-03-00407).

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Elementary Steps in Surface Reactions: Mechanisms, Kinetics and Thermodynamics

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Atomistic–level understanding of surface processes is a key prerequisite for rational design of new catalytic and functional materials. In our studies, we investigate mechanisms, kinetics and thermodynamics of heterogeneously catalyzed reactions and adsorption processes on nanostructured model supported catalysts by combination of multi-molecular beam techniques, infrared reflection-absorption spectroscopy and single crystal adsorption calorimetry. By employing these methods under well-defined ultra high vacuum conditions, we study mechanistic details of complex multi-pathway surface reactions, such as hydrocarbon transformation in presence of hydrogen or selective hydrogenation of multi-unsaturated hydrocarbons. The ultimate goal of our research is obtaining detailed correlations between reactivity, selectivity and the particular structure of the catalytic surface.

Specifically, it will be shown that selective hydrogenation of the C=O bond in acrolein to form an unsaturated alcohol is possible over Pd(111) with nearly 100 % selectivity. However, this process requires a very distinct modification of the Pd(111) surface with an overlayer of oxopropyl spectator species that are formed from acrolein during the initial stages of reaction and turn the metal surface selective towards propenol formation.

In the second part, a mechanistic picture of interaction of water with model $Fe_3O_4(111)/Pt(111)$ surface will be discussed. A combination of single crystal adsorption calorimetry and infrared spectroscopy was employed to determine the adsorption and dissociation heats of water and identify the surface species. We show that water dissociates readily on iron oxide surfaces forming a dimer-like hydroxyl-water complex and proved that the generally accepted model of water dissociation to two individual OH groups is incorrect.

ORAL PRESENTATIONS

Catalytic Activity of Nanoporous Gold: Insights from a Computational DFT Study

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Recently, the research on nanostructured gold catalysts has been extended to gold alloys with less noble metals. Several recent studies reported high catalytic activity of Au-Ag nanoalloy catalysts for alkene epoxidation, low-temperature CO oxidation, and other reactions, in many cases exceeding that of monometallic Au or Ag catalysts. One special case is “nanoporous gold” (np-Au), an unsupported gold catalyst with a 3D sponge-like structure [1]. The ability of nanoporous gold to activate molecular oxygen has been attributed to a small amount of Ag impurities contained in the material. Previous theoretical and experimental studies by the authors [2-4] suggested that Ag impurities should facilitate the adsorption and dissociation of O_2 on np-Au. However, previous theoretical work suggested that a large amount of Ag was needed to significantly change the O_2 dissociation barrier [3,4], while the surface concentration of Ag is actually low.

In this study, we investigate a possibility for a direct reaction of CO and methanol with O_2 on np-Au. We use theoretical modelling on the basis of DFT. The stepped and kinked Au(321) surface has been chosen as a realistic model to represent gold surfaces with a high density of low-coordinated sites, such as those present in np-Au.

We find that, although on pure gold the adsorption strength of O_2 is too low, just a small amount of silver impurities renders it strong enough for a reaction to be feasible, at least at ambient pressure. The activation barriers for a direct reaction with O_2 (< 0.3 eV for $CO + O_2$ and < 0.5 eV for $CH_3OH + O_2$) are much lower than that for O_2 dissociation, > 0.7 eV.

These results suggest that the main mechanism of CO or methanol oxidation on nanoporous gold in a reactor should be via a direct reaction with O_2 as opposed to initial O_2 dissociation assumed in earlier studies.

Acknowledgement. This work was supported by the German Research Foundation, grants MO 1863/2-2 and MO 1863/4-1.

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S1 OP_{20}-02

Structure, Spin and Doping Effects in Oxygen Dissociation on Gold Clusters

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Gold nanoclusters have gained considerable attraction because of the high technological potential for applications in heterogeneous catalysis, electrocatalysis, nanophotonics, and biosensing. The activity of the supported gold particles was observed in different reactions involving molecular oxygen, *i.e.* oxidation of CO, primary alcohols, amines, C_3H_6, direct synthesis of H_2O_2. In some cases, the activation of O_2 via O-O bond dissociation determines the mechanism of the process including activity and selectivity. The oxygen dissociation on Au_n has been extensively studied at the atomic level, but the factors promoting the formation of active $O_{(s)}$ has been under debate.

Here we present the spin-crossing mechanism of oxygen dissociation on gold and gold-doped clusters based on spin–polarized DFT/PBE level in the scalar–relativistic approach. The models presented the special fragments of mono- and bimetallic nanoparticles: the low-coordinated Au sites (Au_{20}, Au_8), Ag or Pd residue on the flat gold terraces ($Au_{19}Ag$, $Au_{16}Ag_4$, $Au_{19}Pd$, Au_7Pd), Ag atoms segregated on Au(111) surface at the low-coordinated top and edge sites (Au_4Ag_{16}), Au atom separating of the multi-atomic Ag or Pd sites ($AuAg_{19}$, $AuPd_7$), and the low-coordinated Ag or Pd sites (Ag_{20}, Pd_8) [1, 2].

There is no information about spin of Au_nO_2 complex near the dissociation barrier, several singlet and triplet pathways corresponding to the oxidation of Au_{20} through peroxo intermediates have been examined in details. The calculation revealed that in $Au_{20}O_2$ and $Au_{19}AgO_2$ complexes the spin inversion from triplet to singlet state occurs on the last step corresponding to O–O bond rupture through singlet transition state. Taking into account the spin-crossing in oxygen dissociation on the clusters, the activation energies decreases by 10÷29 kJ/mol, but the values remain high due to the magic nature of the clusters and high values of vertical spin excitation energies. The calculated activation energy of O–O bond rupture on the facet–edge triangular fragments of the clusters were lower than those on the vertex–edge fragments and decreased with increasing Ag or Pd content.

The information helps to clarify the spin mechanisms of controlling the reactivity of magic gold and silver clusters toward oxygen, and will be useful for theorists, who study the reactions of oxygen and transition metal clusters including catalytic process.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-01-00310, and grant Leading Scientific School NSh-3171.2014.3.

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S1 OP$_{20}$-03

A Density Functional Study of Active Oxygen Species at Ceria-supported Silver Clusters

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Catalytic activity of the silver based oxidation catalysts is related to the properties of oxygen species formed on interaction of O_2 with various supported silver species (Ag islands, isolated cations, dispersed Ag_2O and $Ag_n^{\delta+}$ clusters). In the current communication molecular adsorption (MA) and dissociative adsorption (DA) of O_2 at Ag, Ag_3 and Ag_4 species deposited at $Ce_{21}O_{42}$ nanoparticle is studied.

A silver atom located at the {100} nanofacet of $Ce_{21}O_{42}$ binds O_2 molecule weakly (<0.2 eV for O_2 coordinated in end-on mode), whereas O_2 binding to Ag atom localized at the {111} nanofacet is rather strong (~1.3 eV for bridging AgOO{Ce} isomer with O_2 adsorbed in η^2-mode). DA of O_2 at Ag atom anchored at the {111} nanofacet is unfavorable: OAgO{Ce} DA-complex with one oxo-ligand in bridging position between Ag and Ce atoms and the other oxo-ligand coordinated to Ag atom is ~2 eV less stable than the most stable AgOO{Ce} MA-complex. The energy barrier for transformation of the OAgO{Ce} isomer into the lowest-energy isomer is ~0.4 eV. More stable DA structure is created when oxo-ligand at Ag atom forms a covalent bond with a neighboring O atom of $Ce_{21}O_{42}$ framework; this results in creation of a new superoxo O-O group. Such structure with one O-ligand left is ~1.0 eV less stable than the lowest-energy isomer; the corresponding transformation barrier is ~0.8 eV.

Both MA-bridging Ag_nOO{Ce} and OAg_nO{Ce} DA-structures are formed upon O_2 adsorption at Ag_3 and Ag_4 species supported on the {100} and {111} nanofacets with binding energies in the range of ~0.5-1.1 and 1.4-2.0 eV, respectively. Strong binding and specific O-O bond lengths of AgOO{Ce} structures characterizes them as stable superoxo-like species. The energy increments due to O_2 dissociation are in the range of ~0.5-0.9 eV. Calculated O_2 dissociation barriers at Ag_3 and Ag_4 clusters are 1.5-2.1 eV, indicating low rates for oxidation of supported Ag_3 and Ag_4 species. It is to be expected that active atomic oxygen of the small oxidized clusters will be rapidly consumed under conditions of catalytic conversions and that the superoxo groups will be left as dominating active oxygen species. Also our calculations show that the stability order of the lowest-energy $O_2/Ag_n/Ce_{21}O_{42}$ systems adsorption complexes indicate supremacy of the denucleation trend for the smallest silver species and ultimate preference for AgOO{Ce} MA-structures.

Acknowledgement. This work was supported by the Presidium of the Russian Academy of Sciences. Authors thanks Siberian Supercomputer Center (Novosibirsk) and Center of Collective Use (Krasnoyarsk) for provided computational resources.

S1 OP$_{20}$-04

Mechanistic Insights into Oxidation of Organic Compounds with H_2O_2 Catalyzed by Ti-containing Polyoxometalates

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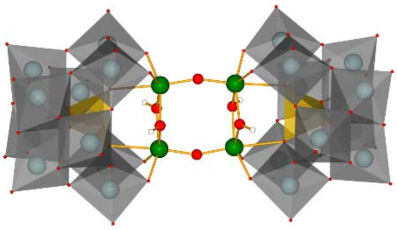
Titanium-substituted polyoxometalates (Ti-POMs) may serve as tractable soluble models of Ti centres in heterogeneous catalysts [1]. Mechanistic studies using Ti-POMs may shed light on the mechanisms of H_2O_2 activation over different types of Ti centres. Two catalytic H_2O_2-based reactions, alkene epoxidation in the presence of the sandwich type polyanion $[HTi_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{7-}$ (**1B**) and thioether sulfoxidation in the presence of $[\{\gamma\text{-}SiTi_2W_{10}O_{36}(OH)_2\}_2(\mu\text{-}O)_2]^{8-}$ (**1D**), have been studied using a combination of kinetic modelling and DFT calculations. It was demonstrated that dimer **1D** undergoes hydrolysis to produce monomeric form $[\gamma\text{-}H_2SiTi_2W_{10}O_{38}(OH)_2]^{4-}$ (**1M**) prior to the formation of active peroxo species [2].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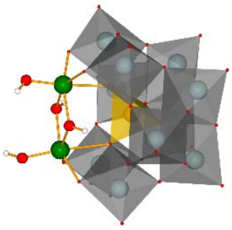
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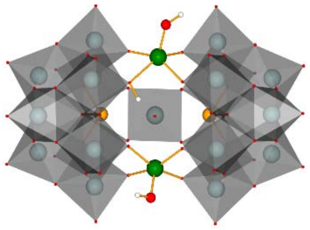
1B

Both reactions involve the formation of an active Ti(IV) hydroperoxo complex (Ti-OOH) *via* interation of Ti-OH group of POM and H_2O_2 and subsequent oxygen atom transfer from Ti-OOH to organic substrate. Oxygen transfer from both α- and β-positions in hydroperoxo group was computationally probed. For both reactions, β-oxygen transfer revealed a lower energy barrier than α-oxygen transfer. The energy barrier of β-oxygen transfer to thioether is only a bit smaller than that of the α-oxygen transfer for $[\gamma\text{-}H_2SiTi_2W_{10}O_{38}(OH)(OOH)]^{4-}$ (**2M**) (22.9 versus 24.2 $kcal\cdot mol^{-1}$) [2]. For $[HTi_2(OH)(OOH)As_2W_{19}O_{67}(H_2O)]^{7-}$ (**2B**), the barrier of β-oxygen transfer to alkene (14.7$kcal\cdot mol^{-1}$) is significantly lower than that of α-oxygen transfer (21.0 $kcal\cdot mol^{-1}$). The energy barriers of β-oxygen transfer from **2M** and **2B** calculated by DFT are close to the values determined from kinetic modelling study, which equal to 18.4 and 14.0 $kcal\cdot mol^{-1}$, respectively.

These results were rationalized in terms of the Ti coordination environment. In **2B,** 5-coordinated Ti centre significantly favours β-oxygen transfer due to lack of flexibility of the Ti coordination sphere. In contrast, 6-coordinated Ti centre in **2M** has a more flexible environment, which results in the lower energy difference for α- and β- oxygen transfer.

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Correlation between Structure and Activity of Catalytic Centres

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The concept of active sites is fundamental to heterogeneous catalysis since the catalytic surface exhibits activity only under special arrangement and chemical composition of surface layer [1]. The part of active site is often assigned to surface imperfections which behaviour is then interpreted at a qualitative level. The activity is generally enhanced at steps if the surface is not highly reactive and on the contrary, the contribution of undercoordinated sites is much less relevant on highly reactive surface. However, the exact nature and the mechanism of catalytic promotion of active sites is still a matter of discussion [2]. The report highlights a realistic model for quantitative relationship between local structure and activity of catalytic centres on the basal metal planes as applied to NH_3 synthesis and $NO+H_2$ reaction [3].

The sum of bonds Σ lost by adjacent surface atoms forming the adsorption site M_n, in comparison with bulk atoms, is taken for evaluation the local imperfection, while the reaction enthalpy at that site is considered as a measure of activity. The comparative study of M_n sites (n = 1 - 5) at perfect planes of Pt, Rh, Ir, Fe, Re and Ru is performed by semi-empirical calculations with respect to heat of dissociative N_2 adsorption Q_N and heat of $N_{ad} + H_{ad} \rightarrow NH_{ad}$ reaction Q_{NH}. The opposite $Q_N(\Sigma)$ and $Q_{NH}(\Sigma)$ variations have specified the "resonant" catalytic centres in NH_3 synthesis. The Ru and Re center particularly consists of two atoms typical of $(11\bar{2}0)$ and $(11\bar{2}1)$ planes known as most active single crystals. The resonant Σ for Fe can be provided by polyatomic centres Fe_{2-5} including a site responsible for most activity of the Fe(111) crystal face among others. The Ir center includes 4 atoms typical of (100) and (110) planes. The resonant Σ for Pt and Rh are not accessible due to steric factors, while the model predicts an extraordinary catalytic activity for clusters of 2-4 atoms.

The calculations have revealed deepened surface defects to enable the weakly bound, but much inclined to hydrogenation N_{ad} state as well as the larger by 5-8 power equilibrium NH_{ad} coverage against perfect terraces. This makes the grain boundary to be an active center for the wave nucleation in spatiotemporal phenomena observed on the Rh tip under $NO + H_2$ reaction [4]. The Σ model can be applied to other adsorption or catalytic processes exhibiting structure sensitivity.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 14-03-00285.

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S1 OP$_{20}$-06

Mechanistic Aspects of Transmetallation in Three- and Five- membered Metallacyclic Intermediates

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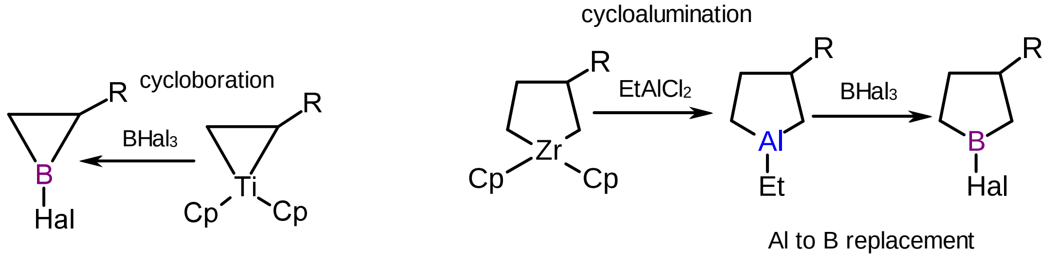
The transmetalation, i.e. the reaction of ligand exchange between metals, is widely used in synthetic practice. For example, transmetalation is a key stage in the cross-coupling reactions, which mechanism is being widely discussed in the literature only in the application to known synthetically important processes, such as the Negishi, Suzuki and Stille cross-coupling [1], etc. Despite the fact that the reactions of direct olefin cycloboration [2], catalytic cycloalumination [3], and replacement of the aluminum atom in alumolanes [4] by the boron [5] are well known, the mechanism of transmetallation in three - and five-membered metallacyclic systems remains questionable. Thus, the aim of the work is a quantum chemical study (PBE/3z, Priroda 6.0 [6]) on the mechanism of transmetallation of titanacyclopropane and 3-substituted zirkona(alumina)cyclopentanes by the aluminum and boron halides..



As a result, the theoretical models of the transmetalation mechanisms for the three- and five-membered metallacycles have been suggested. It is found that titanacyclopropane transmetalation runs through two steps *via* an intramolecular transformation of the product of $BHal_3$ insertion in the metallacycle, while the Zr-Al and Al-B transformations of five-membered systems are multistage process, which proceed via 1,4-dialumina- or 1,4-diboron-derivatives.

Acknowledgement. This work was supported by the Russian Foundation of Basic Research, grant 14-03-00295.

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Hysteresis Effect and Coexistence of the Steady State and Self-oscillations under CO Oxidation over Pd Foil

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Under study of CO oxidation reaction over Pd foil in a plug-flow reactor the hysteresis effect is observed during reactor heating and subsequent cooling in the gas mixture ($P(O_2)/P(CO) \geq 2.5$). Namely, under reactor heating the sharp increase of the CO conversion at certain temperatures is observed, while under cooling the CO conversion decreases more gradually, and the self-oscillations are observed in some prolonged temperature range. It is noteworthy that CO conversion under reactor cooling is characterized by smaller values than under heating. Application of XPS showed that after several heating/cooling cycles the surface of Pd foil, which initially was in metallic state, became partially oxidized, i.e. covered by surface oxide like 2D-PdO, which under heating in the gas mixture transformed into the thick layer of PdO phase.

At the present time there are some kinetic models, which consider the reversible oxidation of the Pd surface and qualitatively describe the relaxation oscillations under CO oxidation reaction (for example, see STM model [1]). In [2] we developed the model which is based on the STM redox mechanism and takes into account stepwise dependences of the rate constants of some reaction steps on the concentration of adsorbed oxygen on the surface. Under such prepositions this modified STM model allowed us to describe the multi-mode self-sustained oscillations under CO oxidation reaction that was experimentally observed over Pd/Al_2O_3. Basing on the experimental data, we assume in this work that under steady state conditions the surface of the foil consists of the mixture of bulk PdO and 2D-PdO. In accordance with modified STM model, the reaction of CO oxidation is accompanied by the reversible oxidation of 2D-PdO into bulk PdO, and the constant of the CO and oxygen interaction changes sharply at certain ratio of 2D-PdO and PdO coverages. In result, the presented modified kinetic model was capable to explain both the effect of hysteresis in the clockwise direction and the origin of self-oscillations during cooling the reactor. The developed mathematical model is in good agreement with the experimental data.

Acknowledgements

This work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (project no. V.44.1.16).

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S2 OP$_{20}$-01

Active Sites of the Functionalized Coals and Carbons for Oxygen Reduction in Fuel Cell and Friedel-Crafts Reaction

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Coal and carbon have a variety of forms, structures and properties, and a challenge to supply to a new age of catalysis as catalysts in a sustainable society; i.e., a free-noble metal catalyst for the oxygen reduction reaction (ORR) in a polymer electrolyte fuel cell and a catalyst for the Friedel-Crafts alkylation of phenol instead of strong acids and zeolites in a basic chemical medium. The active sites of various coals and carbons modified with nitrogen-, oxygen- and iron-doping for the two reactions were studied based on the compositions, structures and the surface properties using several analytical methods. The effects of nitrogen-doping of the substances on the formation of the defect structure with pyridinic and pyrrolic nitrogens, of iron addition on the promotion of the activities and deterioration and of oxygen-doping of the carbons on the Friedel-Crafts reaction of phenyl were studied.

The nitriding of coals formed many edges of disordered and defective carbons and the destruction of the graphite layers (nanocarbon structure) and increased the pyridinic and pyrrolic nitrogens based on the XPS and TEM [1]. The active sites were formed with both the iron and the nitrogen-doped carbons, although the iron overlapped the nitrogen sites and restrained the ORR activity of the functionalized coals.

The functionalized carbons for the ORR were studied to elucidate the catalytic properties of the active sites doped with nitrogen and iron. The active sites of the nitrogen-doped graphite for the ORR were generated on the pyrrole-NH and pyridine-NH$^+$ converted from pyridine-N by attacking the proton. The pyridinic group (=N) as a basic site was changed to an acid site (-NH) to create the active site. The oxidized carbons hardly catalyzed the ORR. The 0.5 wt% iron-doped graphite had an extremely improved ORR of 0.82 V for iron tetraphenylporphorin/carbon. The iron formed sites different from the nitrogen species sites, but more iron addition overlapped with these species sites.

The iron was formed on the graphite carbons as a reaction site and facilitated the Friedel-Crafts alkylation of phenol with *tert*-butyl bromide [2], while the nitrogen species sites as the base catalyst by nitriding did not catalyze it. The oxidized carbon catalyzed the bromination to yield bromophenols rather than the Friedel-Crafts alkylation. The iron was formed on the graphite as a reaction site and activated the alkylation, while the functional oxygen group promoted the bromination as acid sites.

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Mechanism of Ethanol Reforming into Syngas on Complex Oxides Promoted by Pt/Ni+Ru

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This work presents results of studies of the mechanism of ethanol partial oxidation, steam and dry reforming into syngas for nanocomposite catalysts with a high oxygen mobility and reactivity required to provide coking stability (Pt/PrSmCeZrO, La(Pr)$Ni_{0.95}Ru_{0.05}O_3$/Mg-Al_2O_3, Ru+Ni/$MnCr_2O_4$, Ru+Ni/$MnCr_2O_4$/Mg-Al_2O_3 [1, 2]) by using transient kinetic methods (H/D and ^{18}O SSITKA, chemical relaxations, pulse titration studies) combination with microcalorimetry and FTIRS *in situ*. Surface species (ethoxy, adsorbed ethanol, acetaldehyde, acetate, etc) were identified and their thermal stability and reactivity were estimated. Acetate species were shown to be spectators for all types of catalysts. Transformation of ethoxy species by dehydrogenation is a fast step, while the rate-determining stage is the C-C bond rupture in thus formed acetaldehyde on metal sites yielding CO and H_2. Ethanol transformation in pulses fed to catalysts in the steady-state (ss) proceeds with the rate and products selectivities close to those in mixed pulses of ethanol with oxidants. The step of the catalysts reoxidation by oxidants (CO_2, H_2O, O_2) is fast producing, along with CO (or CO_2 for O_2 pulses due to acetates oxidation) and H_2, reactive oxygen species rapidly migrating along the surface/domain boundaries to metal sites. Hence, steady-state reaction of EtOH reforming is described by a simple redox scheme with independent stages of EtOH and oxidants activation. The strength of oxygen bonding with the ss surface corresponds to bridging M_2O forms (heat of O_2 adsorption ~ 600 kJ/mol for fluorite and perovskite-like supports, and ~400 kJ/mol for spinel).Transformation of ethoxy species on the acid sites of alumina-supported catalysts produces C_2H_4 and $(C_2H_5)_2O$ by-products via dehydration route. This impact of this side reaction is minimized by suppressing alumina support acidity with Mg addition and increasing redox ability of supported oxides (adding Pr to perovskites and increasing Mn content in spinel).

Acknowledgement. Support by FP7 BIOGO project, Russian Ministry of Education and Science and V.45.3.8 BBF project of BIC is gratefully acknowledged.

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S2 OP_{20}-03

The Self-sustained Oscillations in CO Oxidation and Structural Transformations of Platinum Metals Supported on Carbon Materials

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The reaction of CO oxidation is the main model reaction for development of catalytic mechanisms in heterogeneous catalysis. The kinetic studies of this reaction are accompanied by complex dynamical behaviour which involves critical phenomena, hysteresis and self-sustained oscillations. Being highly sensitive to the state of the active component the CO oxidation reaction provides essential information about the structural transformations of the catalyst in the reaction conditions. In this work we used TEM and XPS to study the transformations of structural and electronic state of palladium and platinum responsible for the oscillatory behaviour. We used carbon supports with different structure and surface properties - few-layer graphene (FLG) and nanofibers (CNFs). We also studied how N-doping influences the properties of carbon materials and, therefore, the state of the supported metal.

Initially palladium and platinum form well dispersed nanoparticles on the surface of carbon supports. The self-sustained oscillations were observed during cooling of the studied samples in the reaction mixture. Surprisingly the oscillatory behaviour was observed for the catalyst Pd/N-CNF during heating as well. The XPS data allowed us to reveal the changes in the ratio between the oxidized and the metal state of Pd/Pt in the initial catalysts and the catalysts after reaction. The oscillations observed during cooling were found to be related to the redox transition of the active component. According to TEM data this process is accompanied by changes in dispersion and arrangement of the nanoparticles. In the case of FLG the nanoparticles interact weakly with the support and start to sinter and migrate to the defective areas such as sheet folds and edges. The defective surface of carbon nanofibers anchors the nanoparticles stronger and the changes we observed are generally connected with restructuring of the particles surface. The doping of carbon supports with nitrogen changes the defective structure of carbon and forms new defective areas for stabilization of Pd and Pt. TEM and XPS data has shown that the oscillations observed during heating are connected with strong redispersion of metal and with its incorporation in the carbon support.

Thus, the thorough catalytic experiments with detailed investigation by TEM and XPS allowed us to reveal the occurrence of two types of oscillation mechanisms – the known redox mechanism and the mechanism related to intercalation of metal into graphene layers.

Acknowledgement. This work was supported by the Skolkovo Foundation (Grant Agreement for Russian educational organizations no. 3 of 25.12.2014).

In Situ Study of the Activation Bimetallic Catalyst for Multi-walled Carbon Nanotubes Growth

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Multi-walled carbon nanotubes (MWCNTs) are known as one of the most promising materials for various applications due to their remarkable mechanical, chemical, and electronic properties. Properties of MWCNTs significantly depend on their structure (defectiveness, diameter distribution, morphology of agglomerates, concentration of impurities etc.) which in turn depends on the type of catalyst (nature and dispersion of active metals, nature of support and promoters) and on reaction conditions used during nanotube production. It was found that bimetallic catalysts are more effective than monometallic. In the present paper, we study the formation of the active component of various bimetallic catalysts during MWCNT growth using in situ synchrotron radiation X-ray diffraction analysis (SRXRD) and in situ XPS in combination with ex situ HRTEM, solid-state ^{59}Co NMR, and gas chromatography. HRTEM, Raman data, thermal dependence of conductivity and magnetoresistance measurements were used to characterize relationship between MWCNT defectiveness and catalyst composition. Bimetallic oxide catalysts were produced via polymerized complex route based on the Pechini-type method, which provides the production of highly dispersed oxide systems containing homogeneously distributed metal ions of active components and support. MWCNTs were synthesized in a flow integral reactor via ethylene decomposition on the catalyst surface at 600-680ºC (C_2H_4 : Ar mixture 1:1, 15–60 min).

According to the XRD data, catalyst active components (alloyed metal particles) are solid or at least contains crystalline core during CNT growth. At the same time alloy particles smaller than 5-7 nm are roentgen-amorphous in the conditions of the reaction. Sintering rate of active metal particles during catalyst activation is an important factor, which determines the diameter distribution of growing MWCNTs. For the first time we have obtained data confirming a stepwise formation of bimetallic alloy. It was found that cobalt particles are formed at the first stage of catalyst reduction (Fe-Co catalysts). These primary particles promote (via spillover of activated hydrogen) the reduction of Fe species with the subsequent formation of the alloy. We observed a linear dependence of a ratio of intensities of 2D (two-phonon scattering) and D (disorder-induced) bands (I_{2D}/I_D) on the mean diameter of MWCNTs produced with two different types of catalysts. It should be mentioned that each type of catalyst provides the linear dependence with its own specific slope. The difference in slope can be explained in terms of differences in kinetics and energy parameters of the main steps of MWCNT growth for different type catalysts. The graphene fragments have been proposed to form a mosaic structure of nanotube walls .The obtained data can be used to provide the process kinetic model development and to optimize the synthesis conditions to produce MWCNT with controlled properties.

Acknowledgement. This study was partially supported by grant of the Ministry of Science and Education of RFMEFI60714X0046.

S2 OP_{20}-05

Parahydrogen Enhanced NMR for Mechanistic Studies: from Exploring New Catalytic Systems to Microfluidic Reactor Imaging

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Parahydrogen applications in NMR vary from production of highly polarized substances for NMR/MRI sensitivity boosting to mechanistic studies of chemical reactions consuming H_2 as a reagent. Both of these fields attract a considerable attention among specialists. The use of parahydrogen is based on the hyperpolarization of nuclear spins arising due to the so-called parahydrogen-induced polarization (PHIP). Commonly, PHIP is produced when parahydrogen, the readily available nuclear spin isomer of H_2, participates in chemical processes such as catalytic hydrogenation leading to highly enhanced NMR signals of reaction products.

Here, we present our results on studying metal-free H_2 activation and microfluidic reactor NMR imaging assisted by the use parahydrogen. At the first part, we consider pairs of various sterically separated (‘frustrated’) Lewis acids and Lewis bases (FLPs), which were reported to split dihydrogen. We have found that molecular tweezers, i.e., the unimolecular FLPs containing functional centers connected by a chelating molecular link, are capable to produce PHIP of tweezers-captured parahydrogen molecules [1]. Despite the progress in FLPs chemistry and applications, a detailed mechanism of H_2 splitting by FLPs is still debated. We present a systematic study of PHIP effects observed for series of ansa-aminoborane compounds differing in structure. In particular, we discuss new paths of hydrogen activation in addition to ones reported [2]. In the second part, we consider microfluidic reactor imaging. NMR imaging is one of the rare candidates for in situ monitoring of physico-chemical processes, since it has versatile and rich toolkit for mass transport visualization. However, conventional NMR imaging techniques suffer from low sensitivity, which makes studies of microfluidic reactors practically impossible. We show that by combining remote-detection (RD) NMR and (PHIP) we can overcome the limitations. We used this technique for imaging the mass transport, adsorption effects and progress of gas-phase hydrogenation reaction inside cylindrical micro-scale packed-bed reactors of 150-800 μm in diameter [3].

Acknowledgement. This work was supported by the Russian Science Foundation (grant #14-13-00445) and RFBR (14-03-93183-MCX-a, 16-03-00407 A).

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Metathesis of C_2H_4 and 2-C_4H_8 to C_3H_6: Effect of Support and Kind of MoO_x and WO_x Species on Selectivity and Reaction Pathways

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The metathesis of C_2H_4 and 2-C_4H_8 has become an attractive commercial route for producing polymer-grade C_3H_6 on WO_x-based catalysts above 523 K [1]. MoO_x-containing counterparts are promising alternative since they operate at lower temperatures [2]. Isolated and polymerized MeO_x (Me=Mo or W) species are assumed to catalyze the reaction [2]. It is also known that acidic properties of the catalysts affect their activity. However, the relationships between the above catalyst properties and metathesis performance including 2-/1-butene isomerization are still not fully established. Therefore, the present work was aimed at elucidating: i) the effect of the structure and Brønsted acidity of MeO_x species on their activity and ii) mechanistic and kinetic aspects of C_3H_6 formation over differently structured MeO_x species.

Catalysts with Me (Mo or W) loading of 0.15 and 1.5 Me/nm^2 on various Al_2O_3-SiO_2 (0-70 wt.% SiO_2) supports were prepared by incipient wetness impregnation with ammonium heptamolybdate. They were characterized by N_2 adsorption, ICP, XRD, UV-Vis and Raman spectroscopy, H_2-TPR and IR pyridine adsorption. Metathesis reaction (C_2H_4/trans-2-C_4H_8/N_2=5/5/1) was carried out in continuous flow fixed-bed reactors. Mechanistic aspects of C_2H_4 and trans-2-C_4H_8 interaction with Me-carbene species of different structure were elucidated by temporal analysis of products (TAP).

Our characterization study revealed that all catalysts with 0.15 Me/nm^2 possess highly dispersed MeO_x species, while those with 1.5 Me/nm^2 and SiO_2 content in Al_2O_3-SiO_2 higher than 20% contain small amounts of crystalline MeO_3 in addition to polymerized MeO_x sites. Brønsted acidity of MeO_x species was established to determine the rate of C_3H_6 production [3], while the structure of MeO_x species influences the reaction pathways leading to C_3H_6 [4]. C_3H_6 is directly formed through metathesis of 2-C_4H_8 and C_2H_4 over polymerized MeO_x species. Contrarily, highly dispersed MeO_x species initially isomerize 2-C_4H_8 to 1-C_4H_8 followed by the metathesis of 2- and 1-C_4H_8 to C_3H_6 and C_5H_{10}.

To clarify the effect of the kind of MeO_x species on reaction pathways of C_3H_6 formation, we investigated the kinetics of C_2H_4 and trans-2-C_4H_8 interaction with the catalysts in the TAP reactor. It was established that Me-carbenes formed from highly dispersed MoO_x adsorbed C_2H_4 stronger than those originated from polymerized MeO_x. Moreover, Mo-carbene species resulted from trans-2-C_4H_8 bound C_2H_4 weaker than those formed from C_2H_4, i.e. consisting of one or two carbon atoms.

In summary, the kind of MeO_x structures was found to determine C_3H_6 selectivity in the metathesis of C_2H_4 and 2-C_4H_8. Compared to isolated tetrahedral MeO_x species, their polymerized octahedral counterparts show significantly lower activity for isomerisation of 2- to 1-C_4H_8 thus hindering non-selective metathesis of these butenes. In addition, they reveal higher ability to engage C_2H_4 in C_3H_6 formation.

Acknowledgement This work was supported by DFG (project KO 2261/3-1, Li 2047/1-1).

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S2 OP$_{20}$-07

Cross-Metathesis between Polynorbornenes and Poly(1-octylene) Mediated by Grubbs' Catalysts

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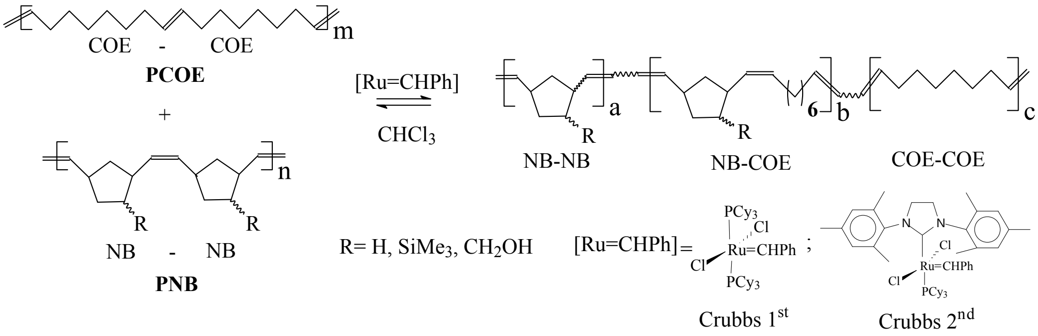
Olefin metathesis became one of the powerful methods in modern organic chemistry and polymer synthesis. However until now cross-metathesis between polymers has remained outside the attention of scientific community. Only recently a few publications devoted the polymer cross-metathesis (PCM) as a new approach to synthesis of multiblock-copolymers have appeared [1,2]. In this study, we carried out the cross-metathesis between polynorbornenes (PNB) and poly(1-octenylene) (PCOE) using the 1st and 2nd generation Grubbs' catalysts.



PCM in d-chloroform mediated by Grubbs' catalysts was studied by monitoring the kinetics of carbenes transformation and evolution of the dyad composition of polymer chains with in situ 1H and ex situ 13C NMR spectroscopy. At the first stage of the reaction all the initial Ru-benzilydene carbenes were transformed into Ru-polyoctenamer carbenes. Polynorbornene-bound carbenes are detected in very low concentrations throughout the whole process thus indicating their higher reactivity, as compared with the polyoctenamer-bound ones. The second stage - interpolymeric reactions - proceeds much slower. Its rate is limited by the interaction of polyoctenamer-bound carbenes with polynorbornene units, which is hampered, presumably due to steric reasons. Introduction Me_3Si- and $HOCH_2$- substituents in norbornene reduced the rate of PCM substantially. Grubbs 2nd turned out to be much more active than Grubbs 1st catalyst and gave the possibility to obtain multiblock statistical copolymers in the short time.

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Synergetic Effect of Ni_2P/SiO_2 and γ-Al_2O_3 Physical Mixture in Hydrodeoxygenation of Methyl Palmitate

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The transition metal phosphides represent the substantial interest as the promising systems for the hydrodeoxygenation (HDO) of oxygen-containing compounds from renewables, such as the triglyceride-based feedstocks. HDO of aliphatic esters into hydrocarbons proceeds through a complicated reaction network, including metal and acid-catalyzed reactions (dehydrogenation, hydrogenolysis of C-O and C-C bonds, hydrolysis and dehydration). Methyl palmitate (MP) conversion was shown is the rate-limiting stage of overall HDO reaction over silica-supported Ni_2P catalysts that are usually studied in the HDO of aliphatic esters [1]. Taking in mind the different possible routes of methyl palmitate hydroconversion (metal-catalyzed hydrogenolysis or acid-catalyzed hydrolysis) we speculated that addition of material with the acid sites to Ni_2P/SiO_2 catalyst could lead to acceleration of MP hydrodeoxygenation. To verify the above hypothesis the catalytic properties of supported Ni_2P/SiO_2 catalyst mixed with the inert material (silicon carbide) or with acidic γ-Al_2O_3 were compared in HDO of methyl palmitate.

Ni_2P/SiO_2 catalyst's precursor was prepared by incipient wetness impregnation of SiO_2 with an aqueous solution of $Ni(CH_3COO)_2{\cdot}4H_2O$ and $(NH_4)_2HPO_4$ (Ni/P ~1/2) followed by drying and calcination. The calcined precursor (0.5 ml, particle size – 0.25-0.50 mm, ~2.5 wt.% of Ni) was mixed with the SiC or Al_2O_3 (4.1 ml, particle sizes – 0.10-0.20 mm) and loaded into the reactor. After *in-situ* reduction of catalysts their catalytic properties were evaluated in trickle-bed down-flow reactor (3.0 MPa, H_2/feed - 600 Nm^3/m^3, 250-330 ^oC) on the bases of GC analysis of liquid and gas phases. XRD and TEM were used to confirm the formation of Ni_2P nanoparticles.

It was found that conversions of methyl palmitate and overall O-containing compounds increased with the temperature growth for both catalytic systems. But the activity of Ni_2P/SiO_2–γ-Al_2O_3 system in MP conversion was much higher in comparison with Ni_2P/SiO_2–SiC one. The second feature of Ni_2P/SiO_2–γ-Al_2O_3 system was the noticeable difference in conversions of MP and overall O-containing compounds in contrast with Ni_2P/SiO_2 catalyst that demonstrated the coinciding of these values along with negligible amounts of O-containing intermediates indicating that conversion of MP was the rate limiting stage of overall HDO reaction over Ni_2P/SiO_2 catalyst. The tentative reaction scheme and hypothesized mechanism of MP hydrodeoxygenation with the participation of metal and acid sites have been proposed. The obtained results led us to conclusion that γ-Al_2O_3 acid centers provide additional route for MP transformation trough the acid-catalyzed reaction of MP hydrolysis with the formation of palmitic acid and methanol.

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S2 OP$_{20}$-09

New Approach to Reactivity Umpolung of Aliphatic Nitro Compounds. The Mechanistic Consideration

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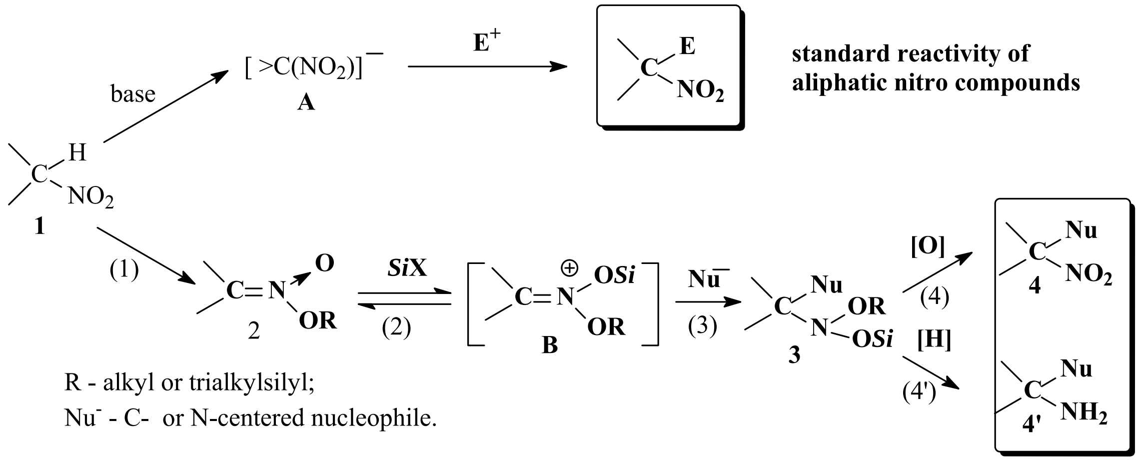
Aliphatic nitro compounds behave usually as α-C nucleophiles (Scheme 1, upper part)[1]. Here we suggest a quite new algorithm of reactivity umpolung for aliphatic nitro compounds that includes four steps.



R - alkyl or trialkylsilyl;
Nu⁻ - C- or N-centered nucleophile.

Scheme 1.

Initial aliphatic nitro compounds **1** have transformed on the first step into silyl- or alkyl nitronates **2** *via* standard procedures. Then reversible generation of cations **B** was realized by treatment of products **2** with power electrophiles containing R_3Si-group. The key step of this sequence is the stereoselective coupling of cationic intermediates **B** with appropriate nucleophiles to give the respective nitroso acetals **3.** Finally the latter can be oxidized into functionalized nitro compounds **4** or on the contrary reduced into functionalized amines **4'**. One could discuss this sequence as really catalytic process (R_3SiX – the catalyst).

Cations **B** have observed through dynamic NMR and their thermodynamic parameters were determined as well. The reactivity of cations **B** was evaluated within the universal scale of reactivity suggested by Prof. H. Mayr[2]. The coupling stereocontrol is achieved *via* evident preference of *trans-anti-parallel* approach of nucleophile against to arising lone pair electrons of nitrogen atom. The coupling (stage (3)) has general second order (the first order by each reagent).

The conclusions mentioned above allows one to use effectively this approach in target organic synthesis.

Acknowledgement. This work supported by the RFFI, grant 15-03-05703.

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Photocatalytic Hydrogen Evolution under Visible Light over Me/$Cd_{0.3}Zn_{0.7}S$ (Me = Au, Pt, Pd): Transformation of Metal co-Catalysts During the Irradiation

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Hydrogen as environmental friendly and high-energy fuel has attracted attention all over the world for the last decade. Photocatalytic water splitting under the visible light is a very promising and interesting method of the H_2 production. $Cd_{1-x}Zn_xS$ solid solution with a controllable bandgap width and band-edge position is an efficient photocatalyst for H_2 production under visible light. To improve the photocatalytic activity of $Cd_{1-x}Zn_xS$ solid solution, many modification approaches have been developed. CdS and $Cd_{1-x}Zn_xS$ have usually been coupled with noble metals such as Au, Pt, and Pd acting as co-catalyst. Earlier it has been shown that for platinum deposited on $Cd_{1-x}Zn_xS/Zn(OH)_2$ an increase in nanoparticle dispersity with further aggregation of the nanoparticles during the photocatalytic hydrogen evolution is observed [2]. The transformations of Au and Pd on the surface of $Cd_{1-x}Zn_xS$ during the hydrogen evolution have not been discussed before, while these processes can affect the photocatalytic performance.

In present research, photocatalysts Me/$Cd_{0.3}Zn_{0.7}S$ (Me = Au, Pd, Pt) were investigated in cyclic experiments on the photocatalytic hydrogen evolution under visible light. The mechanism of activation/deactivation of Me/$Cd_{0.3}Zn_{0.7}S$ photocatalysts was explained using XPS, HRTEM, and XRD techniques. The initial activation of all the photocatalysts during the hydrogen evolution was observed. The rates of the hydrogen evolution over Au/$Cd_{0.3}Zn_{0.7}S$ and Pt/$Cd_{0.3}Zn_{0.7}S$ reach the plateau after 7.5-9 hours of the reaction whereas in the case of Pd/$Cd_{0.3}Zn_{0.7}S$ the rate of the hydrogen evolution grows for 6 hours and then becomes to fall. These peculiarities are likely connected with the initial metal state: palladium exists in PdO form while gold and platinum are in the metallic state.

Acknowledgement. The work was supported by base budget project V.44.2.11 and additionally was partially supported by RFBR via project # 15-33-20458 mol_a_ved, RF President Grant MK-3141.2015.3, and the Skolkovo Foundation (Grant Agreement for Russian educational organizations no. 5 of 30.12.2015).

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S2 OP_{20}-11

Active Sites in Ni-containing Catalysts for Selective Phenylacetylene Hydrogenation

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Styrene is an intermediate product of the first step of phenylacetylene hydrogenation. It readily undergoes further hydrogenation to give ethylbenzene. Modification of adsorption properties of active sites seems to be a promising way to improve styrene selectivity.

In this work *in situ* and *ex situ* study (DSC, TPR, XPS, EXAFS etc.) of Ni-containing catalysts supported on nanodiamond (ND) was performed to reveal both the structure of active sites and the role of metal-support interaction in their formation. ND supported catalysts were prepared by the impregnation method. Precursor decomposition was monitored by DSC-MS.

Temperature programmed reduction (TPR) study of monometallic Ni/ND catalysts revealed two forms of supported Ni particles differed in the reduction temperature. These forms of Ni were attributed to the different strength of Ni-support interaction. It was suggested that oxygen-containing functional groups on ND surface participated in metal precursor coordination during catalyst preparation. The coordination on Ni atoms in the catalysts was studied by extended X-ray absorption fine structure (EXAFS) spectroscopy using wavelet transform with modified Morlet function. Comparison of the experimental and model EXAFS data for ND supported Ni, NiO, $Ni(CH_3COO)_2$, and $NiCO_3$ confirmed the presence of Ni–O–C bonds between Ni and ND. Catalytic tests in phenylacetylene hydrogenation showed that the active sites comprised strongly bonded nickel were more selective in styrene formation.

In order to vary the adsorption strength, Ni-containing catalysts were modified by the addition of Cu and Zn. TPR of non-reduced monometallic and bimetallic catalysts precursors testified that the influence of second metal on the active sites depended on the metal nature. *In situ* TPR combined with EXAFS spectroscopy was performed to clarified the role second metal in the reduction of NiO. During the preparation Zn and Ni competed for similar adsorption centers on ND surface, while Cu and Ni occupied different sites. As a result the number of strongly bonded nickel sites in NiZn/ND catalyst decreased. Since these sites were responsible for styrene formation, this led to low phenylacetylene conversion and styrene selectivity. In the case of CuNi/ND Cu only modified the adsorption characteristics of the catalysts. Owing to different role of Cu and Ni, high styrene selectivity of CuNi/ND catalyst didn't decrease phenylacetylene conversion.

Acknowledgement. This work was supported by Russian Scientific Foundation (14-33-00018) and Lomonosov Moscow State University Program of Development.

S2 OP$_{20}$-12

Effects of Magnetic Field and Oxygen on Catalytic Hydroperoxide Decomposition in Mixed Micelles with Cationic Surfactants

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Hydroperoxides (LOOH) are the primary products of hydrocarbon and lipid oxidation. Cationic surfactants (S) have been found to form mixed micelles together with amphiphilic hydroperoxides and catalyze their decomposition into free radicals. The formation of mixed micelles {mLOOH..nS} was studied and confirmed by NMR, dynamic light scattering (DLS), and tensiometry. In micelles with cationic surfactants, the peroxide bond evidently is located in a strong electrical field of the electrical double layer with strength of ~105—107 V·m^{-1}, weakening this bond and stimulating the homolytic decomposition. The activation energy of the LOOH thermal decomposition is 90—120 kJ mol^{-1}, whereas in micelles with cationic surfactants the activation energy decreases to 40—60 kJ mol^{-1}. Radicals formed in the micelles react with an LOOH excess and peroxide radicals $LO_2{\cdot}$ are delivered to the volume:

$$mLOOH + nS \Leftrightarrow \{mLOOH\text{–}nS\} \rightarrow LO_2$$

Unpaired electrons of radicals formed are carriers of spin magnetism and can interact with magnetic fields. It is known that magnetic effects can appear only in multispin systems containing at least two spins, i.e., radical pair (RP). Magnetic fields can induce spin triplet-singlet transitions in such pairs and change their spin state and reactivity. The retardation effect of oxygen and static magnetic field on the yield of radicals during tert-butyl hydroperoxide decomposition in the reverse mixed micelles with cetyltrimethyl ammonium bromide (CTAB) has been discovered. Similar effects of oxygen and external magnetic field (60—150 mT) on the yield of radicals are observed in the catalytic decomposition of hydroperoxides in the presence of acetylcholine. Acetylcholine chloride (ACh) is a quaternary ammonium salt but contains no bulky hydrophobic substituent; so ACh has no surface activity. We have found that ACh forms larger and less ordered mixed microaggregates {mLOOH..nACh} and catalyzes the LOOH decomposition to free radicals in organic solvents similarly to cationic surfactants. In the case of ACh, the rate of radical initiation (Wi) decreases in the presence of oxygen by 24%. The decrease due to the magnetic field (150 mT) is equal to 40%. In the case of {mLOOH..nCTAB}, the field dependence of magnetic effect MEB = (Wi0 - WiB)/Wi0 was studied and high magnetic effect ME = 60% at 150mT in the absence of O_2 has been measured. It is noteworthy that the magnetic field effect reduction is observed in the presence of paramagnetic particles such as oxygen and relatively stable radicals.

Possibly, the formation of several types of diffusional radical pairs affected by the magnetic field in the micellar aggregate is a reason for the anomalously high magnetic effect. The influence of oxygen and magnetic field on the properties of the electrical double layer in which hydroperoxide decomposes to radicals also is discussed.

S3 OP$_{20}$-01

Interplay between Lewis & Brønsted Acid Sites Vanadia-based Catalysts for NH_3-SCR: a Combined *Operando*, Isotopic and Chemometric Study on an Integral Monolithic Reactor

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We perform *operando* FTIR-MS study on the Brønsted-Lewis sites interplay in an integral monolithic reactor during NOx selective catalytic reduction (SCR) using isotopic labeling and chemometric analyses. Indirect hard modeling allows discerning the vibrations of adsorbed ammonia and water overlapping bands. *Operando* IR studies of pre-adsorbed ammonia shows that adsorbed ammonia is either used for the SCR reaction, or converted into the ammonium ion, which then participates in the SCR reaction. Spatial maping along monolith channels complement works performed on kinetically restricted pelletized or powdered catalysts with valuable information on secondary effects from the water produced upstream. Chemometric indirect hard modeling allows discerning bands from adsorbed ammonia and adsorbed water, and thus evaluating the interplay between Lewis and Brønsted acid sites on vanadia based catalysts.

Acknowledgement. This work was supported by Spanish MINECO CTQ2014-57578-R, Danish "Otto Mønsted" Visting professor for M. A. B., and FEDER-Region Basse the Normandie "chaire d'excellence" for M.A.B.

The Formation of Dissolved and Oxidic Oxygen in Supported Platinum Particles and Their Reactivity towards Hydrogen

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To understand the mechanism of action of heterogeneous catalysts in the reactions of oxidative catalysis, it is important to get information about the state of active oxygen species taking part in the reaction. In this paper, XPS method is used to study the formation of platinum-oxygen species in the reaction of model catalysts Pt/TiO_2 with NO_2 and subsequent reduction of these species with hydrogen.

Pt/TiO_2 samples of approximately the same platinum content were prepared by deposition of platinum nano-particles by platinum evaporation in vacuum onto a thin film of TiO_2 on a FeCrAlloy substrate. Samples were treated in a preparation chamber of XPS spectrometer (SPECS) with NO_2 at pressure of 10^{-5} mbar according to a technique described in Ref. 1 or with H_2 at pressure varying in the range of 1-10 mbar. Pt 4*f* spectra were analysed calculating a double derivative of a function describing the Pt $4f_{7/2}$ line, which allowed us to determine the number of platinum states with different oxidation degrees [2].

When a Pt/TiO_2 sample reacted with NO_2 at room temperature, a solution of oxygen atoms in platinum particles was formed at the initial stage. The dissolution of oxygen in platinum manifested itself in a gradual shift of the Pt $4f_{7/2}$ line from its original binding energy (*BE*) value of 71.6 eV up to 72.5 eV. At that, the line maintained an asymmetric shape characteristic of metallic state. With increasing NO_2 exposure, a mixture of oxides PtO (*BE* 73.0 eV) and PtO_2 (*BE* 74.6 eV) was produced. When the sample pre-treated in NO_2 was step-by-step heated in vacuum from room temperature up to 120°C, first PtO_2 reduced into PtO, and then PtO and dissolved oxygen (Pt-O_{dis}) disappeared simultaneously to return platinum particles to the original metallic state.

The room-temperature reaction of hydrogen with a sample containing three different platinum species – Pt-O_{dis}, PtO, PtO_2 – also resulted first in reduction of PtO_2 into PtO. After PtO_2 was consumed, hydrogen began to react with PtO. Pt-O_{dis} disappeared right in the moment when PtO consumption was completed.

Recently, we had found that oxygen dissolved in platinum particles revealed a much higher reactivity towards hydrogen as compared with anionic oxygen which was a part of platinum oxide particles [3]. Based on this fact, we can assume that the NO_2 treatment of the Pt/TiO_2 samples resulted in oxygen atoms dissolved in the bulk of platinum particles and coating of the surface of the particles with a layer of platinum oxides. Thus, more reactive O_{dis} appeared to be not available for the reaction with H_2 until the surface oxide layer was reduced.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-23-00146.

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S3 OP_{20}-03

Iron Oxide Nanophases Mobility in and out $LaFeO_3$ Perovskite Lattice in Three-Ways Catalysis Probed by *In Situ* Raman Spectroscopy and Surface Analyses

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Meeting the requirements expressed by the European Commission towards the reduction of raw materials contents, $LaFeO_3$ based perovskites with severely reduced content in noble metal were targeted as potential active materials for 3-ways catalysis (TWC). The latter simultaneously combines the conversion of CO, NO and hydrocarbons. Prepared on purpose for counterbalancing the excess La/Fe ratio generally observed on solids surface and promote the presumed redox-active iron species, La-deficient catalysts were shown to exhibit higher reaction rates than the stoichiometric ones [1]. We propose here an *in situ* Raman investigation of the $La_{0.67}FeO_3$ catalyst under selected atmospheres which are relevant in TWC.

Hematite-like nano-domains were found to reversibly precipitate on the perovskite surface upon heating in oxidative atmosphere. Occurring around 300°C, this new phase, characterized by Raman lines at 212 and 275cm^{-1}, was shown to be also favoured upon partial hydration up to 400°C. When subjected to CO/He conditions, this phase is not visible anymore, and is regenerated under NO/He flow. Looking more in details at the structural fingerprints of the perovskite structure, involving phonon modes suggest that the enhancement of the catalytic activity towards 3-ways catalysis rely on the mobility of FeO_6 octahedra from the $LaFeO_3$ lattice to a Fe-rich oxide phase. The latter was shown to be strongly modified under the different model steps and seems to retain active sites of sound interest for 3-ways catalysis. In order to support this first set of findings, surface analyses including LEIS and XPS were appointed for investigating powdered and thin model surfaces, making it possible to draw an original picture of the mobility of iron entities in and out the perovskite lattice and generalise the concept of self-regeneration of catalysts [2] to nano-domains of transition metal oxides.

Acknowledgements: This work was supported by the European Commission in the frame of the FP7 project NEXT-GEN-CAT funded under the Grant Agreement # 280890.

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Formation and Structure of Active Centres in Supported Ziegler-Natta Catalysts for Olefin Polymerization on the Base of New Experimental Data

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Supported Z-N titanium-magnesium catalysts (TMC) are the most important catalysts for production of polyethylene (PE) and polypropylene (PP), but so far many important issues about formation and structure of active centers of these catalytic systems are under discussion. Earlier [1] we have found TMC with very low titanium content (≤ 0.1wt.% of Ti, TMC-0.1) show super high activity at ethylene polymerization due to high content of active centers. It was shown TMC-0.1 contains mainly isolated Ti(III) ions after interaction with AlR_3 cocatalyst as distinct from usual TMC with high titanium content (2-4 wt.% of Ti) which contain mainly Ti(III) ions as EPR invisible surface associates [2]. So we believe TMC-0.1 catalyst is suitable and real model to study the formation and structure of active centers in supported ZN catalyst and theirs reactivity in olefin polymerization.

We have found firstly the correlation between content of isolated Ti(III) ions in catalysts prepared and activated by different methods and activity in ethylene polymerization. Moreover we have identified firstly by EPR technique the surface Ti(III) species with titanium-alkyl bond. We believe these species are the real precursors of active sites in supported Z-N catalysts. The structure of these species anchored on the 110 face of activated magnesium dichloride is calculated by DFT method.

TMC with low titanium content produces at propylene polymerization mainly atactic PP. We have used the preparative TREF procedure to get quantitative data on the formation of separate fractions with different stereoreguliarity for PP samples produced over TMC with different Ti content (0.1 and 3.5 wt.%) and PP samples obtained at polymerization in the presence of external donor. Data obtained evidence on the transformations of the part of aspecific centers (AS) in TMC-0.1 to the stereospecific centers of different types (IS1, IS2, IS3) at interaction with AlR_3 and external donor. The scheme of these transformations are proposed and discussed.

Acknowledgement. The work was partially supported by the Ministry of Education and Science of Russian Federation and supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (project V 44.2.1).

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S3 OP_{20}-05

Para-, Superpara/Ferromagnetic Particles in the Ziegler Type Catalytic Systems: Structure and Reactivity

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It has been over 60 years since the discovery of Ziegler type catalysts, which had an enormous influence on the development of catalytic science in general, and polymerization, oligomerization, dimerization processes of olefins, in particular [1,2]. Ziegler type catalysts are complex systems combining transition metal complexes with aluminum-organic compounds (AOC), a catalytic action which is currently associated with the structures formed during the interaction of the components of the catalyst system. These structures in most cases are highly reactive. Isolation and study of these species, complexes by direct structural methods is currently quite challenging, and therefore, studies related to the identification, establishing their composition and structure are based mainly on the methods of optical and magnetic spectroscopy [3,4]. This paper presents the results of studies of the magnetic complexes in catalytic systems based on Co (Ni) and aluminum-organic compounds, their structure and reactivity. In situ electron magnetic resonance (EMR) spectroscopy in combination with gas chromatography/mass-spectrometry (GC/MS) technique is used to identify simultaneously the magnetic species and the gas-phase products on line conditions, to establish their transformation as a function of reaction duration, reaction conditions (reaction temperature, composition of catalytic system) participation of magnetic species in conversion of olefins. Para-, superpara/ferromagnetic intermediate complexes, particles in these systems, the products of their reactions with ethene, propene, butene are identified, their role as catalytically active species in these reactions is discussed. The EMR spectra of magnetic intermediates, most of which were obtained for the first time and is absent in the world literature are given. Experimental examples of evidence of the direct coordination of the transition ion with olefin in the system of di- and oligomerization of olefins are given.

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CO Oxidation on the Bimetallic Pd-Au/HOPG Catalysts: NAP XPS and MS Investigation

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Bimetallic systems attract the great interest of many scientific groups due to its ability to induce the significant improvement of catalytic properties compared to monometallic catalysts [1-2]. Among these systems the Pd-Au catalysts is one of the most frequently studied ones because they have exhibited high catalytic activity in a number of industrially important reactions. Although a large number of publications devoted to study of bimetallic Pd-Au systems has been 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 also temperature of calcination will affect the surface composition causing the big difference between Au/Pd atomic ratios in the bulk and surface [1-2]. 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-Au catalysts is necessary to understand the nature of active sites and help to optimize the catalyst composition for the best activity, selectivity and stability.

On the first step formation of the model bimetallic Pd-Au/HOPG catalysts has been investigated with XPS and STM [3]. The optimal temperature for the Pd-Au alloy formation ~ 400°C was found 400°C. The regularities for the preparation of Pd-Au/HOPG model catalysts with controlled particles size and Au:Pd atomic ratio were developed. The prepared model bimetallic Pd-Au/HOPG catalysts were investigated in CO oxidation with combination of in-situ XPS and MS techniques. It was shown that the prepared Pd-Au/HOPG samples started to be active in CO oxidation reaction at 100ºC. The redistribution of Au and Pd atomic concentration on the surface in the course of the reaction was investigated using in-situ XPS. It has been shown that the Au/Pd atomic ratio enhances in active state.

Acknowledgement. This work was supported by the Skolkovo Foundation (Grant Agreement for Russian educational organizations no. 5 of 30.12.2015)

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S3 OP$_{20}$-07

Kinetic Studies of Green Catalytic Processes of Wood Oxidative Delignification

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Advanced processes for obtaining cellulose from wood by ecologically friendly ways are based on the application of "green" delignification reagents (oxygen, hydrogen peroxide) and effective catalysts. This presentation summarizes the results of kinetic studies of wood oxidative delignification processes in the presence of soluble H_2SO_4 and solid TiO_2 catalysts.

Air dry saw dust (fraction 2–5 mm) of aspen wood, birch wood, abies wood, pine wood were used as initial raw material. Catalytic processes of wood oxidative delignification were studied with the use of stirring fixed-bed reactors. FTIR, XRD, SEM and chemical methods were used for study the solid products and catalysts. Low molecular mass products were identified by GC, HPLC and GC-MC methods.

The processes of wood delignification by H_2O_2 have the similar kinetic parameters regardless of the difference in wood origin and catalyst nature. They are described by the first-order equation, the activation energies are 76–91 $kJ \cdot mol^{-1}$. The established kinetic parameters points to the insignificant role of diffusion limitations at used conditions of wood delignification. The oxidative delignification of hardwood (birch and aspen) proceeds with a higher rate as compared to softwood (abies and pine) since the softwood lignins have a closed-packed structure constructed from guacyl-type units.

Taking into account the similar kinetic parameters the same mechanism of wood oxidative delignification for soluble H_2SO_4 and solid TiO_2 catalysts was supposed. Oxidative depolymerization of lignin apparently proceeds via homolytic mechanism in the presence of studied catalysts which initiate the formation of hydroxyl ($\dot{O}H$) and peroxyl ($\dot{O}OH$) radicals from hydrogen peroxide.

The catalytic delignification of wood by H_2O_2 allows to obtain the microcrystalline cellulose by one-step process thanks to simultaneous implementation of reactions of lignin, hemicelluloses and amorphous part of cellulose depolymerization. The deep oxidation of lignins with the rupture of aromatic rings take place in wood catalytic delignification with H_2O_2.

The more selective oxidation with the predominant formation of vanillin from softwood and the mixture of syringaldehydes and vanilline from hardwood was observed in the processes of wood lignins aerobic oxidation in alkaline medium at 160 °C in the presence of $CuSO_4$ catalyst. It was shown that the cellulose obtained in the process of wood lignin aerobic oxidation hydrolyzes much easier than the initial wood. At optimum conditions the pine wood was processed into vanilline (up to 18 % wt. based on lignin) and cellulose (84–93 % wt. based on the initial wood) or glucose (yield up to 70 % wt. based on cellulose).

The reported study was supported by Ministry of Education and Science RF (Project RFMEFI607 14 X0031).

S4 OP$_{20}$-01

Unified Kinetic Analysis of Solvent Effects in Complex Catalytic Reactions

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Analysis of the solvent influence on various organic reactions catalyzed by organometallic complexes, enzymatic and heterogeneous catalysts has been a subject of numerous contributions along the years. Catalytic performance might be considerably influenced by the applied solvents, which are typically classified either according to their chemical bonds; using physical constants or in terms of acid-base behavior or solute-solvent interactions.

The solvent effects in catalytic reactions comprise not only interactions with the substrate and the catalyst, but also, in case of multiphase processes, solubility of gases in the liquids as well as binding of the solvent to the surface of a heterogeneous catalyst or to catalytic species for the case of homogeneous catalysis.

Although there are many studies on the solvent effects, there are surprisingly few kinetic models of complex multistep catalytic reactions, where the solvent effects would be incorporated in the rate equations going beyond considerations of mass transfer (gas-liquid or liquid-liquid solubility) and solvent binding/adsorption.

In the current work a mathematic framework was developed for analysis of solvent dependent reaction rates in the case of complex catalytic reactions by incorporating solvent permittivity into the rate expressions. The theoretical approach was used to treat several generic reaction mechanisms and address also selectivity in various catalytic reactions. Comparison with representative data for homogeneous, heterogeneous and enzymatic catalysis [1-3] shows applicability of the developed equations for describing activity and selectivity to accurately account for experimental observations. As an example enantiomeric ratios at different solvent permittivity for acylation of alcohols in toluene-acetonitrile mixtures are presented for different alcohols in Figure 1 and compared with the theoretical predictions.

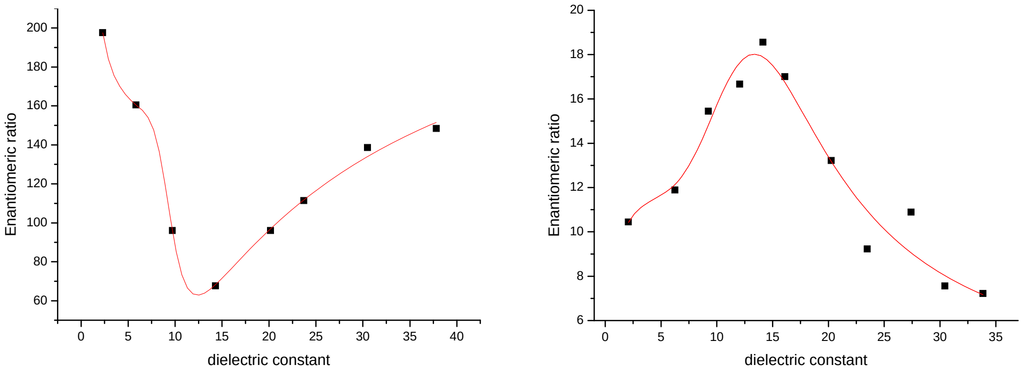

Figure 1. Dependences of enantiomeric ratio on solvent permittivity for acylation of alcohols in toluene-acetonitrile mixtures (data from [3]).

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S4 OP$_{20}$-02

Aminopyridine Manganese Complexes Catalyzed Asymmetric Epoxidation with Various Oxidants: Evidence for Multiple Mechanisms

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Catalytic asymmetric epoxidation of olefins remains the major synthetic tool to access chiral epoxides – useful building blocks in organic synthesis. Manganese aminopyridine complexes (Fig. 1A) are promissory *bioinspired* catalysts, that display high efficiencies (1000 to 10000 TN) and enantioselectivities (up to 99 % *ee*) in the epoxidations of olefins with H_2O_2 [1]. Also, these complexes were found to catalyze the epoxidation of olefins with other oxidants, such as peracetic acid, *t*BuOOH, PhIO with similarly high enantioselectivities. In this work, we report a mechanistic study of these systems, with focus on the influence of oxidants and additives on the epoxidation stereoselectivity.

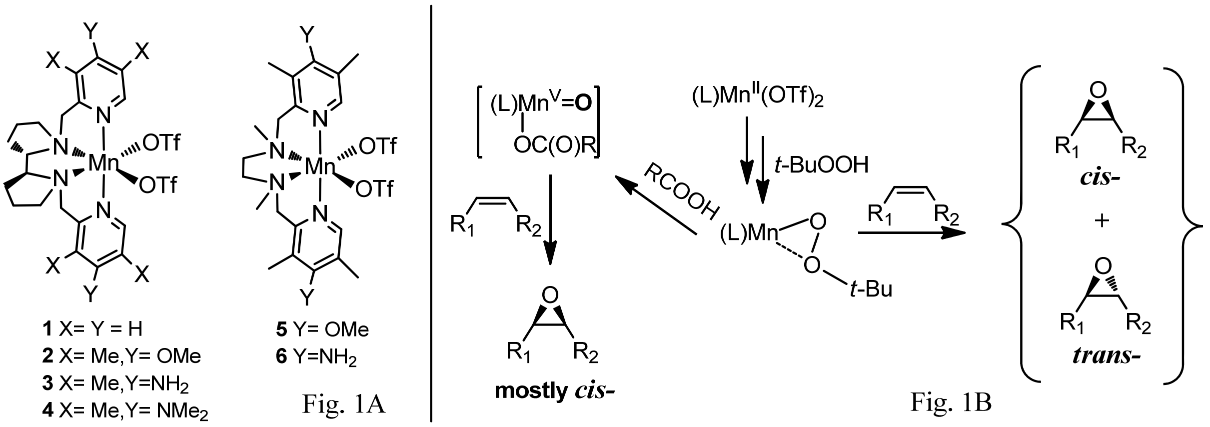

Figure 1. Aminopyridine Mn complexes (A) and plausible mechanism of epoxidation by alkylhydroperoxides (B).

The oxidations by catalyst systems **Mn**/alkyl hydroperoxide most likely occur via oxygen transfer from [(L)Mn-alkylperoxo] species to the alkene with formation of relatively long-lived acyclic, presumably radical intermediates. In the presence of added carboxylic acid (or water), the mechanism is diverted to the [LMn^V=O] driven oxidation, similar to that by catalyst systems **Mn**/H_2O_2/carboxylic acid (Fig. 1B). For oxidations with catalyst systems **Mn**/iodosylarenes, catalytic and ^{18}O-labelling data provide evidence in favor of predominant Lewis-acid activation mechanism, with the [LMn(OIAr)] adduct as the oxygen transfer agent. The epoxidations with peroxycarboxylic acids very likely occur via concerted oxygen transfer from the Mn acylperoxo intermediate to the olefin; zero incorporation of ^{18}O (from added $H_2{}^{18}O$) into the epoxide rules out the participation of high-valent oxomanganese intermediate.

Acknowledgement. This work was supported by the RFBR (#16-33-00014 and #14-03-00102).

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"One-Pot" Hydrolytic-Dehydration of Cellulose into Glucose and 5-Hydroxymethylfurfural over Solid Acid Catalysts. Kinetics and Reaction Intermediates Study

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Glucose is a valuable carbohydrate which has a wide industrial application, including the production of 5-Hydroxymethylfurfural (5-HMF). 5-HMF being one of the platform molecules is promising for wide-application in chemical industry (plastics, pharmaceutics etc.) and fuel production. We previously developed solid acid catalysts based on carbon Sibunit and Nb/ZrO_2 [1] which allow obtaining high yields of glucose (up to 46%) and 5-HMF (up to 22%) from inedible cellulose in a "one-pot" process hydrolytic-dehydration. The aim of this work was a study of kinetics and reaction intermediates as well as an elucidation of the mechanism and kinetics modeling.

The Sibunit based carbon catalysts were prepared via sulfonation by fuming H_2SO_4 at 200 °C. Zirconia was synthesized from $Zr(O^iPr)_4$, impregnated with niobium oxalate and calcined at 450 ºC. The one-pot hydrolysis-dehydration of mechanically activated cellulose was conducted under hydrothermal conditions at 180 °C. The products were analyzed by HPLC.

Cellobiose, glucose, fructose and 5-HMF appeared to be the main intermediates. Mannose, furfural, levulinic and formic acids, formaldehyde were also detected. For elucidation the mechanism of catalytic action and the role of the catalysts the intermediates (ctllulose, glucose, mannose, fructose and 5-HMF) degradation over the most active Sibunit and NbO_x/ZrO_2 was studied. On the basis of the results obtained the total process scheme was proposed and heterogeneous mechanism of the cellulose depolymerization was suggested. The dissolution of cellulose appeared to be a limiting step of the process. Rearrangement of glucose to fructose is also slow reaction. While the hydrolysis of oligosaccharides and the irreversible dehydration of fructose are rapid steps. Moreover there are different ways of glucose transformations. On the basis of the kinetics data the kinetics modeling was conducted for the cellulose hydrolysis-dehydration process. The kinetic parameters such as the reaction rate constants and the orders of the reactions were evaluated.

Acknowledgement. This work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (project V.46.4.4) and as well as by the Russian-French GDRI "Biomass".

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S4 OP_{20}-04

Catalytic Behaviour of Supported Cu_2O in Gas-Phase C-N Coupling Reaction: Influence of Deactivation Phenomena from Continuous-Flow Kinetic Observations

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Industrial synthesis of fine chemicals, drugs, agrochemicals, etc. involves the C-N coupling reaction as a key step, performed mainly as amination by homogeneous Buchwald-Hartwig Pd-ligands catalysts [1-2]. Although highly effective, such systems present important drawbacks: cost and availability of the noble metal [3], difficult catalyst separation and ligands reacting in the synthesis conditions. Efforts were therefore driven towards heterogeneous ligand-free catalytic systems based on nonprecious metals, such as copper [4].

Catalytic tests in batch conditions (autothermal pressurized autoclave) performed in our lab for C-N coupling between aniline and bromobenzene revealed conversions of aniline (after 24 h) of 1.4 % in presence of 1% Cu_2O/Al_2O_3 whereas 1% Cu_2O/ZnO and 1% Cu_2O/TiO_2 led to acceptable conversions of 37 and 40%. These results alone will erroneously correlate with the catalytic activity because the deactivation occurs with different rates, depending on the nature of the support.

The present study was carried out in differential conditions (conversions below 5%), where the effect of the surface poisoning could be clearly distinguished. A kinetic model including parallel and sequential steps for the formation of three reaction products (diphenylamine, triphenylamine and aminodiphenyl) has been proposed. The catalytic activity varies in order: $Cu_2O/Al_2O_3 > Cu_2O/TiO_2 > Cu_2O/ZnO$, indicating thus Cu_2O/Al_2O_3 as the most active catalyst that deactivates fastest. The best balance between the catalytic activity and the resistance to deactivation was observed for Cu_2O/TiO_2. An excess of aniline was also found to reduce the catalyst rate of deactivation. Characterization of the catalysts by XRD, XPS and H_2-TPD provided support for the evidenced kinetic results.

Acknowledgement. This work was supported by the Romanian UEFISCDI Project PN-II-ID-PCE-2011-3-0060ctr. 275/5.10.2011.

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Detailed Kinetic Study of Methanol Steam Reforming over Novel Pt/In_2O_3/Al_2O_3 Catalyst in a Microstructured Recycle Reactor

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A kinetic study of methanol steam reforming over bimetallic Pt/In_2O_3/Al_2O_3 catalyst was carried out. The kinetic measurements were performed in a microstructured monolithic reactor with an external recycle free of temperature and concentration gradients. By the help of residence time distribution measurements it could be verified that the reactor showed the behaviour of an ideal continuously stirred tank reactor (CSTR). The absence of external and internal concentration gradients could be proven by corresponding experiments and theoretical diagnostic criteria.

Previous investigations showed that the optimum temperature range for the operation of the bimetallic Pt/In_2O_3/Al_2O_3 catalyst exceeds 300°C at a steam-to-carbon ratio (S/C-ratio) of 1.5 [1]. Detailed investigations of the nature of the active surface performed by Barbosa et al. revealed the formation of a $PtIn_2$ alloy by XRD measurements when operating the Pt/In_2O_3/Al_2O_3 catalyst under reducing conditions [2]. The kinetic measurements revealed that in the temperature range from 310°C to 355°C the molar rate of methanol consumption mainly depends on the methanol partial pressure, especially at higher temperatures, whereas there is only minor dependence on the water partial pressure. Carbon dioxide has no inhibiting effect, whereas hydrogen showed a weak inhibiting effect.

The measured kinetic data were fitted to four formal kinetic rate models and one rate model, which was derived from mechanistic considerations.

The model discrimination revealed that the rate law derived from a mechanism, which assumes the dehydrogenation of an adsorbed methoxy-species as rate determining step, described the measured kinetic data second best. Optimum agreement with a maximum deviation of 13.5 % between observed and predicted molar rates of methanol consumption was obtained when applying a Langmuir-Hinshelwood Hougen-Watson rate law (LHHW) assuming dissociative methanol and molecular water adsorption on the catalyst surface.

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S4 OP$_{20}$-06

Mechanism of Oxidation of C-H Bonds by Homogeneous Vanadium Substituted Polyoxomolybdates

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The reactivity of various vanadium-substituted polyoxometalates with different structures and oxidation potentials was compared for the electron transfer-oxygen transfer oxidation of anthracene and dihydroanthracene as model substrates. Electron transfer initiates the C-H bond activation. Analysis of reactivity via an outer sphere electron transfer model demonstrates that in addition to the oxidation potential, the polyoxometalate structure and charge are important parameters in the electron transfer reaction. A further comparative study for electron transfer and oxygen transfer reactivity showed that the eventual formation of the oxygenated product, although initiated by electron transfer was dependent on other factors.

Mechanistic Aspects of the Gas Phase Acetoxylation of Toluene over Pd-Sb/TiO$_2$ Catalyst

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The acetoxylation of toluene is a promising alternative route for the manufacture of benzyl alcohol (BOL) via benzyl acetate (BA) and its subsequent hydrolysis. During the last decade, a highly active and selective Pd-Sb/TiO$_2$ catalytic system was developed in our group [1, 2]. However, the mechanism of this reaction was still unknown. To close such gap, we performed steady-state and transient kinetic studies in combination with (micro-) kinetic modelling. In order to gain deeper insights, the Pd-Sb/TiO$_2$ catalyst samples were also characterized by various techniques like TPR/TPO, in situ FTIR, and XPS.

Pd-Sb/TiO$_2$ catalyst was prepared by impregnation method and the contents of Pd and Sb are 10 and 16 wt%. Steady-state isotopic transient kinetic analysis (SSITKA) was carried out in an integral reactor at 210 °C and 2 bar. Thereby, $^{16}O_2$ was replaced by $^{18}O_2$ and the transients of labelled products were recorded. To elucidate the number of surface oxygen species participating in the reaction, the transients of labelled products were modelled using an integral reactor model and kinetic equations for each individual reaction step. Initial reaction rates for the formation of BA and benzaldehyde (BAL) were experimentally determined by steady-state tests.

The results showed that BA and the main by-product BAL are formed in parallel reaction pathways. This statement was also confirmed by their similar activation energy indicating a common rate-limiting step in their formation. Moreover, separate experiments were carried out by dosing BOL instead of toluene to get new insights into the nature of intermediates formed. Such studies showed that BOL is not the intermediate in the formation of BA due to its selective conversion to BAL even in the presence of acetic acid. Further mechanistic insights were obtained from transient kinetic studies. A step input from inert flow to the reaction mixture indicated the favoured decomposition of acetic acid into CO_2 and H_2O at low surface coverages. The tests performed even in absence of gas phase O_2 also showed the formation of CO_2 (by decarboxylation of acetic acid) and H_2O (formed with lattice oxygen). This fact suggests that lattice oxygen participates in the formation of oxygenated products.

The results revealed that two surface oxygen species are involved in the reaction. The rate constant (from SSITKA) for the incorporation of unselective oxygen species into the lattice was high and hence the selectivity towards BA is also high. The deduced rate equations for the initial reaction rates of BA and BAL formation could fit the experimental data very well and confirms the assumption of toluene activation as rate-limiting step.

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S4 OP$_{20}$-08

Reactive Oxygen Species and Kinetics of Oxidative Coupling of Methane over NaWMn/SiO$_2$ Mixed Oxide Catalyst

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NaWMn/SiO$_2$ oxide system is a unique catalyst for the oxidative coupling of methane (OCM). First, it provides with the highest selectivity to target products (C$_2$ hydrocarbons) at high conversions of methane. Secondly, unlike other efficient OCM catalysts, it contains two components (W and Mn) capable of changing their oxidation state during the OCM reaction. The latter correlates with the results of kinetic measurements [1] according to which the OCM kinetics over this catalyst can be described in the framework of the Mars-van-Krevelen (stepwise oxygen removal-replenish, or redox-type) mechanism. Recently we demonstrated that NaWMn/SiO$_2$ can be reduced by H$_2$ and methane and reoxidized by O$_2$ in the conditions that mimic the steady-state OCM reaction [2].

A more detailed study of the lattice oxygen of the system under discussion has revealed the presence of two types of reactive species that differ in their properties; they are further denoted as [O]-1 and [O]-2. The [O]-1 form is present in the amount of ~345 μmole O$_2$ per gram, which is equivalent to the total oxygen associated with W and Mn (corresponds to $W^{6+} \leftrightarrow W^0$ and $Mn^{3+}/Mn^{4+} \leftrightarrow Mn^{2+}$ transitions). It can be reversibly removed from the system by its reduction with H$_2$ and methane at ≤800°C. The amount of reactive oxygen in [O]-2 form is much less (16 μmole O$_2$ per gram); it can be reversibly removed from the sample by heating in inert atmosphere in the temperature range between ~640 and 800°C. In this temperature range the rate of molecular oxygen desorption can be described by the 2-nd order equation. The latter indicates that this oxygen is present in the system in a monatomic form.

Both [O]-1 and [O]-2 can be considered as candidates for the participation in the redox catalytic cycle. Also, they both can be restored by re-oxidation with molecular oxygen which starts at temperatures above 200°C and becomes practically instantaneous at temperatures typical for OCM reaction. This observation apparently contradicts to the results of kinetic measurements according to which in the framework of the Mars-van-Krevelen description the rate of re-oxidation is comparable to the rate of the active site reduction with methane. This implies that the catalyst active sites are re-oxidized via a different mechanism, namely by the direct interaction of surface OH-groups with O$_2$ molecule without the formation of intermediate oxygen vacancies. A reconsidered version of Mars-van-Krevelen scheme is suggested and discussed.

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Sterically Hindered Isobutylaluminum Aryloxides as Metallocene Activators in Homo- and Copolymerization of Olefins

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Metallocene catalysts are currently considered as the most versatile transition metal catalysts for production of different homo- and copolymers of olefins with tailor-made properties [1-4]. Metallocene catalysts contain two components, a metallocene complex and a cocatalyst (or activator). The most effective cocatalyst in modern metallocene catalysis is polymethylalumoxane (MAO) [5,6]. However the benefits of MAO as activator in practice are compensated by its drawbacks such as high cost at necessity to use it in high molar excess to pre-catalysts (up to 10^3–10^4 mol/mol) and instability under the long-term storage resulting in loss of activating features and irreproducibility of polymer characteristics formed in the presence of aged activator. So, economically it would be extremely advantageous to replace MAO by new effective, stable, and low cost activators.

Here we report the new class of effective activators. We have synthesised the set of isobutylaluminium aryloxides with tert-butyl group in the 2,4 and 6 positions of aryloxy group. It was shown that such compounds are very effective activators of metallocenes in homo- and copolymerization of ethylene and propylene, and terpolymerization of ethylene, propylene, and 5-ethylidene-2-norbornene.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 15-03-02307-a.

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S4 OP_{20}-10

A Kinetic and Mechanistic Study on the Heterogeneously Catalysed Aqueous Phase Amination and Isomerization of Biogenic Alcohols

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The catalytic amination of biogenic platform chemicals such as isohexides[1] is of major importance for the utilization of renewable resources in the production of polymers and plastics such as polyamides.[2] In this work we demonstrate for the first time the amination of sugar alcohols in aqueous solutions using Ru/C as a commercially available solid catalyst.[3]

Catalysts were screened and reaction conditions investigated and optimized at temperatures of 140-180°C. We found for the amination and the isomerization, that occurs as a side reaction, that a certain partial pressure of hydrogen is required for the reaction to occur. So far, the mechanism was expected to be based on the hydrogen autotransfer mechanism ("borrowing hydrogen") comprising three reaction steps: 1) an initial dehydrogenation of the alcohol to the ketone, 2) the formation of the imine with ammonia, and 3) the subsequent rehydrogenation to yield the primary amine, as proven for the homogeneously catalysed amination. Despite following the same reaction route without overall hydrogen consumption the hydrogen autotransfer mechanism apparently can be excluded when using a solid catalyst since a certain coverage of the active species on the catalysts surface with hydrogen is required to enable the reaction and shift it towards the products. Hence, reaction kinetics of both reactions, the amination and the isomerization, were investigated and in case of the isomerization also modelled to gain insights into the reaction path and mechanism. Results of the kinetic study and isotope labeling experiments carried out with D_2O/H_2 proved that besides the hydrogen autotransfer mechanism apparently a second mechanism based on a direct hydride exchange occurs in parallel and plays a key role in the formation of intermediate species and by-products.

Overall, investigation of the reaction kinetics and the mechanism of the amination and isomerization of isohexides gave valuable insights into the aqueous phase catalytic conversion. The basic understanding is essential for further process development also concerning the catalytic conversion of biogenic alcohols in general.

Acknowledgement. This work was supported by the German Federal Ministry of Food and Agriculture via the Fachagentur für Nachwachsende Rohstoffe, grant 22024111.

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Kinetic Modelling of One-Pot Alcohol Amination over Gold Catalyst

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One-pot alcohol amination giving complex amines is of great importance in organic synthesis, providing access to valuable alkyl amines widely used as pharmacophores in numerous biologically active compounds, dyes, agrochemicals and functionalized materials. Synthesis generally consists of three consecutive steps: dehydrogenation of an alcohol to a reactive aldehyde, which reacts with an amine to produce a corresponding imine and finally hydrogen transfer from the alcohol to the imine *via* metal-hydride intermediates with the amine formation. Despite a high potential of the process from the industrial viewpoint the reaction kinetics has been described only to a limited extent. In the present work, the main attention is focused on the investigation of the main kinetic regularities of one-pot alcohol amination with the further development of the kinetic model.

One-pot myrtenol amination with aniline over Au/ZrO_2 catalyst was studied in a batch reactor in the temperature range 413-453 K under nitrogen pressure [1]. To explore the main kinetic regularities each step as well as the overall process were investigated in details over Au/ZrO_2 catalyst, ZrO_2 and without any catalyst. The impact of non-catalytic reactions, namely the second step of aldehyde condensation with aniline, was estimated during the build-up of the kinetic model. Special attention was given to study of the catalyst deactivation. Based on the data obtained for myrtenol amination over Au/ZrO_2 catalyst the reaction mechanism was proposed. Catalyst deactivation and the non-catalytic reaction were taken into account in this kinetic model, along with the main reaction routes. The system of differential equations was solved numerically with the backward difference method by minimization of the sum of residual squares with non-linear regression analysis using the Simplex and Levenberg-Marquardt optimization algorithms implemented in the modelling and optimization software ModEst. Comparison of the kinetic model with experimental data through numerical data fitting shows high degree of explanation confirming applicability of the proposed mechanism as well as the deactivation function to describe experimental data of the title reaction. The developed model is generic one and can be used for a number of other hydrogen borrowing reactions.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 16-33-60028.

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S5 OP$_{20}$-01

The Pathways of 2,4,6-Trinitrobenzoic Acid Transformation in the Aqueous-Phase Hydrogenation. Development of Advanced Pd/Sibunit Catalysts for Exhaustive Hydrogenation

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The catalytic hydrogenation of trinitroaromatic compounds is of interest for development of theoretical bases of the liquid-phase hydrogenation of organic compounds, and has practical importance for utilization of explosives. Strong adsorption of trinitroaromatic on the surface of catalysts, high exothermic effect, and side-reactions between the intermediates to polymers initiate studies that aim both to reveal the effect of reaction conditions on the rate and conversion and to obtain new stable catalytic systems. Our study examined the effect of 2,4,6-trinitrobenzoic acid (2,4,6-TNBA) hydrogenation parameters and conditions of the catalyst synthesis on the process rate and selectivity. The work was aimed to reveal the directions of 2,4,6-TNBA transformations in the aqua-phase catalytic reaction.

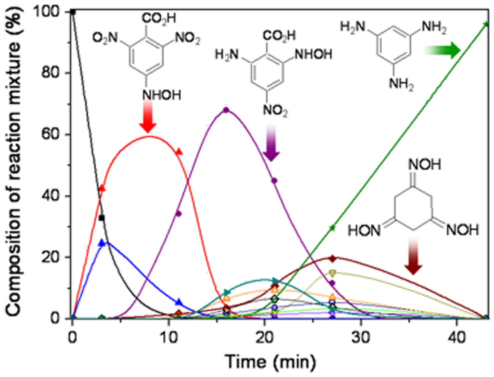

Fig. 1. The change of reaction mixture composition during TNBA hydrogenation

The mesoporous carbon material Sibunit was chosen as a support for the palladium catalysts. The Pd/C catalysts, C(Pd)=0.5-5.0 wt.% was synthesized by the hydrolytic precipitation of palladium polyhydroxo complexes (PHC) on the surface of carbon followed by the reduction of palladium with sodium formate. Particle size was determined by TEM and CO chemisorption. The ^{1}H and ^{13}C NMR spectra were recorded on an Avance-400 (Bruker) NMR spectrometer. The hydrogenation was studied in different media and water with the addition of $NaHCO_3$ was found to be the most efficient solvent. The hydrolysis of H_2PdCl_4 was performed with precipitants containing the K^+, Na^+ and Li^+ cations and the CO_3^{2-}, HCO_3^- and OH^- anions. The relationship between palladium particle size and the catalyst activity was found. The suggested conditions of the hydrogenation of 2,4,6-TNBA (hydrogenation in an aqueous medium at a temperature of 50°C, pressure 0.5 MPa and $g_{TNBA}/g_{cat} = 400$) made it possible to perform a complete hydrogenation of all nitro groups and to selectively produce 1,3,5-triaminobenzene. The NMR analysis of reaction mixtures at consecutive steps of the reaction allowed us to obtain unique information on the composition of intermediate transformation products and to propose a scheme of consecutive and parallel reactions occurring in the hydrogenation.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 16-03-00601

S5 OP$_{20}$-02

Phosphate-catalyzed Isomerization of Aldoses into Ketoses and Their Recovery Using Anionic Extraction

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Isomerization of aldoses into ketoses has attracted great attention as an efficient method for production of valuable and/or rare saccharides [1]. Ketoses are in demand as sweeteners, precursors for cosmetic and pharmaceutical formulations, as well as substrates for platform chemicals. In this work, we propose a three-step process for preparation of ketoses presented in Figure 1. The first step is isomerization of aldoses into ketoses using water as solvent and soluble Na_2HPO_4+NaH_2PO_4 as catalyst. The second step is recovery of ketoses by selective anionic extraction due to complexation of phenylboronic acids (PBAs) with ketoses. A selective extraction of ketoses into organic phase is feasible due to much larger complexation constants of ketose-PBA compared to aldose-PBA. After extraction, the aqueous phase containing the phosphate catalyst and the rest of aldose can be recycled. In the third step, ketose can be re-extracted from the organic phase with an acidic solution, whereas the organic phase containing PBA can be re-used for extraction (Figure 1). We showed high efficiency of the proposed method for isomerization of glucose, mannose, galactose, xylose, arabinose, and lactose [2].

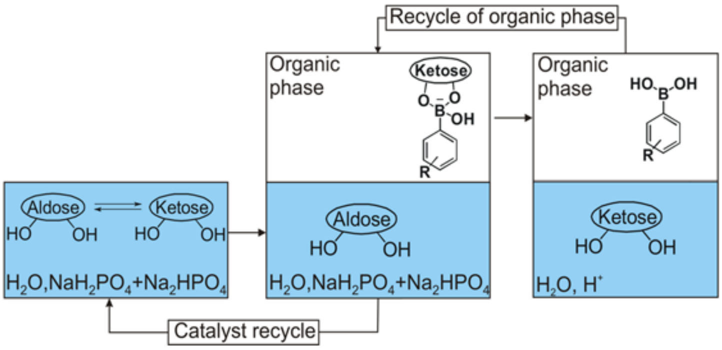

Figure 1. Representation of synthesis and recovery of a ketose

Isomerization of glucose into fructose was investigated in details. Mechanistic studies of the isomerization in the presence of Na_2HPO_4+ NaH_2PO_4 suggest that the reaction proceeds via formation of an enediol anion detected by UV-spectroscopy. Kinetics studies indicate that the isomerization is catalyzed by OH^- anions as basic active species. Selective extraction of fructose occurs due to complexation with PBA. Complexation was studied by ^1H, ^{13}C and ^{11}B NMR, ESI-MS as well as using model saccharides. The results evidence a preferentially extraction of ketose in pyranose form upon formation of 1,2-bidentate and 1,2,3-tridentate phenylboronate esters. Variation of chemical composition of PBAs as well as optimization of reaction conditions enabled extraction of up to 76% of ketose from an aldose-ketose mixture with 78-100% selectivity.

We acknowledge funding of the Alexander von Humboldt Foundation and the Bayer Foundation.

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S5 OP_{20}-03

Catalytic Activity of Carbon-encapsulated Metal Nanoparticles

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The interaction of metal nanoparticles with the carbon shell or support plays a significant role in catalysis. Carbon shell is believed to prevent the catalytic action of metal surface. However, recent studies [1–3] demonstrated that the defects in ordered carbon shell could be the active sites for the activation of reagents. In addition, surface metal carbides formation is often the first step of metal-carbon interaction, and such carbides may also contribute to catalytic performance.

In this work the influence of preliminary surface carbide formation, synthesis conditions and synthesis medium composition on the coverage of transition metal nanoparticles (Pd, Ni, Fe) was compared for carbon-encapsulated nanoparticles, synthesized by two methods. In the first method, molten Me suspension was evaporated in a flow of inert gas that contained light hydrocarbons [4]. The second technique was based on the direct pyrolysis in an inert atmosphere of wood sawdust impregnated with metal nitrate solution [2]. Both methods resulted in carbon-encapsulated nanoparticles with the reduced metal core of 2.5–5 nm in size depending on the synthesis conditions. The structure of the carbon shell and the chemical state of metal in the core were studied by TEM, XPS, Raman spectroscopy, TPR etc. Catalytic action in vapor-phase and liquid-phase chlorobenzene hydrodechlorination was compared for metal-carbon systems, synthesized by the two methods. It was found that the defects in the graphene shell, if its thickness is 1–3 monolayers, and the presence of catalytically active metal in the subsurface layer, even in form of carbide, provided catalytic action in gas-phase reductive reactions at elevated temperature. However, carbon-encapsulated metal nanoparticles were not active in liquid-phase reactions of a similar nature.

Acknowledgement. This work was financially supported by Russian Science Foundation (14–33–00018). The authors acknowledge partial support from Lomonosov Moscow State University Program of Development for providing access to the XPS facility.

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S5 OP$_{20}$-04

Ti-Salan/Salalen Based Catalyst Systems for the Environmentally Benign Asymmetric Oxidation of Thioethers to Sulfoxides with H_2O_2

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In this work, we present the new catalyst systems based of Ti-salan and Ti-salalen complexes, capable of oxidizing prochiral thioethers to chiral sulfoxides with H_2O_2 with good to excellent stereoselectivities. Using these catalysts, the blockbuster anti-ulcer drugs esomeprazole (Nexium) and dexlansoprazole (Kapidex), having up to 96 % optical purity, were synthesized. Thess catalyst systems provide a more efficient, green and technically simple alternative for the industrially exploited von Unge process for the synthesis of esomeprazole.

The effects of steric bulk and electronic properties of chiral ligands of the Ti-salan and Ti-salalen complexes (Figure 1) on the sulfoxidation enantioselectivity has been systematically examined. Remarkably, the sulfoxidation enantioselectivity was shown to vary with temperature in a nonmonotonic fashion, with maximum *ee*s attained at ca. 273 K, representing a rare example of *isoinversion relationship*. The consistent reaction mechanism has been proposed on the basis of experimental and DFT data.

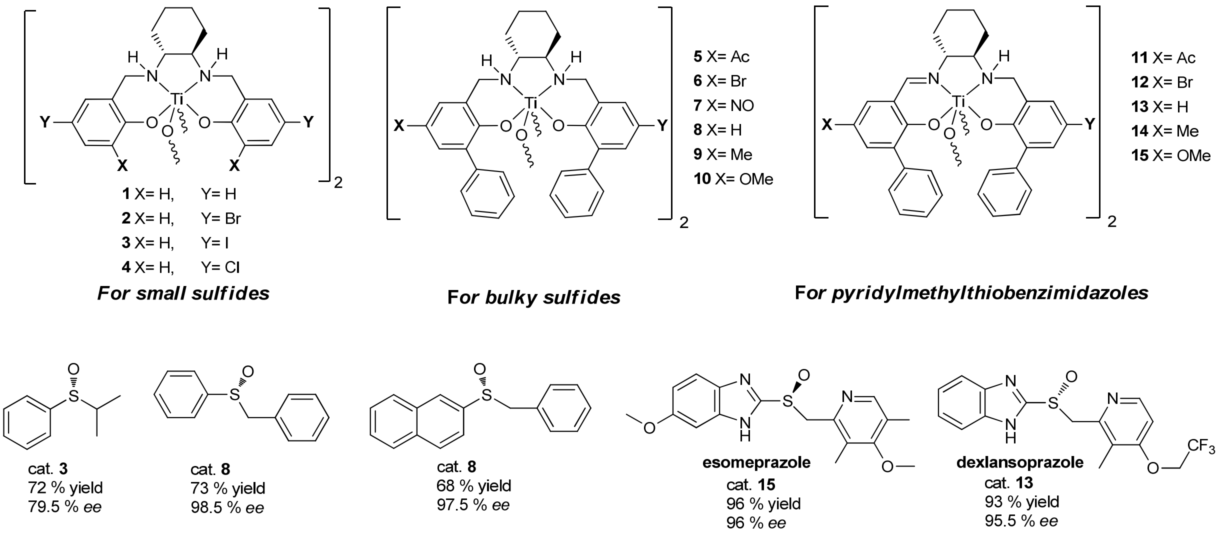

Fig. 1. Examples of Ti(IV) salan (**1-10**) and salalen (**11-15**) complexes, and chiral sulfoxides.

Acknowledgement. Financial support from the Russian Foundation for Basic Research (#14-03-00102 and #16-29-10666) is gratefully acknowledged.

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S5 OP_{20}-05

Highly Active Ternary $NiCoMoS/Al_2O_3$ Hydrotreating Catalysts Based on Co_2Mo_{10}-Heteropolyacid and Nickel Citrate

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The hydrotreating of petroleum cuts and residues is the central refining process in the production of clean fuels that meets the actual ecological requirements. The changing feedstock quality and involvement of unconventional hydrocarbon resources (oil shales, bituminous oils, bio-raw materials, etc.) into the hydroprocessing require the development of more active catalysts. The aim of this work was to investigate the co-promotion effect in $NiCoMoS/Al_2O_3$ catalysts based on Co_2Mo_{10}-heteropolyacid and nickel citrate.

Co(NiCo)MoS/Al_2O_3 catalysts were prepared by means of the incipient wetness technique via impregnating the γ-Al_2O_3 with mixed water solutions of Co_2Mo_{10}HPA and cobalt and/or nickel carbonate. Co(NiCo)/Mo atomic ratio was the following: 0.17 – 0.45. The catalysts were studied by N_2 adsorption, XRD, HRTEM and XPS methods. The catalytic activity was evaluated in HDS reactions of individual sulfur-containing compounds (DBT, 4,6-DMDBT), oxygen-containing compounds (dodecanoic acid and guaiacol) and in hydrotreatment of diesel.

It was found that adding the Co(Ni) citrate to Co_2Mo_{10}/Al_2O_3 catalyst significantly altered the active phase morphology. The average slab length increased from 3.0 to 4.1 nm in Co_x-Co_2Mo_{10}/Al_2O_3 catalysts and to 3.6 nm in Ni_x-Co_2Mo_{10}/Al_2O_3 counterparts. The average stacking number of the MoS_2 crystallites grew from 1.4 to 2.0 with loading the Co or Ni. Increasing the Co content in the Co_x-Co_2Mo_{10}/Al_2O_3 catalysts decreased the Co percentage in the CoMoS phase and led to the growth of Co fraction in cobalt sulphide. With the increase of Ni content in Ni_x-Co_2Mo_{10}/Al_2O_3 catalysts the Ni percentage in the NiCoMoS phase decreased from 47 to 25 rel. % and the Co percentage in the NiCoMoS phase was constant and equal to ~ 62 rel. %. For both series of the catalysts, activity in DBT HDS passed through maximum at 0.33 of the atomic ratio (Co+Ni)/(Co+Ni+Mo). Ni_x-$Co_2Mo_{10}S/Al_2O_3$ catalysts indicated higher rate constants in DBT HDS than Co_x-$Co_2Mo_{10}S/Al_2O_3$ counterparts at the same metal content. It was concluded that Ni_1-Co_2Mo_{10}/Al_2O_3 sample with minimal Ni/Mo ratio had mixed Ni-Co-Mo sites with high turnover frequencies values.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 15-33-20511.

Design of Pt,Pd-doped Mn-Hexaaluminate Catalyst with High Efficiency and Stability in Methane Oxidation

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Previously, we have discussed a non-additive increase of the catalytic activity in the high-temperature oxidation of methane over Mn-alumina catalysts after their modification by Pd [1, 2]. These catalysts are perspective for the catalytic combustion chamber of small gas turbines [3-5]. Characterization of fresh catalysts by TPR-H_2, XRD and HRTEM has shown that their initial oxidative activity is associated with 2-5 nm sized PdO particles, having intimate contacts with metallic Pd (100-300 nm) and imperfect Mn-hexaaluminate [2].

Here TPR-O_2, in situ XRD and in situ XPS were used to identify a role of the nanoscale state of noble metals and manganese cations in the synergetic effect in the catalytic activity and the high-temperature stability of the Pd-Mn-hexaaluminate catalyst and Pt-doped samples. The positive effect on the methane oxidation activity was shown to be indeed due to high-dispersed PdO layer located on the surface of metallic Pd particles. Mn^{3+} cations in the spinel blocks of Mn-hexaaluminate also promote the improvement of the catalytic activity and stability. The PdO transformation to metal and Mn^{3+} to Mn^{2+} reduction were reversible under the reaction conditions. A decrease of the fraction of highly active PdO nanoparticles due to both a change of Pt loading in the catalyst above Pt/Pd=0.3 and high-temperature sintering of Pd metal particles under the reaction conditions result in lowering of the catalytic activity of PtPd-doped $MnLaAl_{11}O_{19}$ samples.

PtPd-alloy formation, that was observed in spite of PdO, by TPR-H_2, HRTEM, XRD and XPS in the catalyst with Pt/Pd=0.3 correlates well with its high water and SO_2 tolerance, although it possesses lower methane oxidation activity compared with PdO.

Therefore, the design of effective and stable catalysts was found to include the optimum content of the catalytically active PdO nanoparticles as well as the sulfur tolerant and water resistant particles of PtPd alloy. Both types of noble metal particles are located on the surface of the imperfect particles of Mn-hexaaluminate. Their content is controlled by the Pt/Pd ratio and a preparation mode.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research (grant 15-03-05459-a).

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S5 OP₂₀-07

Mechanism of Dimethoxymethane Steam Reforming to Hydrogen-Rich Gas over Alumina Supported CuO-ZnO and CuO-CeO_2 Catalysts

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Dimethoxymethane (DMM) is a liquid under normal conditions and therefore it is easily stored and transported. It is worth emphasizing that DMM is noncorrosive, nontoxic material with a wide scope of applications. These facts together suggest that DMM is a promising feedstock for production of hydrogen-rich gas for polymer electrolyte membrane fuel cells applications. Catalytic steam reforming of DMM is one of the most efficient method for production of hydrogen-rich gas:

$$C_3H_8O_2 + 4H_2O = 3CO_2 + 8H_2 \quad (1)$$

Recently efficient bifunctional CuO-CeO_2/γ-Al_2O_3 [1] and CuO-ZnO/γ-Al_2O_3 [2] catalysts have been suggested for this reactions. It was shown that those catalysts provided complete DMM conversion under atmospheric pressure, T~300 °C, GHSV = 10000 h^{-1} with hydrogen productivity of ~15 L H_2/h·g_{cat} and CO content in hydrogen-rich gas below the equilibrium value.

The present work reports results of kinetic experiments on DMM steam reforming and characterization of catalysts by number of methods, such as TPR, XRD, TEM, EDX, HAADF-STEM, FTIR in situ, N_2O titration of Cu sites). Based on the data, role of each component, nature of active sites and mechanism of the reaction are discussed. Particularly, we show that:

1) DMM steam reforming proceeds via a consecutive two-step reaction mechanism – first step is a hydration of DMM to methanol and formaldehyde (reaction 2) and the second step is steam reforming of the produced methanol/formaldehyde to hydrogen-rich gas (reactions 3,4).

$$C_3H_8O_2 + H_2O = 2CH_3OH + HCHO \quad (2)$$

$$CH_3OH + H_2O = CO_2 + 3H_2 \quad (3)$$

$$HCHO + H_2O = CO_2 + 2H_2 \quad (4)$$

Besides this reactions, a reserve WGSR proceed to produce carbon monoxide.

2) The catalytic performance in DMM steam reforming is associated with the γ-Al_2O_3 Brønsted acid sites and alumina supported copper-ceria or copper-zinc oxide species, which are responsible for DMM hydration and methanol/formaldehyde SR, respectively.

Acknowledgement. This work was supported by the RFBR grant 14-03-00457a and by the project V.44.2.9.

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S5 OP_{20}-08

Kinetic and Mechanistic Aspects of One-Pot Valeric Acid Transformation into Alkane over Pd (Pt)/MO_x

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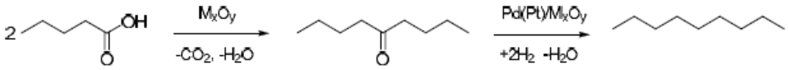
Abundant amounts of carboxylic acids are produced during thermolysis of biomass, anaerobic fermentation of sugars and biological processes. Valeric acid (VA), a product of levulinic acid conversion [1], can be converted to hydrocarbons through dimerization of two VA molecules to one ketone molecule with the removal of water and carbon dioxide followed by hydrodeoxygenation (HDO) into *n*-nonane over Pd and Pt catalysts in H_2 [2]. The goal is to study the mechanism of decarboxylative coupling followed by HDO as well as to develop a heterogeneous catalyst for one-pot production of a high-energy-density C9 alkane. Both catalytic reactions were studied separately in order to be performed over Pt or Pd on an amphoteric metal oxide under optimal reaction conditions.



One-pot VA conversion and 5-nonanone HDO was carried out in a fixed bed flow reactor over zirconia and ceria supported 2% Pd and Pt, VA was dimerized over amphoteric oxides ($m_{catalyst}$=0.5 g, fraction 0.25-0.5 mm, 573-678K, 1-10 bar H_2 (flow rate 10-33 cm^3/min)). The reaction products were analyzed by “Chromos 1000” GC (FID) with Stabilwax-DA (50 m/0.32 mm/0.5µm) at 373-473 K with ramp 10K/min. Catalysts were characterized by XRD, XPS, HRTEM. UV-Vis and FTIR were used for the mechanistic studies (293-423K).

Kinetic regularities and mechanistic aspects of VA ketonization and one-pot synthesis, as well as 5-nonanone HDO were determined. Using FTIR and UV-Vis ketonization over zirconia was shown to start at room temperature. Different chemisorption forms of valeric acid on Lewis acid sites were found: monomolecular and bimolecular monodentates as well as chelating and bridging bidentates that could be a part of the reaction mechanism previously reported [3]. Two approaches to the mechanism of VA ketonization could be proposed different in the carboxylate forms generated in the first reaction step. After the carboxylates are formed and α-H atom is abstracted from one of them to give an anion radical, the latter attacks the second carboxylate adsorbed on the same or neighboring metal species to produce β-ketoacid followed by decarboxylation forming the desired ketone. The ratio between Lewis acid (M^{x+}) and base (O^{-2}, OH^-) sites is crucial in providing catalytic activity of metal oxides in VA ketonization as well as Pd (Pt)/MO_x activity in one-pot VA conversion giving *n*-nonane.

Acknowledgement. Financial support from RFBR Grant No. 15-03-09329 related to catalyst synthesis and characterization is gratefully appreciated.

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S5 OP$_{20}$-09

Prompt Metal Dusting of Model Ni-based Alloys: Mechanism of Active Sites Formation Followed by CNM Growth

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A phenomenon of spontaneous degradation of the bulk Fe- and Ni-based alloys occurred in the strongly carburizing atmosphere (CO, C_xH_y etc.) is well known as "metal dusting" [1]. Progressive disintegration of bulk item gives rise to appearance of disperse metallic particles functioning as active catalytic sites for the growth of carbon nanostructured materials (CNM). This process is now implemented as an alternative way for production of such valuable products as carbon nanotubes and nanofibers [2]. As it was shown in our previous study [3], a slow process of carbon erosion can be significantly accelerated by using the chlorinated hydrocarbons as a carbon-containing substrate.

The principle scheme for the mechanism of the active sites formation as a result of metal dusting of the bulk Ni-Cr alloy is presented in Fig. 1.

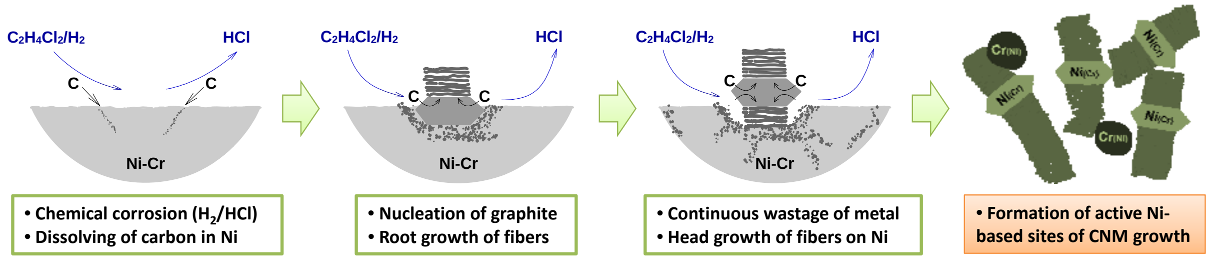

Fig. 1. Schematic mechanism of metal dusting of the bulk Ni-Cr alloy occurred during decomposition of 1,2-dichloroethane at 550-720°C.

A controllable process of prompt metal dusting of bulk Ni-based alloys in aggressive reaction media can be considered as a new concept to prepare active and effective catalysts for synthesis of carbon nanomaterials. Catalytic properties of thus self-organized Ni-M/CNM systems could be tuned purposefully by changing the nature and loading of alloying metal M.

In presented research the series of model Ni-M (M = Cu, Fe, Mo) bulk alloys synthesized by mechanochemical activation method have been studied as precursors in similar process. The mechanism of formation and evolution of the active sites as well as peculiarities of catalyzed CNM growth will be discussed in details.

Acknowledgement. This work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (V.45.3.5).

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CO/CO_2 Hydrogenation and CO Disproportionation over Small Co Particles Supported on Carbon Nanotubes

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It is well known that the surface oxidation of carbon nanotubes (CNT) leads to the significant changes in the support structure and dispersion of metal in CNT supported Co catalysts [1, 2]. In this work the role of metal crystallinity in the hydrogenation of carbon oxides over Co/CNT catalyst was studied. Co crystallinity was tuned by the different degree of the oxidation of CNT support surface. Pure CNT were refluxed in nitric acid at the different temperatures and decorated by Co using impregnation technique. TEM images combined with nanodiffraction patterns revealed the presence of amorphous particles of Co species (~2 nm) in the catalyst supported on more oxidized CNT. This catalyst was almost inactive both in CO and CO_2 hydrogenation. TEM investigation after CO hydrogenation showed the carbon shell formation on the surface of amorphous particles which testified CO disproportionation. The mechanism of the catalytic process in the case of extremely small Co species was proposed based on the TEM results and literature data.

Acknowledgement. The work was partially supported by RFBR research project No. 16-29-06439 ofi_m.

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OP$_{10}$-02

ESR Investigation of Nitrobenzene Hydrogenation over Au/Al_2O_3 Catalyst

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Au/γ-Al_2O_3 catalysts are known to provide high chemoselective hydrogenation of nitroarenes to aniline, however, the exact mechanism of chemoselective hydrogenation of nitroarenes to anilines over Au/Al_2O_3 catalyst is still unclear and is discussed in the literature [1-3].

Some authors applied ESR technique to study the interaction of Al_2O_3 surface with nitroaromatic compounds. For example the behavior of γ-Al_2O_3 based systems in the liquid solution of TNB in toluene was investigated few years ago [4]. It was shown, that electron transfer takes place between TNB and –OH group of the γ-Al_2O_3 surface.

Here we report the data on the mechanism study of hydrogenation of nitrobenzene over Au/Al_2O_3 catalyst via ESR method *in situ*. The ESR technique was applied to reveal the radicals formed in the system as the result of the interaction of nitrobenzene with active sites of the Au/Al_2O_3 catalyst surface. The spectra registered are attributed to the immobilized radicals while there is no detectable ESR signal is observed for the solution over the samples. The specific hyperfine splitting of nitro-radicals detected indicates the influence of neighboring gold nanoparticles while for the γ-Al_2O_3 the HFI splitting three times higher is observed. The nitro-radicals detected should be considered as the intermediate species for the catalytic hydrogenation of nitrobenzene to aniline. It was confirmed providing simultaneous GC-MS analysis of reaction mixture with the registration of ESR spectra *in situ* which displayed the severe drop of the resonance absorption intensity during the reaction.

Acknowledgement. We are grateful to B.L. Moroz for providing the samples. The work was performed in the framework of joint Scientific and Educational Center of Energy efficient Catalysis of the Boreskov Institute of Catalysis and NSU with the support of Federal Agency of Scientific Organization (V.44.1.15).

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OP$_{10}$-03

XPS Study of Oxidized Rhodium Species Active in CO Oxidation Reaction

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Being an active component of many industrially important reactions, rhodium has attracted attention of the scientists over the last 50 years. Thorough investigation of the oxidized species stabilized on the surface of rhodium and Rh-based catalysts plays a key role in the understanding of the mechanisms of their catalytic action. In our work we studied the highly oxidized rhodium surface using X-ray photoelectron spectroscopy (XPS). The nature of the oxidized species, their thermal stability and reactivity in CO oxidation reaction were established. The obtained results were compared with the data for Rh/CeOx powder catalysts in order to shed light on the influence of Rh-CeOx interaction on the oxygen reactivity.

The radio-frequency (RF) discharge in an oxygen atmosphere was applied to prepare highly oxidized rhodium surface. Thermal stability and reaction probability of the obtained oxidized species were analyzed by a step-by-step heating and CO titration, respectively. The Rh/CeOx catalysts were synthesized by coprecipitation of Rh and Ce nitrates with subsequent calcination in air at 450^{0}C-1000^{0}C. The catalytic activity of the samples was studied with temperature-programmed reactions (TPR -CO+O_2 and TPR-CO).

The RF-oxidation of the rhodium foil resulted in the formation of Rh_2O_3 and/or Rh^{4+}/Rh^{3+}OOH species characterized by the Rh3d$_{5/2}$ spectrum at 308.4 eV (Figure 1a). The obtained oxidized species had a thermal stability about 250^{0}C and demonstrated noticeable reactivity towards CO oxidation at temperature above 100^{0}C. However, their interaction with CO was inhibited by the formation of carbonaceous species on the surface. The Rh/CeOx samples showed main peak in Rh3d spectra at 309.2 eV (Figure 1b) related to Rh^{3+} species in a Rh_xCeO_y solid solution. The interaction with CO for these samples started already at room temperature and proceeded without inhibition, pointing to a crucial role of Rh-CeOx interaction in a low-temperature catalytic activity.

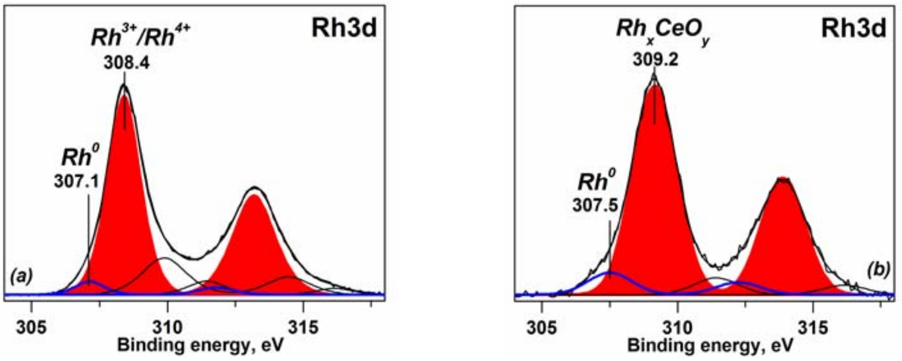

Figure 1. The Rh3d spectra of (a) highly oxidized Rh foil, (b) calcined Rh/CeOx catalyst.

Acknowledgement. This work was partially supported by the Ministry of Education and Science of the Russian Federation (President's grant for young scientist MK-6911.2016.3).

OP$_{10}$-04

Insights on the Mechanism for the Heterogeneous Iso-Butane/Butene Alkylation over Solid Catalyst

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The present work is focused on the development of efficient catalysts for producing of alkylate and on new energy-saving technology of production gasoline based on the use of alkylate. The purpose of this research is to analyze the mechanism of heterophase alkylation reactions on ZrO_2-Al_2O_3/HY catalyst based on experimental results.

The alkylation of iso-butane with 2-butene was performed in a plug-flow reactor operated in continuous mode. Operating parameters of the process: temperature range (20-100) °C; pressure 17 atm; paraffins / olefins ratio 19/1, space velocity 3 h^{-1}.

Formation of C_4-C_{14} components is described by the following basic stoichiometric equations. This assumption was based on the analysis of the reaction routes [1], and experimental data of the composition of the alkylate:

Step	Reactions	Rate equations	E_a, kJ/mole
1	$C_4H_{10} + C_4H_8 \rightarrow C_8H_{18}$	$R_1 = k_1 \cdot C_{C_4H_{10}}$	14.4
2	$C_8H_{18} + C_4H_8 \rightarrow C_{12}H_{26}$	$R_2 = k_2 \cdot C_{C_4H_{10}} \cdot C_{C_8H_{18}}$	26.8
3	$C_{12}H_{26} + C_4H_8 \rightarrow C_{16}H_{34}$	$R_3 - k_3 \cdot C_{C_4H_{10}} \cdot C_{C_{12}H_{26}}$	23.8
4	$C_{16}H_{34} \rightarrow C_6H_{12} + C_{10}H_{22}$	$R_4 = k_4 \cdot C_{C_{16}H_{34}}$	28.4
5	$C_{10}H_{22} + C_4H_8 \rightarrow C_{14}H_{30}$	$R_5 = k_5 \cdot C_{C_4H_{10}} \cdot C_{C_{10}H_{22}}$	51.2
6	$C_6H_{12} + C_4H_{10} \rightarrow C_{10}H_{22}$	$R_6 = k_6 \cdot C_{C_6H_{12}}$	15.6
7	$C_{14}H_{30} \rightarrow C_{10}H_{22} + C_4H_8$	$R_7 = k_7 \cdot C_{C_{14}H_{30}}$	38.2

Formation of light hydrocarbons C_4-C_6 occurs mainly due to cracking of C_{14} - C_{16} hydrocarbons, which are formed by stepwise C_4-C_{12} alkylation.

Activation energy of primary TMP-formation reaction (14.4 kJ/mole) is lowest from observed reactions. Therefore reaction rate is limited by diffusion of the reactants.

Acknowledgement. Work is carried out in accordance with the grant №381 of the Russian Government to support research conducted under the guidance of leading research scientists at Russian institutions of higher education on the topic: "The process of alkylation of isobutane with light olefins on solid catalysts using reactive distillation technology" contract №14.Z.50.31.0013, on 03/19/2014.

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Metal-Promoter Interface in Selective Alcohol Oxidation: Understanding the Synergetic Effects of P-promoted Ag Catalysts

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Promoters are widely used in catalysis to facilitate the effectiveness of the catalysts. Silver is known to show high activity in alcohol oxidation, and phosphorus compounds promote the process performance. In the present work using density functional theory approach we would like to characterize synergetic action of silver and phosphorus compounds in activation and transformation of alcohols exemplified by ethylene glycol (EG). To the best of our knowledge, there were a few attempts to look at the metal-promoter interface (MPI) of alcohol oxidation catalysts from theoretical point of view, while experiment-based interpretations are not unambiguous. Thus, the present work is focused on new insights on the nature of MPI of promoted alcohol oxidation catalysts and synergetic action of metal and promoter.

Multiple systems containing neutral Ag_n (n=1÷10; 20) relaxed clusters and/or adsorbate/intermediate and/or phosphate model component were calculated as described in [1] using the Gaussian'09 program package installed at SKIF "Cyberia" supercomputer of Tomsk State University. Hexametaphosphoric acid (HMPA, reflects the hydroxylated catalyst surface sites) and polyphosphate structure (PP, represented by H-less HMPA structure) were considered as promoter component models based on known experimental results [2]. Ethylene glycol was used as an alcohol adsorbate.

MPI was shown to play a crucial role in activation and transformations of EG over P-promoted Ag catalysts and contain the most energetically preferable surface sites for these processes. The processes were found to take place due to synergetic effect between silver, promoter and Ag-bound oxygen species. Mechanisms of O-H bond activation and C-H bond scission were discussed. Several P-containing oxametallocycles were shown to form at the MPI. Cluster size effect was considered, and odd-even alterations were revealed for bare and HMPA-supported Ag_n clusters. Several active oxygen species were considered at the MPI, including those in 3-fold sites of Ag clusters, terminal P=O and P-O-H as well as bridging P-O-P groups. Their roles in transformation of EG and process intermediates (i.e., ethylenedioxy, 2-oxoethoxy, etc.) were discussed.

Acknowledgement. This work was supported by The Tomsk State University Academic D.I. Mendeleev Fund Program in 2015-2016.

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OP_{10}-06

Catalytic Hydrogenation of Silicon and Germanium Tetrachloride

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The catalytic reduction of $SiCl_4$ and $GeCl_4$ by hydrogen to silicon and germanium powder was carried out over a modified nickel chloride catalyst. The effects of nickel chloride surface on the reaction were intensively investigated. The results show that modified nickel chloride surface play an important role in reduction the value of the activation energy and reaction temperature of the catalytic hydrogenation $SiCl_4$ and $GeCl_4$.

The chromatograms and mass spectra of the main products formed in the reaction of silicon and germanium tetrachloride reduction, obtained in the study, indicate that the following reactions occur when the process is performed:

$ECl_4 + 2H_2 \rightarrow E\downarrow + 4HCl$ ($T = 423 - 623$ K, E = Si/Ge) (1)

$ECl_4 + 4H_2 \rightarrow ECl_2\downarrow + 2HCl$ ($T = 523 - 573$ K, E = Si/Ge) (2)

$ECl_2 + HCl \rightarrow HECl_3$ (only for E = Si) (3)

$n\ ECl_2 \rightarrow (ECl_2)_n$ ($T < 373$ K, E=Si/Ge) (4)

As a part of the study reduction of silicon/germanium tetrachloride with hydrogen in the presence of catalyst based on modified nickel chloride (II) was carried out. It was found that the reaction (1) takes place with a high degree of conversion at 623 K (Table 1), and that the reaction (2) is a side reaction and leads to the formation of silicon / germanium dichlorides which are polymerized in $(ECl_2)_n$.

Table 1. Quantitative characteristics of catalytic reduction reactions with $SiCl_4$ and $GeCl_4$.

Reaction	Conversion (%) 423 (K)	Conversion (%) 623 (K)	Reaction order	E_a ($NiCl_2$) ($kJ \cdot mol^{-1}$)*	$HSiCl_3$ yield (mol. %)
(1), E = Si	85.3	100	0.04	2.898	10 - 12
(1), E = Ge	53.1	98.9	0.175	5.507	-

Formation of dichlorosilylene / -germylene was discovered by pyrolysis gas chromatography-mass spectrometry. The resulting knowledge has helped to assume the reaction mechanism which is based on the formation of $SiCl_2$ and $GeCl_2$ in the reaction zone.

This study will be useful in understanding the reduction of $SiCl_4$ and $GeCl_4$ with hydrogen and provides information regarding the development of a $SiCl_4$ converter for a Siemens reactor to produce poly-Si in the solar cell industry and produce Ge nanopowders with minimum energy consumption.

Acknowledgement. This work was financially supported by the Ministry of Education and Science of the Russian Federation in the Framework of the Basic Part of the State Task, Project No. 2897.

OP$_{10}$-07

Regularities of Electrochemical Aromatic C-H Fluoroalkylation Using Ni and Fe Complexes

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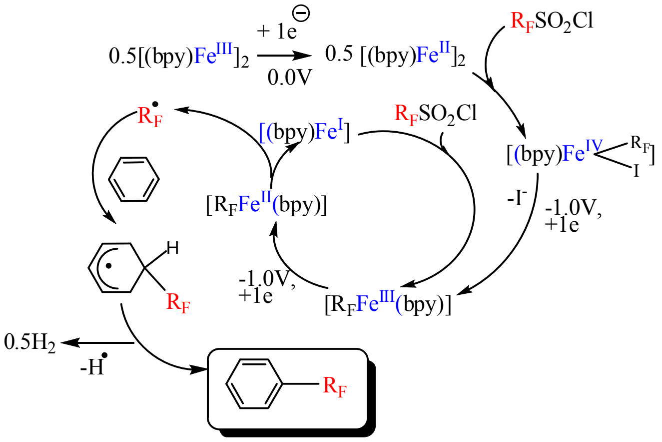
The increasingly broad realization of the key role of organofluorine compounds in numerous areas has recently attracted many new scientists to the field. The development of new methods for the selective introduction of fluorine and fluorine containing groups into organic molecules for biologically active and other useful materials has become hot area

Catalytic methods to incorporate the trifluoromethyl group into arenes have yet to be developed. There is a rich history of stoichiometric trifluoromethylations of aryl halides using copper, however the first example of a process catalytic in copper to couple the trifluoromethyl group with aryl iodides was only recently reported in 2009 [1].

We aimed to develop an iron-based electrocatalytic method for the perfluoroalkylation of both simple and compicated arenes. Our goal was to utilize relatively inexpensive CF_3SO_2Cl as R_FX precursors, together with an accessible and nontoxic iron compound as a catalyst.



Perfluoroalkylation of aromatic and hetero-aromatic compounds by CF_3SO_2Cl catalyzed by $[(bpy)FeCl_2]_2$ under electrochemical conditions was investigated. Fluoroalkylation of benzene derivatives, naphthalene, coumarine derivatives, anthracene, and caffeine was realized under mild reaction conditions with high product yields. The mechanism of electrochemical transformation was proposed to be a radical process based on ESR and CV studies[2-3].

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-23-00016.

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OP$_{10}$-08

Bioinspired Nonheme Iron Catalysts for Oxidation: Remarkable Effect of Carboxylic Acid Additive on the Electronic Structure of the Active Oxoferryl Species

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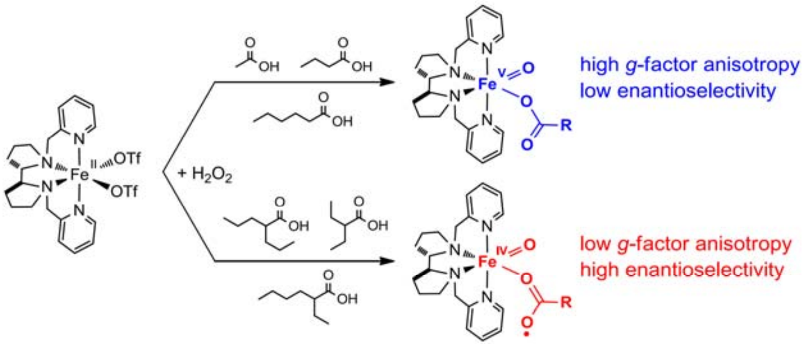
The development of efficient and selective oxidations under mild conditions inspires researchers to design biomimetic catalysts – synthetic models of nonheme iron oxygenases. The systems based on iron complexes bearing polydentate *N*-donor ligands, H_2O_2 as an oxidant and carboxylic acid as a co-catalytic additive have been intensively investigated recently. Previously, it was discovered that introducing electron-donating substituents at the pyridine rings of the ligand can improve the yields and enantioselectivities of epoxidations catalyzed by aminopyridine-iron complexes. However, the role of carboxylic acid in the metal complex-catalyzed epoxidation reactions with H_2O_2 has not been clearly understood.

Herein, we report the detection of two types of active species in catalyst systems Fe^{II}((*S*,*S*)-PDP)/H_2O_2/RCOOH depending on the nature of added carboxylic acid. For carboxylic acids with tertiary α-carbon atom (2-ethylhexanoic, valproic, 2-ethylbutyric acids), the active species displays an EPR spectrum with small anisotropy of *g*-factor ($g_1 = 2.07$, $g_2 = 2.01$, $g_3 = 1.96$). For carboxylic acids with primary and secondary α-carbon atom (acetic, butyric and caproic acids), the active species exhibits an EPR spectrum with large anisotropy of *g*-factor ($g_1 = 2.7$, $g_2 = 2.4$, $g_3 = 1.7$). The latter intermediates are similar to the previously reported oxoiron(V) species $[((S,S)\text{-PDP})Fe^{V}{=}O(OC(O)R)]^{2+}$ (type 1), while the former are best represented as their electronic isomers $[((S,S)\text{-PDP})Fe^{IV}{=}O(^{\bullet}OC(O)R)]^{2+}$ (type 2). The catalyst systems displaying intermediate of the type 2 show better enantioselectivities toward epoxidation of electron-deficient olefins (chalcone and benzylideneacetone), than those displaying intermediate of the type 1 (*ee* 83% *vs.* 62%, and 58% *vs.* 23% at 0 °C). Higher enantioselectivity of the catalyst systems with branched carboxylic acids is probably due to the additional stabilization of the active species via delocalization of the unpaired electron over the carboxylic moiety.



Acknowledgement. This work was supported by the RFBR, grants 14-03-00102 and 16-33-00014.

OP10-09

Mechanistic Studies of Selective Oxidation of Alkylarenes with H_2O_2 Catalyzed by γ-Keggin Divanadium-substituted Phosphotungstate

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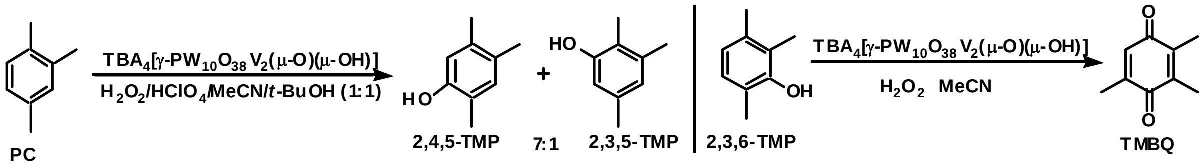
The selective oxidation of aromatic rings of alkylarenes with atom efficient and green oxidants, e.g. H_2O_2, is a challenging goal. Aromatic oxidation of alkylbenzenes [1,2] and alkylphenols [3] can be efficiently catalyzed by a divanadium-substituted polyoxometalate (V_2-POM), $TBA_4[\gamma\text{-}PW_{10}O_{38}V_2(\mu\text{-}O)(\mu\text{-}OH)]$. In this work, we report studies on the mechanisms of the catalytic action of this POM in the oxidation of two representative arenes, pseudocumene (PC) and 2,3,6-trimethylphenol (TMP), by experimental and theoretical methods, including ^{31}P and ^{51}V NMR spectroscopy, kinetic modeling and DFT calculations.



The oxidation of PC in the presence of V_2-POM proceeds with high selectivity of the aromatic nucleus hydroxylation and unusual regioselectivity, leading to a mixture of 2,4,5- and 2,3,5-trimethylphenols (TMP) with the ratio of 7:1 [2]. The lack of side-chain oxidation products evidences in favor of heterolytic mechanism of the H_2O_2 activation over V_2-POM while the absence of 2,3,6-TMP among the phenolic isomers allows suggestion that steric factors prevail over electronic ones. The presence of acid co-catalyst and *t*-BuOH is crucial for this reaction. Studies on PC oxidation by DFT implicated a peroxo complex, $[\gamma\text{-}PW_{10}O_{38}V_2(O_2)]^{3-}$ (**I**), as the main active species. The energy barrier for oxygen transfer calculated by DFT is close to that determined from the kinetic modeling study. The role of acid and *t*-BuOH is, most likely, to facilitate the formation of **I** from hydroperoxo species $[\gamma\text{-}PW_{10}O_{38}V_2(\mu\text{-}O)(\mu\text{-}OOH)]^{3-}$ (**II**) formed upon interaction of V_2-POM with H_2O_2. In contrast, the oxidation of alkylphenols, including 2,3,6-TMP, smoothly proceeds without acid co-catalyst and *t*-BuOH, producing *p*-benzoquinones (BQ) with high yields (90-100%) and H_2O_2 efficiency (80-90%) [3]. Importantly, 3,5-dimethylphenol undergoes oxidation to 3,5-dimethyl-BQ. These facts allow suggestion that less sterically hindered hydroperoxo complex **II** might be involved in the oxidation of alkylphenols.

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OP10-10

Propylene Glycol Oxidation with Hydrogen Peroxide over UiO-66

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Metal-organic frameworks (MOFs) have attracted increasing attention as catalysts due to a unique combination of properties. Zirconium terephthalate UiO-66 is a MOF with unprecedentedly high thermal and hydrothermal stability [1]. Moreover, Zr-containing catalysts are known for their high ability to activate the green oxidant, hydrogen peroxide. In this work, we explored the mechanism of the selective oxidation of propylene glycol (PG) to hydroxyacetone (HA) over UiO-66 using aqueous hydrogen peroxide as oxidant.

PG conversion and HA selectivity are strongly affected by the nature of solvent (acetonitrile, *tert*-buthanol, ethylacetate, dimethylcarbonate, methanol, or water). The solvent of choice is acetonitrile where HA selectivity attained 85 % at 13 % substrate conversion after 3 h. Side products, such as acetaldehyde, acetic and formic acids, formed in the result of C-C bond cleavage. HA overoxidation products, methyl glyoxal and pyruvic acid, were not observed. Hot catalyst filtration tests confirmed truly heterogeneous nature of the catalysis. Zirconium content in the filtrate did not exceed 3 ppm, corroborating the absence of the active metal leaching. Although PG/H_2O_2 molar ratio was close to 1, PG and H_2O_2 conversions were 13 and 24 %, respectively, in acetonitrile (i.e., the oxidant utilization efficiency was ~75 %). At the same time, H_2O_2 conversion was close to 100 % in water while PG conversion was only 5 %, which indicates that unproductive decomposition of the oxidant is significant. The reason for such different catalytic performances in the two solvents can be tentatively rationalized in terms of adsorption constants. In acetonitrile, the adsorption constants of PG and HA on UiO-66 are 290±50 and 42±12 M^{-1}, respectively. We may suppose that PG molecules block zirconium active sites and thus suppress adsorption and unproductive decomposition of the oxidant. The PG oxidation rates were similar under inert atmosphere and in air, indicating that hydrogen peroxide is the sole oxidant in the system. Additives of a conventional radical chain scavenger, e.g. ionol, produced no rate-retarding effect. Therefore, the catalytic performance of the UiO-66/H_2O_2 system differs markedly from the recently studied Cr-MIL-101(100)/TBHP systems, where contribution of O_2 into the PG oxidation process was substantial and the reaction was strongly inhibited by ionol [2]. Further studies are in progress to clarify the mechanism of the PG oxidation over UiO-66.

Acknowledgement. This work was supported by “Tomsk State University Academic D.I. Mendeleev Fund Program” in 2016.

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Influence of Platinum Precursor on the Formation of Active Sites of Bifunctional Catalysts of One-Step Vegetable Oil Hydrocracking

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Hydrocracking of fat and oil raw materials is highly demanding technology of the production of diesel fuels components with improved environmental and operational properties. The main objective of this research was studying the effect of the nature oxide supports (γ-Al_2O_3 (A), ZrO_2 (Z), ZrO_2-Al_2O_3 (ZA), B_2O_3-Al_2O_3 (BA), B_2O_3-ZrO_2 (BZ)) and platinum precursors (H_2PtCl_6 (^{a}) and $[Pt(NH_3)_4]Cl_2$ (^{b})) on the properties of Pt-containing catalysts for hydrocracking of vegetable oil.

The catalysts were characterized by N_2 adsorption, XRD, TPR-H_2, chemisorption of H_2, TPD-NH_3, FT-IR adsorbed CO and HRTEM techniques. The catalytic tests were carried out in a continuous flow fixed bed reactor at temperature of 380°C, pressure of 4.0 MPa, WHSV of 1.0 h^{-1}, H_2/feed ratio of 1400 (v/v), TOS of 20 h. The purified sunflower oil was used as the feedstock. Contents of gasoline (IBP-150°C), diesel (150-350°C) and heavy gas oil (350°C-FBP) in liquid product were determined by simulation distillation.

Borate-containing catalysts Pt/BA, Pt/BZ are X-ray amorphous and characterized by high levels of acid sites. All the catalysts which produced using anionic precursor $[PtCl_6]^{2-}$, have greater dispersion of the metal, compared with catalysts obtained by the cationic precursor $[Pt(NH_3)_4]^{2+}$. This is due to sorptive fixing of the $[PtCl_6]^{2-}$ ions on the surface of supports. Platinum dispersion on catalysts with alumina support is higher than dispersion on zirconia based systems due to developed textural characteristics. According to the catalytic tests all systems provide complete hydrodeoxygenation vegetable oil. On the catalysts Pt/BA^a and Pt/BZ^a the yield of the diesel fraction (80.7 and 72.7 wt.%) is higher than on systems Pt/BA^b and Pt/BZ^b (77.4 and 69.1 wt.%, respectively). Diesel fractions obtained on the catalysts Pt/BA^a and Pt/BZ^a, also contain large amounts of iso- and cycloalkanes (28.3 and 60.7 wt.%) compared with diesel fractions formed on systems Pt/BA^b and Pt/BZ^b (19.2 and 31.3 wt.%). This fact is due to the greater acidity of borate-containing systems, synthesized using anion precursor platinum. Furthermore, the presence of these hydrocarbons in the diesel fraction formed on Pt/BA and Pt/BZ catalysts may be associated with a predominance of Brönsted acid sites on catalyst surface. Catalysts Pt/A, Pt/ZA and Pt/Z, characterized by the acidity of Lewis type, contribute to the preferably n-alkanes formation (up to 97.5-94.0 wt.% in the diesel fraction). It is shown that all platinum-supported systems, regardless of the state their hydrogenated components, are effective catalysts for hydrocracking of vegetable oils. Using the catalysts Pt/BA and Pt/BZ, prepared with H_2PtCl_6 is preferred because of the formation of large amounts of iso- and cycloalkanes, potentially providing good cold flow properties of diesel fuels.

OP_{10}-12

Metal-induced Oxidative Phosphorylation of Aromatic Compounds

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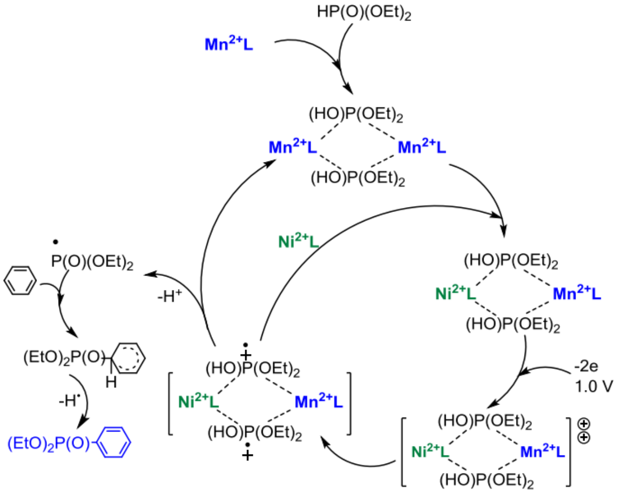
The preparation of aryl phosphonate through the direct phosphorylation of C-H bond of aromatic substrates remains one of the most important approaches because it corresponds to the principles of green chemistry, namely, atom economy, single-step, low-waste, etc. The desired catalytic conditions in this context are particularly attractive, given the fact that the catalytic reactions of aromatic compounds phosphorylation are limited. Perhaps benzene in this row is one of the most difficult substrates, given that its structure has no favourable C-H substitution factors, i.e., functional groups, activating bonds or directing functionalization. Typically, if it is possible to select conditions for the phosphorylation of benzene, its derivatives give even higher yields.



Electrochemical catalytic reactions of aromatic compounds direct phosphorylation are particularly attractive. We assume that it would be possible to realize the phosphorylation of benzene derivatives, coumarin and caffeine by taking advantage of electrochemical metal complex catalysis.

We have provided a one-stage method of direct electrochemical phosphorylation of aromatic C-H bonds resulting in dialkyl aryl phosphonates (aryl = benzene derivatives, coumarin derivatives, caffeine). The process takes place under mild conditions (room temperature, normal pressure), and at a reagent ratio of 1:1, thus providing a product with a high yield (70%) and 100% conversion when a bimetallic catalyst system Mn^{II}bpy/Ni^{II}bpy) is used. The success achieved through a fast catalytic cycle and the rapid regeneration of metal catalysts on the electrode.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-23-00016.

In Situ and Operando X-ray Absorption and Emission Spectroscopy: Probing SCR-relevant Cu Species in Cu-CHA Zeolite

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X-ray absorption and emission spectroscopies (EXAFS, XANES, XES) are known to be very powerful tools for structural and electronic characterization of catalytically active metal centers in various types of materials. Making use of the modern state-of-the-art synchrotron sources, these methods are perfectly suited for various kinds of *in situ* and *operando* catalytic experiments. Element selectivity of XAS and XES techniques represent a significant advantage as well, since minor or disordered species are often the focus of interest in catalysis.

Cu-CHA zeolite, known for its outstanding performance in NH_3-assisted selective catalytic reduction (SCR) of NO_x, has been an example of a very successful application of X-ray absorption and emission techniques. Since catalytically active sites in this material are likely to be relatively low-abundance isolated Cu ions incorporated in the cavities of the zeolite framework, element selective methods were a logical choice for the characterization task.

In the present study we used EXAFS, XANES and XES methods complemented by DFT calculations to shed light on Cu local environment in the activated state of the catalyst [1] and reaction-relevant conditions [2,3], and consequently to develop a consistent scheme of the SCR reaction [3]. In particular, it was proved possible to decouple the oxidation and reduction parts of the SCR reaction, by exposing the catalyst alternately to a mixture containing NO and O_2 and a mixture containing NH_3 and NO. Indeed, it was indicated by a very pronounced preedge XANES peak that the sample was reduced upon interaction with NH_3+NO and reoxidized after switching back to NO+O_2. Conversely, the interaction with NH_3 alone did not lead to such prominent reduction, converting only about a quarter of Cu(II) sites to Cu(I). Reduction upon interaction with NO alone was even less likely, resulting in purely Cu(II) species.

Acknowledgement. This work was supported by the Megagrant of the Russian Federation Government no. 14.Y26.31.0001. K.A.L. acknowledges the support from the Scholarship of the Russian President for young scientists СП-2796.2016.

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OP10-14

In Situ Palladium Hydride and Carbide Formation in the Palladium Nanoparticles during Catalytic Reactions

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Palladium catalysts are widely used in industry to selectively hydrogenate alkynes in the alkyne/alkene mixtures. The high selectivity of the palladium-based catalysts in semi-hydrogenation of alkynes was a subjects of numerous studies during the last 50 years [1-2]. The formation of carbide and hydride phases in the catalyst was reported to be responsible for selectivity and catalytic performance [3]. However, the issue is still under debate. The aim of the current work, is to investigate the structure-activity relationship of the working palladium-based nanocatalyst using simultaneously *in situ* X-ray absorption spectroscopy, X-ray diffraction, and mass spectrometry.

By applying recently developed technique [4-5], which combines theoretical simulations and fitting procedure, we obtain information on the type of the phase (carbide or hydride) and the amount of carbon or hydrogen atoms in the palladium lattice from X-ray absorption near-edge structure (XANES). As a proof of principle, this technique was applied to observe Pd-C and Pd-H species in the steady-state conditions when the catalyst was exposed to pure hydrogen, acetylene and a mixture of these gasses. Then, the structure of the catalyst was controlled in situ during the catalytic hydrogenation of ethylene. We observed that phase transitions occurring in palladium nanoparticles lead to dramatic changes of the catalytic activity. We found that palladium carbide phase and pure palladium demonstrated extremely high catalytic activity in ethylene to ethane hydrogenation, while β-PdH showed very surprisingly low activity. After continuous exposure to ethylene and hydrogen mixture, stable carbide phase formed in the nanoparticles. This phase provided high conversion of ethylene to ethane irrespective on the amount of hydrogen in the gas mixture.

Acknowledgement. This work was supported by the Mega-Grant of Ministry of Education and Science of the Russian Federation 14.Y26.31.0001.

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OP$_{10}$-15

In Situ XPS and XRD Study of Mixed Mn-Zr Oxide Catalysts Reduction

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Solid solutions based on ZrO_2 exhibit high catalytic activity in a number of practically important reactions. Mn-Zn mixed oxides can effectively catalyze the gas-phase oxidation of hydrocarbons or chlorcarbons. Although there is an agreement that the catalytic performance of these catalysts is determined by their redox properties, the exact mechanism for these reactions is not clear yet. Mn cations can enter the lattice of ZrO_2 with the formation of solid solutions $Mn_xZr_{1-x}O_2$, 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, under reduction conditions, a segregation of manganese with the formation of dispersed MnO_x may occur on the surface of the solid solution $Zr_{1-x}Mn_xO_2$.

One of the main ways to study redox properties of different oxides is a temperature-programmed reduction technique. On the basis of its results, it is possible, for example, to draw some conclusions about the presence of various forms of manganese oxides. However, TPR is an indirect method that allows monitoring only the absorption of hydrogen rather than the change in structural characteristics of catalysts and in the charge state of Mn and Zr cations. The aim of this work was to obtain detailed information on various stages of the reduction of Mn-Zn mixed oxides. The study was carried out using a combination of methods: temperature-programmed reduction, in situ XRD and in situ XPS.

A series of mixed Mn-Zr oxides with different molar ratios Mn/Zr have been prepared by coprecipitation of manganese and zirconium nitrates. It has been found that at low Mn/Zr ratios, when the Mn content is below 30 atom %, the catalysts are single-phase solid solutions ($Mn_xZr_{1-x}O_{2-\delta}$) based on a ZrO_2 structure. According to XPS data, manganese in these solutions exists mainly in the Mn^{4+} state. An increase in the Mn content mostly leads to an increase in the number of Mn cations in the structure of the solid solutions, but a part of manganese form Mn_2O_3 and Mn_3O_4 in crystalline and amorphous states.

The reduction of these oxides with hydrogen was studied by a temperature-programmed reduction technique, in situ XRD, and near ambient pressure XPS in a temperature range from 100 to 650 °C. It was shown that the reduction of the solid solutions $Mn_xZr_{1-x}O_{2-\delta}$ proceeds via two stages. During the first stage, between 100 and 500 °C, Mn cations incorporated into the solid solutions $Mn_xZr_{1-x}O_{2-\delta}$ undergo the partial reduction. During the second stage, at temperatures between 500 and 700 °C, Mn cations segregate on the surface of solid solution.

Acknowledgement. This work was supported by the RSF project №14-23-00037.

OP$_{10}$-16

Kinetic Study of the Low-Temperature Steam Reforming of Light Hydrocarbons in the Presence of Methane over the Ni-based Catalyst

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Processing and utilization of associated petroleum gas (APG) is one of the key tasks ensuring the progress of gas-and-oil producing industry. One of the promising methods of APG utilization is low-temperature catalytic steam reforming of light hydrocarbons (LTSR), that enriches the initial gas mixture with methane. Recently, we have shown [1,2] the possibility of APG LTSR over the Ni-Cr catalyst.

This work reports our new results on kinetic study of LTSR of model mixtures of light hydrocarbons (CH_4, $C_2H_6 - C_5H_{12}$), which composition is close to the realistic APG, over the Ni-Cr catalyst at T = 200-350 °C and atmospheric pressure. Two-stage macrokinetic model was suggested to describe the process. It includes the reactions of steam reforming of C_{2+}-hydrocarbons and CO_2 methanation:

1) $C_nH_{2n+2} + 2nH_2O \rightarrow (3n+1)H_2 + nCO_2$
2) $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

It was shown, that reaction (2) occurs in a quasi-equilibrium mode at T > 250 °C and the LTSR process is limited by the reaction (1). For the model methane-propane gas mixture the reaction orders with respect to CH_4, CO_2, H_2, H_2O and C_3H_8, as well as apparent activation energies were estimated. The obtained reaction orders were confirmed for other light hydrocarbons.

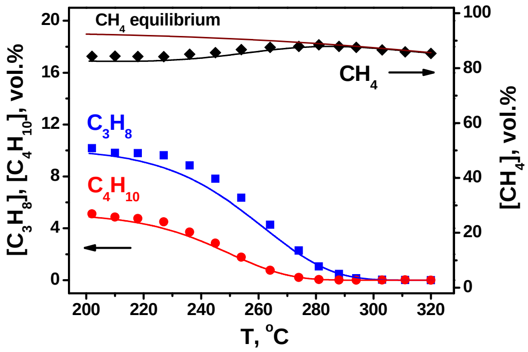

Fig. 1. The temperature dependencies of CH_4, C_3H_8 and C_4H_{10} concentrations (on dry basis) in the LTSR of model mixture. $H_2O/C = 0.5$. Points - experiment, lines - modelling.

Within the proposed model the kinetic parameters were optimized and numerical simulation of LTSR of model APG mixtures was performed. Comparison of the simulated and experimental data for the model methane-propane-butane mixture (Fig. 1) shows that proposed model describes well the observed dependences and so, can be used for catalytic reactor design.

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The Role of Oxygen in Deactivation of DeNOx Platinum catalysts. *In Situ* XPS and $N^{15}O$ Kinetic Study

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It is well known that chemical state of catalyst strongly depends on reaction conditions such as temperature, gas pressure and gas phase composition. As result in some cases application of the *in situ* technique is the only way to elucidate the mechanisms of catalytic reactions.

In the present work *in situ* X-ray photoelectron spectroscopy (XPS) study with mass-spectrometry gas phase analysis of the NO involved reactions on Pt/Al_2O_3 and bulk Pt catalysts was performed in wide range of temperature. Spectroscopy data was compared with results of ^{15}N isotopic kinetic studies performed in a static reactor equipped with mass-spectrometry gas phase analysis.

The particular attention was paid to the $NO+CO+O_2$ reaction. Under sample heating condition the shift of the XPS Pt4f line to the higher binding energy was found. Under sample cooling Pt4f line does not return back to the value typical for the metal platinum. The peak shift is not enough to assume the complete platinum oxidation. At the same time *in situ* XPS experiments on NO decomposition and NO involved reactions on bulk Pt catalysts (single crystal Pt(100) and Pt foil) indicate on formation of the two states of oxygen under reaction conditions, namely surface and subsurface oxygen. The amounts of these species strongly depend on sample temperature and gas phase pressure. Oxygen “deactivates” platinum catalysts in DeNOx reactions. So in the case of supported catalysts under O_2 excess shift of the Pt4f line can be explained by the introduction of the oxygen into Pt. Under sample cooling the state of active component is differ comparing with initial one.

During ^{15}N isotopic kinetic studies the size effect in $N^{15}O+CO+O_2$ reaction on Pt/Al_2O_3 was found. Under conditions similar to *in situ* XPS experiments obtained turn over frequency at 150^0C for the catalyst with mean Pt particle size of 7.9 nm is higher comparing with sample with mean particles size of 1.5 nm. Basing on comparison of spectroscopy data with results of catalytic test it can be assumed that observed size effect can be explained by the difference in oxidation resistivity of the platinum particles of the different size.

In situ XPS allowed us to trace the evolution of the catalyst under reaction conditions. Combination of *in situ* XPS with kinetic studies provide important information on catalytic reactions.

Acknowledgement. This work was supported by The Russian Science Foundation, grant 14-23-00146.

OP10-18

Ethanol and CO Oxidation over Ag/SiO_2 Catalysts: Effect of Hydroxyl Coverage of the Support

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The Ag/SiO_2 catalysts attract special attention due to high activity in low-temperature CO oxidation [1], selective oxidation of alcohols into aldehydes [2] and total oxidation of volatile organic compounds [3]. Numerous investigations of Ag/SiO_2 systems were devoted to influence of different gas phase pretreatments and preparation method on state and catalytic activity of silver. However, effect of support properties, namely, concentration of OH-groups, was not thoroughly investigated. The aim of the present work is to show the effect of hydroxyl coverage of silica on the surface and catalytic properties of Ag/SiO_2 catalysts in low-temperature CO oxidation and ethanol selective oxidation. Initial silica was calcined at 550 and 900 °C to obtain catalyst supports with different concentrations of OH-groups. The Ag/SiO_2 catalysts were prepared by incipient wetness impregnation method and denoted as Ag/SiO_2-550 and Ag/SiO_2-900. The prepared Ag/SiO_2 catalyst was tested in the said reactions and characterized by N_2 adsorption at -196 °C, TPR/TPO techniques, TEM, H_2-O_2 titration method and in situ FT-IR spectroscopy of adsorbed CO and ethanol.

It was stated that the oxidative treatment of Ag/SiO_2 catalysts at 500 °C followed by H_2 reduction at 200 °C resulted in formation of highly dispersed Ag particles able to easily adsorb oxygen at RT. However, the nature and quantity of the adsorbed species are different for Ag/SiO_2-550 and Ag/SiO_2-900 samples due to differences in structure and dispersion of silver nanoparticles. Dispersion of Ag nanoparticles for Ag/SiO_2-550 and Ag/SiO_2-900 catalysts was 49.1 and 28.5 %, respectively, which corresponds to mean particle size of 2.7 and 4.7 nm. Moreover, according to TEM, silver particles on the surface of Ag/SiO_2-900 catalyst have defective structure (represented by several crystal domains). Catalytic activity of the Ag/SiO_2-900 catalyst in CO oxidation was higher in comparison with the one for Ag/SiO_2-550. Increasing of catalytic activity may be associated with defective structure of Ag particles which was favourable for adsorption of CO. Silanol groups of silica play important role in ethanol adsorption. Two types of adsorbed species were observed: Physically adsorbed ethanol bonded with OH-group and chemically bonded ethoxy species. Ethanol adsorbed on the OH-groups converted into acetaldehyde on the Ag/SiO_2 interface, while ethoxy species are stable up to 500 °C in the inert atmosphere.

Acknowledgement. This work was supported by “Tomsk State University Academic D.I. Mendeleev Fund Program” in 2016.

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Mechanisms of Heterogeneous Hydrogenation of α,β-unsaturated Carbonyl Compounds and Thiophene Hydrodesulfurization Studied Using Parahydrogen-induced Polarization Technique

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Parahydrogen-induced polarization (PHIP) is a useful method for mechanistic studies of heterogeneous catalytic reactions involving hydrogen. If reaction mechanism includes pairwise addition of two atoms from one hydrogen molecule to the same substrate molecule, the utilization of parahydrogen in this reaction leads to characteristic antiphase line shape and significant enhancement of NMR signals of reaction products and/or intermediates. Observation of PHIP effects allows to rule out the possibility of pairwise hydrogen addition as well as to detect minor reaction products or short-lived intermediates.

Herein, we used PHIP technique for studies of heterogeneous gas phase hydrogenation of α,β-unsaturated carbonyl compounds [1]. PHIP effects were observed in hydrogenation of C=C bonds of acrolein and crotonaldehyde over various supported Pd-, Pt- and Rh-based catalysts, implying the existence of pairwise hydrogen addition route. In contrast, hydrogenation of C=O bond never led to any PHIP effects. Interestingly, in acrolein hydrogenation over some of Pd-based catalysts the NMR signal of CHO group of propanal was also polarized, most likely as a result of minor process involving scission of acrolein C(O)-H bond. In hydrogenation of acrolein and vinyl acetate over Rh-based catalysts polarized signals corresponding to 2-butene were observed in the NMR spectra. 2-butene can be formed by decarbonylation of acrolein or hydrogenolysis of vinyl acetate and subsequent dimerization of resultant C_2 species.

Also thiophene hydrodesulfurization was investigated using PHIP technique [2]. In case of $MoS_2/\gamma\text{-}Al_2O_3$ catalyst butenes and butane were formed, but without any PHIP effects. However, when this catalyst was used in 1,3-butadiene hydrogenation, PHIP effects were observed for the same reaction products. These results demonstrate that in thiophene hydrodesulfurization over $MoS_2/\gamma\text{-}Al_2O_3$ 1,3-butadiene is not formed and the reaction proceeds via formation of dihydro- or tetrahydrothiophene intermediates.

Acknowledgement. This work was supported by RFBR (14-03-00374-a, 14-03-93183 MCX_a and 16-03-00407-a) and MK-4498.2016.3.

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OP10-20

Preparation of Model VO_x/TiO_2 Catalysts by Atomic Layer Deposition

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The monolayer V_2O_5/TiO_2 catalyst has been previously shown to exhibit high activity in the selective oxidation of formaldehyde to formic acid [1], methanol to methyl formate and dimethoxymethane [2], and the selective oxidation of ethanol to acetaldehyde and acetic acid [3]. To clarify the structure of the active sites of vanadium-titanium oxide catalyst the model catalyst was investigated. To prepare the model monolayer VO_x/TiO_2 catalyst we have used the atomic layer deposition (ALD) method. The $TiO_2(110)$ single crystal was used as a support, before ALD process the crystal was cleaned via multiple cycles of Ar^+ sputtering and annealing in UHV at 730°C. The surface cleanness and smoothness of $TiO_2(110)$ were controlled by XPS, HREELS, and LEED. Vanadium (V) oxytriisopropoxide (VTIP) was used as a precursor. The deposition cycle consisted of exposition of the sample in the VTIP vapor at 190°C to form a layer of adsorbed precursor molecules and subsequent treatment in oxygen at 350°C to remove the carbon-containing ligands from the surface.

The process of growth of vanadium oxide films was studied by LEED, XPS, and HREELS. The formation of epitaxial layer of vanadium oxide film on the surface of $TiO_2(110)$ crystal was evidenced by blurring reflections on the LEED-image of the single crystal surface. XPS study revealed that after the VTIP deposition vanadium presents in the fully oxidized state (V^{5+}) and partially reduced V^{4+} and V^{3+} states. The further treatment in oxygen results in the full oxidation of vanadium to V^{5+}. According to our estimation, 0.25 monolayer of VO_x forms on the crystal surface during one deposition cycle. It was shown that the monolayer $VO_x/TiO_2(110)$ catalyst is thermally stable up to 350°C in the oxygen atmosphere.

Adsorption of methanol on the model catalyst was studied by XPS, LEED and HREELS. It was shown that methanol dissociates to form methoxy and hydroxyl groups starting with room temperature. Thus, deposited VO_x film could be used as a model catalyst to study selective oxidation of methanol.

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

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OP_{10}-21

CO and Soot Oxidation with CeO_2-ZrO_2 Mixed Oxides in the Absence of Oxygen

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During the last few decades, Ceria-based materials have received much attention in applied catalysis, thanks to their notable redox properties and OSC that allow quick intake and release of oxygen. Moreover, it has been observed that inserting aliovalent cations, like Zr^{4+} and Pr^{3+}/Pr^{4+} into Ceria framework gives more surface oxygen vacancies (structural defects) as well as redox active sites (1-3). In the present work, sets of nanostructured Ceria (Figure 1), Ce-Zr (Ce 80 at.%, Zr 20 at.%), Ce-Pr (Ce 80 at.%, Pr 20 at.%) and Ce-Zr-Pr mixed oxide catalysts (Ce 80 at.%, Zr 10 at.% and Pr 10 at.%) have been prepared and their catalytic activity has been tested for CO oxidation, as prototypical reaction for probing the oxidation activity. The catalysts have been characterized by complementary techniques, including powder XRD, FE-SEM, N2 physisorption at -196 °C, H_2-TPR, O_2-TPD and XPS.

As a whole, better results for CO oxidation have been obtained with mixed oxides (oxidation activity scale: Ce-Zr-Pr > Ce-Zr > Ce-Pr) rather than pure Ceria (Figure 2), thus confirming the beneficial role of multicomponent catalysts for this prototypical reaction. Since CO oxidation occurs via a Mars-van Krevelen (MvK)-type mechanism over Ceria-based catalysts, it appears that the presence of both Zr and Pr species into the Ceria framework improves the oxidation activity, via collective properties, such as electrical conductivity, surface or bulk oxygen anion mobility. The Ce-Zr-Pr catalyst, indeed, exhibited easier reducibility and better redox properties, as revealed by H_2-TPR, O_2-TPD and XPS analysis.

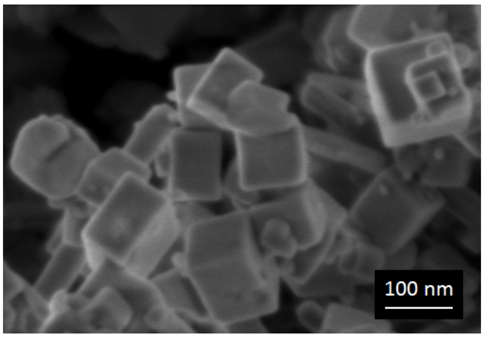

Figure 1. FESEM image of the novel Ce-Zr-Pr catalyst obtained by hydrothermal synthesis.

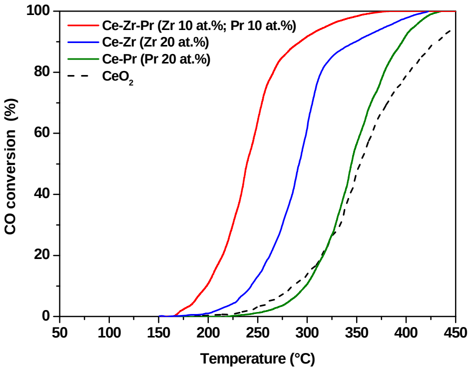

Figure 2. Conversion of CO to CO_2 as a function of temperature.

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Paramelaconite-based Catalysts of Low-Temperature CO Oxidation

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In this work, the catalytic properties of $Ag_2Cu_2O_3$ and CuO nanopowder in CO oxidation were investigated and compared in detail. Paramelaconite surface structure of studied oxides was proposed to be responsible for low-temperature catalytic activity[1].

Mixed silver-copper oxide $Ag_2Cu_2O_3$ and copper oxide were synthesized by precipitation of $AgNO_3$+$Cu(NO_3)_2$ and $Cu(NO_3)_2$ solutions in alkali medium, respectively. The catalytic properties of $Ag_2Cu_2O_3$ and CuO samples in the reaction of CO oxidation were shown to be characterized by high activity in the low temperature range, i.e. 60-130°C. The TPR-CO study revealed the presence of low-temperature reduction shoulder for both the $Ag_2Cu_2O_3$ and CuO samples, which indicated the presence of highly reactive oxygen species. The appearance of low-temperature TPR-CO peak was attributed to the reversible surface transition $Cu^{2+}\rightarrow Cu^{1+}$.

Based on XPS data two oxygen species characterized by O1s binding energies ($E_{b.}$(O1s)) equal to 529.5 and 531 eV with similar reaction properties were observed on initial surface of both $Ag_2Cu_2O_3$ and CuO_x oxides. It may be the reason for close catalytic properties of $Ag_2Cu_2O_3$ and Cu_4O_3/CuO oxides.

$Ag_2Cu_2O_3$ and CuO oxides were additionally studied using *in situ* DRIFTS method. Carbonyls Cu^{1+}-CO groups with vibration frequency ~2100 cm^{-1} were detected on both oxide surfaces as under catalytic CO+O_2 conditions as during reduction by CO at near room temperature indicated the similar chemical environment of Cu^{1+} sites. It should be paramelaconite-like surface with Cu^{1+} sites appeared as result of Cu^{2+} reduction.

The catalytic properties of $Ag_2Cu_2O_3$ and CuO nanopowder in low-temperature CO oxidation were close to each other. Electronic and reaction properties of oxygen species on the surface were also found to be similar for both $Ag_2Cu_2O_3$ and CuO oxides. Metastable Cu_4O_3 oxide can be effortless formed on the surface of CuO nanopowder under reaction conditions. Oxide Cu_4O_3 and mixed silver-copper oxide $Ag_2Cu_2O_3$ are characterized by paramelaconite structure. Unique crystal structure of paramelaconite oxides with oxygen vacancies and low-valence Cu^{1+} sites stimulates the formation of CO and O_2 adsorbed species with high reactivity determining high catalytic activity in CO oxidation at near room temperatures.

Acknowledgement. This work was supported by RFBR, research project No. 16-33-00202.

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OP10-23

Oxidation of Naphthols on Nanocrystalline Pt-Group Metal Catalysts

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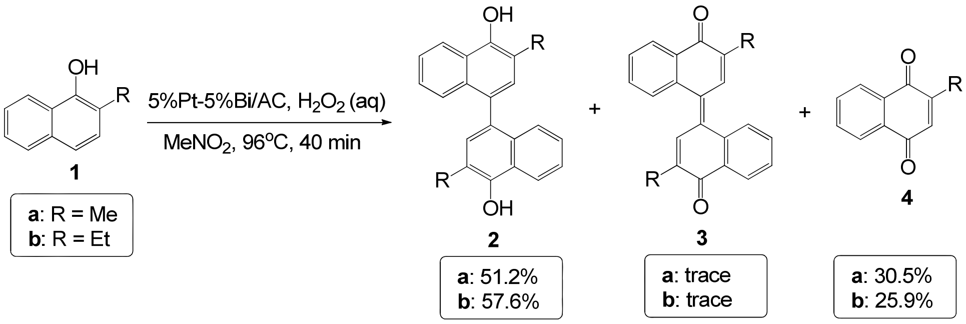
Catalytic oxidative coupling of naphthols is a useful method for the formation of new carbon-carbon bonds in green organic synthesis. In our previous work [1] we reported that in the presence of hydrogen peroxide, precious metals supported on carbon catalyze the reactions shown in Scheme 1. Naphthols with electron-donating groups in 2- and 4-position (e.g. 2-methyl-, 2-ethyl- and 4-methoxy-1-naphthol) can be converted by this method. The products obtained are useful for many pharmaceutical applications, as organic dyes and as ligands in enantioselective catalysis [1, 2]. The outcome of the reaction is influenced by the active metal used (Pt, Pd or Ag), the catalyst modifier (Bi or Sb), the solvent, the reaction temperature, and the physical structure of the catalyst. For example, in methanol under reflux the selectivity shifts, in comparison to Scheme 1, to give 83.0 and 61.1% of **3a** and **3b**, respectively.



Scheme 1. Oxidation of substituted 1-naphthols over promoted platinum catalysts.

The coupling of **1** to **2** competes with the direct oxidation of **1** to **4**. The suggested mechanism for the formation of **2** involves the dimerization of naphthoxy species chemisorbed on platinum. Re-adsorption of **2** can lead to the formation of **3**. The quinone **4** is formed by the direct oxidation of naphthoxy intermediates by chemisorbed perhydroxide.

The mechanistic implications with respect to the various competing reactions and the position of the substituent (2- or 4-position) will be discussed in detail.

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OP10-24

The Effect of Electron-Acceptor Sites on Catalytic Dehydrochlorination of 1-Chlorobutane over Metal Oxide Catalysts

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One of the most intriguing properties of many heterogeneous acid catalysts is their ability to generate organic radical cations after adsorption of aromatic electron donors. The existence of electron-acceptor sites with electron affinities ~7 eV in large quantities on the surface of many conventional oxides is quite remarkable. Electron-acceptor sites of different strength can be characterized using aromatic probes with different ionization potentials.

It was shown earlier that the catalytic activity in dehydrochlorination of 1-chlorobutane over nanocrystalline MgO substantially increases with time due to the MgO conversion to $MgCl_2$. Recently we reported that weak electron-acceptor sites formed due to the MgO halogenation might be responsible for solid-state reaction between nanocrystalline MgO and CF_2Cl_2. In this study we characterized weak electron-acceptor sites formed during 1-chlorobutane dehydrochlorination over several oxides using perylene and anthracene as spin probes, and found a good correlation between their concentrations and the catalytic activity.

The catalytic activity of nanocrystalline aerogel-prepared MgO was found to increase significantly during the 1-chlorobutane dehydrochlorination reaction, which is accompanied by modification of the MgO surface and bulk with chloride ions. No electron-acceptor sites were observed on the surface of initial MgO samples. They appeared only during the reaction. Their concentration normalized per unit mass gradually increased during the reaction due to the surface chlorination. A good correlation was observed between the catalytic activity and the concentration of weak electron-acceptor sites. Commercial MgO sample was substantially less active and showed much lower concentration of electron-acceptor sites.

Al_2O_3 samples are characterized by substantial concentrations of electron-acceptor sites. This made this material much more active, so that similar chlorobutane conversion was achieved at lower temperatures than on nanocrystalline MgO. The catalytic activity and the concentration of electron-acceptor sites increased during the first 20 min on stream due to the surface chlorination accompanied by an increase in the concentration of electron-acceptor sites.

On the contrary, the activity of sulfated alumina catalysts gradually decreased during reaction due to substitution of the sulfate groups for chlorine. Again a good correlation was observed between the catalytic activity in dehydrochlorination of 1-chlorobutane and the concentration of weak electron-acceptor sites as the latter deceased with time on stream paralleling the decrease in the catalytic activity.

Acknowledgement. This study was supported in part by Russian Foundation for Basic Research (Grant 16-03-00267-mol-a).

Electrocatalytic Functionalization of Biologically Important Substrates of Different Classes of Arenes

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In recent decades, the field of fluorinated and phosphonated aromatic molecules has grown rapidly in recent years, and nowadays they are utilized for different applications ranging from pharmaceutical chemistry to materials science. However, the synthetic pathways to these compounds are very complex, often multi-step and characterized by the use of high temperatures, pressures, and expensive reagents and catalyst. Nevertheless, the high value of arenes with fluoroalkyl or phosphonate substituents for medical, agrochemical and engineering industries is the impetus that provokes and promotes exploratory research related to the simplification of the processes of their formation. That is why the aim of the work is to provide a simplified method for the catalytic fluoroalkylation through cross-coupling reaction of organic and fluoroorganic halides, excluding the use of chemical oxidants and reductants as well as phosphorylation through CH-activation of aromatic substrates.

New approaches to the synthesis of organofluorine and organophosphorus compounds were developed, and practically significant biologically active, hydrophobic or plasticizing compounds were produced. The confirmation of reaction routs through the metal (I) or metal (0) active form of the catalyst and the intermediate σ-perfluoroalkyl metal complex deepens the understanding of the mechanisms of catalytic processes involving Ni complex, widely popular in the modern chemistry and chemical technology.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-23-00016.

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OP10-26

In Situ Time-resolved XRD Study of Red/Ox Transformations in Copper Oxide-based Systems

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Copper-containing compounds are widely used as catalysts in various reactions, including CO-PROX [1] and water-gas shift reactions [2] etc. Structure of copper-containing oxide catalysts exhibit high sensitivity to Red/Ox conditions and therefore should be studied by in situ methods. In many real catalysts these studies are complicated due to complex nature of studied systems. Model studies of copper oxide nanoparticles are essential for understanding of reaction mechanisms.

In this work we studied in detail reduction and re-oxidation mechanisms of CuO nanoparticles using *in situ* time resolved X-ray diffraction. The time-resolved studied were performed in Siberian Centre of Synchrotron radiation, Budker Institute of Nuclear Physics, Novosibirsk. X-ray diffraction was measured in a high temperature chamber using fast 1D detector (OD-3M) in the course of CuO nanoparticles reduction. In the contrast to previous studies of bulk CuO powders reduction [3], we found no difference in reaction mechanism under high (1bar) hydrogen supply and under limited hydrogen supply. In both cases it goes through formation of intermediate Cu_2O phase.

The difference of Rex/Ox behaviour of CuO nanoparticles in comparison to bulk material we attempt to explain by extended fraction of (-111) surfaces that under mild reduction conditions can easily be transferred to (202) of Cu_4O_3 and finally to (111) surface Cu_2O. These particular transformations were directly observed by TEM after CuO nanoparticle exposure under electron beam.

The good geometrical similarity between (-111) CuO, (202) Cu_4O_3 and (111) Cu_2O planes can explain an effortlessness of transitions between them and, as a consequence, a high oxygen mobility of CuO nanopowder as provided by TPR-CO study.

Detail understanding of Red/Ox transformations in model CuO nanoparticles was used for studies of activation processes and phase transformations in other copper-containing oxide systems.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 16-33-00202 mol_a.

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Bimetallic PtCu Nanoparticles in PtCu/C Electro-Catalysts

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Nanocatalysts PtCu/C with different distribution of components in bimetallic PtCu nanoparticles (NPs) were synthesized by simultaneous and sequential deposition of Cu and Pt on carbon support. Electrochemical stability of the obtained samples PtCu/C was studied using the cyclic voltammetry. Characterization of atomic structure of as prepared PtCu NPs and obtained after acid treatment was performed by TEM, XRD, and by Pt L_3- and Cu K-edge EXAFS using the technique for determining local structure parameters of the absorbing atom under strong correlations among them [1]. EXAFS derived parameters were used for generation of structural models of PtCu NPs by the method of cluster simulations. For this end, the procedure of visualization of components distribution in the volume of mean PtCu NP using local structure parameters obtained by EXAFS, was suggested. Within this approach, the models of atomic structure of PtCu NPs obtained by the two methods of synthesis, before and after post treatment were revealed.

Acknowledgement. This work was supported by grant 213.01.-07.2014/10ПЧВГ of Southern federal university (RF).

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OP_{10}-28

Atomic Oxygen on Ag(111) Generated via Ozone Decomposition and Its Reactivity towards Methanol

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Oxygen species generated on silver surface attract fundamental and practical interest due to the relevance to epoxidation of ethylene and partial oxidation of alcohols [1,2]. In spite of a large body of existing work in literature, the nature of oxygen spices on Ag(111) is still not clear [3]. O_2 dissociation on the Ag(111) surface and formation of oxygen atoms requires high oxygen pressure which results in reconstruction of the silver surface [4] and leads to the formation of various types of oxygen atoms and subsurface oxygen species [5]. In the current work, we present a novel way of preparation of oxygen layers on the Ag(111) surface under ultra-high vacuum (UHV) conditions where oxygen layer can be prepared at 10^{-9} Torr with suppressed surface reconstruction. For the O/Ag(111) overlayers prepared at 100 K we did not detect any changes in the LEED pattern. For the overlayers prepared at 470 K at low coverages the previously not detected p(5×1) surface structure was found; and at high coverages the c(4×8) structure was detected which previously was observed only at low oxygen coverages [4]. In our experiments we did not detect the commonly observed p(4×4) structure. In TPD experiments, oxygen overlayers prepared without surface reconstruction reveale a single O_2 desorption peak at 560 – 580 K, while at high oxygen coverages (when surface reconstruction takes place) the additional desorption states at 520 – 560 K appear.

The oxygenated Ag(111) surfaces were investigated in methanol oxidation reaction. The TPR experiments of methanol adsorbed on oxygen pre-covered Ag(111) surface reveal that methanol could be oxidized into the two main products: formaldehyde and CO_2. IRAS experiments demonstrate that on the pre-oxidized Ag(111) surface, adsorption of methanol at 100 K leads to the formation of surface methoxy groups which can be further transformed into formaldehyde. On the other hand methanol exposure on O/Ag(111) at 300 K (i.e. at temperature where methanol is not stable on the clean Ag(111) surface) leads to surface formate species which produce only CO_2 upon oxidation. Thus, depending on temperature two different reaction pathways of methanol oxidation were observed.

Acknowledgement. This work was supported by the Scientific and Technical Research Council of Turkey (TUBITAK) (Project Code: 112T589).

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OP$_{10}$-29

Investigation of Hydrogen Transfer Reactions between C_6-Hydrocarbons on the Catalysts with Different Natures

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Intermolecular hydrogen transfer reactions play an important role in many refining processes (catalytic cracking, alkylation, isomerization, etc.). These reactions can also be used as a method of saturation of unsaturated and sulfur compounds [1,2] in the absence of molecular hydrogen. The hydrogen source are the hydrogen donors: paraffins and naphthenes.

Saturation without molecular hydrogen of unsaturated and sulfur compounds can be carried out on acid-base catalysts and containing a noble metal (Pt, Pd) catalysts [3,4]. The intermolecular hydrogen transfers from naphthenes to olefins and sulfur compounds are carried out by different mechanisms on the different nature catalysts. Zeolite-containing catalysts is carried out by transfer of hydride-ions, and catalysts comprising a noble metal - by means of molecular hydrogen.

Disproportionation reaction of cyclohexene - a widely used model reaction of hydrogen transfer. Hydrogens are distributed among three molecules of cyclohexene to form cyclohexane and benzene. The acidity of the support has a great effect on cyclohexene conversion and composition of obtained products. Support with high acidity promotes isomerization, cracking and polymerization reactions resulting in the formation of methylcyclopentenyl, light hydrocarbon gases and cyclohexene dimers. In the case of the catalyst with an inert carrier selectivity of hydrogen transfer reactions reaches 75 %. The second direction of the cyclohexene transformation is dehydrogenation reactions.

Acknowledgement. Financial support for this project was provided by the Ministry of Education of Russian Federation (UIN: RFMEFI60715X0111)

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OP$_{10}$-30

Evaluation of Cu Based Catalysts for Glycerol Hydrogenolysis

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Catalytic glycerol hydrogenolysis represents an interesting alternative route for the production of propylene glycol which is currently produced from petroleum via propylene oxide. Upgrading glycerol, a biodiesel side stream, into the more valuable propylene glycol (PG) will also increase the sustainability and commercial viability of biodiesel production. It has been widely accepted that Cu based catalysts efficiently catalyse glycerol hydrogenolysis [1,2]. Although many researchers have investigated this reaction, very few have focused on a rational catalyst comparison making use of microkinetic modelling, including kinetic and catalyst descriptors.

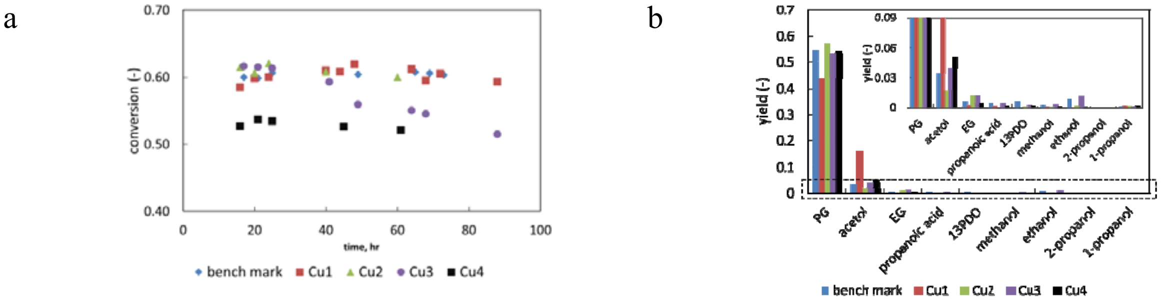

Figure 1: *Comparison of activity and selectivity of various commercial Cu catalysts. a) long term stability of Cu catalysts at T: 503 K, P: 6.5 MPa, W/F_G: 0.55 a. u., F_{H2}/F_G: 5. b) product distribution at T: 503 K, P: 6.5 MPa, W/F_G: 0.55 a. u., F_{H2}/F_G: 5.*

Four commercially available Cu based catalysts were compared to a bench mark catalyst as part of a set of intrinsic kinetic experiments in a high-throughput kinetic mechanistic investigation setup. **Figure 1a** indicates a stable glycerol hydrogenolysis activity for all the catalysts except for Cu3 which was zirconia supported and, hence, is more prone to deactivation [3]. Although stable activity was observed for Cu4, it exhibited a lower initial conversion compared to the other catalysts due to its lower Cu content. **Figure 1b** compares the product distributions obtained with the investigated catalysts. While Cu1 has the lowest PG yield, it leads to a notably high acetol yield such that its total yield of by-products is the lowest of the investigated catalysts. Cu2 combines an interesting PG yield combined with a low production of any of the other products, i.e., acetol and by-products. This differences in the product distribution will be taken into account through adaptation in the kinetic and catalyst descriptors of the microkinetic model.

Acknowledgement. This work was supported by IWT Flanders and ERC grant agreement n° 615456.

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School-Symposium "Quantum-mechanical modeling of catalytic processes"

Kls-1

Innovative Computational Design of Advanced Nanoalloy Materials for Catalysis and Beyond

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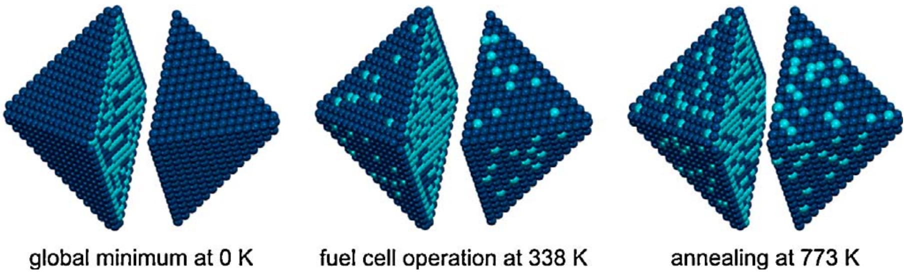
Metal nanoparticles (NPs) are key component of numerous materials. Yet, monometallic NPs are often insufficiently versatile, which limits their use. Conversely, diversity of mixed-metal NPs (nanoalloys) enables tailoring their properties for a given application much easier. It is very hard to experimentally determine the atomically resolved composition (atomic ordering) in nanoalloys. We recently proposed an innovative method to ascertain atomic ordering in nanoalloys by density functional calculations [1]. This method is applicable to combinations of transition metals with each other and with *s*,*p*-elements [1-5]. It allows one to reliably predict stable atomically resolved 3-dimensional structures of nanoalloys, thus guiding their manufacturing. The method also permits to assess structural changes in nanoalloys at elevated temperature, under reaction atmosphere or on a support. We shall outline the method and exemplify its application to nanoalloys based on Pd [1], Pt [2-4] and Ni [5].

Our method renders possible generating databases of structures and energies of alloy NPs spanning the Periodic Table. Its applications deepen the understanding of chemical bonding in nanoalloys and accelerate the discovery of tailor-made nanoalloys. This approach enables real-time simulation of various kinds of nanoalloy particles with thousands of atoms.



global minimum at 0 K fuel cell operation at 338 K annealing at 773 K

Figure 1. Temperature-dependent structures of $Pt_{1638}Co_{1637}$ particles [3]. Pt – dark blue.

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Kls-2

Bonding and Reactivity at Catalytic Interfaces: Modelling Novel Electrodes from Ideal to Realistic Reaction Environments

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Platinum-group metals supported and dispersed on highly reducible oxides are common active catalysts for the industrial synthesis of chemical products and for renewable-energy applications such as fuel cells or artificial photosynthesis. Due to the high price of Pt, the sustainable development of these technologies requires new materials that reduce the content of precious metal without affecting the device efficiency.

I will discuss the challenges opened by these systems to electronic-structure simulations and will present case studies in the context of electrodes for solar energy [1-3] and fuel cells applications [4-8].

We combine DFT simulations with ab-initio molecular dynamics, atomistic thermodynamics, metadynamics, and other enhanced-sampling methods to reveal the new surface chemistry opened by these systems. The calculations are used to characterise the chemical bonding and the reactivity at the electrode active sites in a wide range of compositions and environments, ranging from model surfaces at $T=0K$ in vacuum conditions to realistic wet electrodes at finite temperatures, i.e. chemical reactions at complex solid-liquid interfaces comprising nano-structured surfaces in contact with a solution.

The calculated results allow for rationalising the available experimental data and identify correlations among the reaction mechanisms, thermodynamic efficiency, and local structure of the active sites, thus shedding light on the origins of the amplified reactivity and stability of novel electrodes.

Acknowledgement. This work was supported by the FP7-NMP-2012 project chipCAT under contract number 310191 and by the EU FP7 COST action CM1104.

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DFT Study of Methanol Decomposition on Platinum Clusters

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The clusters of transition metals demonstrate a different chemical behavior than the metal films. For example, the XPS in situ studies of methanol decomposition revealed the increased selectivity of CO formation with its following oxidation on the Pt nanoparticles compared to extended surfaces [1]. The most probable path developed for an ideal massive Pt (111) surface [1,2], begins with O-H bond cleavage and a consecutive abstraction of hydrogen atoms:

$$CH_3OH > CH_3O > CH_2O > CHO > CO$$

In the present study, we theoretically address the intermediates of methanol dehydrogenation reaction at different sites of ideal Pt (111) surface and Pt nanoparticles. All electronic structure calculations were carried out using the Vienna Ab initio Simulation Package (VASP), employed the plane-wave-based projector augmented wave approach and the density functional (DF) gradient-corrected exchange-correlation functional PW91 with a kinetic energy cutoff of 400 eV. Pt substrate was represented with two different models: periodic 2D-slab mimicking the ideal Pt (111) surface and cuboctahedra cluster model Pt_{79} with Pt(111) and Pt(001) facets, which model defect-rich surface.

Our DF study confirms the experimental observation that CO molecules and CH_xOH_y ($x=1$-3, $y=0$-1) intermediates are preferably adsorb at and nearby the low-coordinated atoms of Pt substrate. These intermediate species are by 0.2–0.6 eV more strongly bound at edges and corners of Pt nanoparticles compared to the regular Pt(111) surface. This stabilization is caused by extra flexibility of low-coordinated sites to accommodate adsorbates. The methanol and formaldehyde are weakly adsorbed (0.6-0.8 eV), while the other derivatives are strongly bound (2.3-3.1 eV) and prefer decomposition rather than desorption from Pt_{79} cluster edges. The geometries and energies of all species involved were analyzed, and the decomposition energy profile was mapped out to elaborate the favorable reaction mechanism. The binding energies of CO, which is final reaction product and catalytic poison for Pt, decrease from -1.87 to -1.70 eV, as result of growth of the cluster size from Pt_{79} to Pt_{116}.

Acknowledgement. This work was supported by the RFBR (Russian Foundation for Basic Research), grant 16-33-00578. Computational support was provided by the Siberian Supercomputer Center (www2.sscc.ru).

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SOP$_{10}$-02

Phosphine-protected Gold Clusters: from Structure Prediction to Catalytic Reaction Study

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Protected gold clusters have generated a strong interest, because of luminescence, biological and catalytic properties including the synthesis of tri- and tetra-substituted furans, the oxidation of styrene into benzaldehyde, and the cycloaddition of allenenes [1]. The ligand-protected clusters can be described by the $[(PR_3)_sAu_nX_m]^q$ formula, where Au_n is gold core stabilized by m electron-withdrawing X ligands (SR or Hal) and s weakly bound PR_3 ligands (R=–C_nH_{2n+1}, –C_6H_5) [2]. Despite significant progress in the applications of phosphine-protected gold clusters in catalysis, mechanisms of the formation, as well as the ligands influence on the catalytic properties have not been fully understood yet. Therefore, the study of the phosphine-protected gold clusters using quantum-chemical methods is very promising direction.

Here, we investigated the influence of the different electron-withdrawing ligands X (X= –C≡CH, –CH_3, –SCH_3, –F, –Cl, –Br, –I) on the structure and electronic properties (HOMO-LUMO gaps and the binding energies) of $[Au_4(dpmp)_2X_2]^{2+}$(*dpmp*–bis(diphenylphosphinomethyl)phenylphosphine). There activity of the clusters in decomposition, ligand exchange reaction and oxidation by molecular oxygen was considered. The all-electron calculations were performed within the spin-polarized DFT/PBE and the scalar-relativistic approach in Priroda and NWChem programs. It was shown, that PBE level allows more accurately calculating structure of the $[Au_4(dpmp)_2(C{\equiv}CC_6H_5)_2]^{2+}$ cluster than PBE0, TPSS, TPSSh.

It was found that the X ligand weakly effects on the structure of $[Au_4(dpmp)_2X_2]^{2+}$, but it determines the electronic properties of the clusters. Calculated HOMO–LUMO gap decreases in the order: –F >–Cl >–Br ~–C≡CH >–CH_3>–I >–SCH_3. According to the binding energies, all clusters are stable. Based on the calculation, $[Au_4(dpmp)_2(C{\equiv}CH)_2]^{2+}$ is a suitable precursor for synthesis of variety clusters by ligand exchange reactions. The reactions of O_2 and $[Au_4(dpmp)_2Hal_2]^{2+}$were simulated; superoxo-, peroxo- and oxide-complexes were found. The oxide-complexes are the most stable. The reaction is accompanied by the formation of $OOH_{(s)}$, which is active radical in many catalytic processes. The cluster protected by fluorine ligands indicates the highest reactivity.

Acknowledgement. This work was supported by the Russian Science Foundation 14-01-00310, and the Ministry of Education and Science of the Russian Federation Grant NSh-3171.2014.3.

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SOP$_{10}$-03

DFT Study of the Active Sites of Gold Clusters Anchored by Thiolate, Selenolate and Tellurolate Ligands

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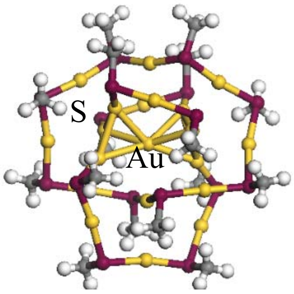
Thiolate-protected gold clusters have attracted considerable interest over the last decade due to their unique structure and properties including catalytic activities in CO oxidation, selective oxidation of styrene, and the chemoselective hydrogenation of α,β-unsaturated ketone to unsaturated alcohol [1]. The clusters are formed by the symmetric Au_n core protected by staple $–(Au–SR)_x–$ fragments in the shell. The interaction of core atoms and atoms in the staple shell determines the cluster’s structure, available active sites, and the mechanism of the catalytic reactions. It should be mentioned that the mechanism of the reactions catalyzed by thiolate-protected gold clusters has been unclear yet.

In this work, we investigated the gold clusters with the composition $Au_{20}(XCH_3)_{16}$ (X=S, Se, Te) with DFT/PBE and SBKJC basis set. The calculations were performed in NWChem, PRIRODA programs. Our aim is to study the effect of the ligand nature on the structure, stability (HOMO–LUMO gap), binding energy of the cluster’s fragments, and electronic properties including vertical ionization potential (VIP) and vertical electronic affinity (VEA). The benchmark calculations of interatomic distances and dissociation energy of Au_2, AuS, $(AuSR)_x$ (x=4÷8), $Au–(AuSR)_4$, $Au_{20}(SR)_{16}$ (R = $–CH_3$, $–C_6H_5$) [2] have been shown, that the DFT/PBE/SBKJC method is exact in calculation of the structure and energy of thiolate-protected gold clusters.



The five isomers of $Au_{20}(XCH_3)_{16}$ (X=S, Se, Te) were calculated [2,3], and the most stable structure is depicted on the figure. For all ligands, the Au_7 core consists of two tetrahedrons, united by a common vertex, which is protected by an octameric ring, one triple and two monomeric staple motifs. The HOMO-LUMO gap decreased in the series of $Au_{20}(SCH_3)_{16}$, $Au_{20}(SeCH_3)_{16}$, $Au_{20}(TeCH_3)_{16}$, which indicating to high stability of thiolate-protected cluster. The stability of the clusters also studied in respect to decomposition in solution or after heating in the reactions including ligand or CH_3 group removing [4]. The $Au_{20}(SCH_3)_{16}$ is the most stable in solution and after heating. The calculated values of VIP decreases in the order $–SCH_3 > –SeCH_3 > –TeCH_3$, in opposite to VEA data. Thus, $Au_{20}(SeCH_3)_{16}$ and $Au_{20}(TeCH_3)_{16}$ have opportunity in the oxidation reactions due to low VIP, the gold atoms in the staple fragments can be active sites.

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SOP$_{10}$-04

DFT Insight into CO Oxidation Catalyzed by Gold-Copper Nanoclusters

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The oxidation of carbon monoxide (CO) to carbon dioxide (CO_2) has attracted great interest in recent years because the reaction has many industrial applications such as in catalytic conversion of automobile exhaust and in fuel cells. As is known, in contrast to Au bulk materials, Au nanoparticles can be used in many selective oxidation reactions, particularly in CO oxidation [1]. Also it has been shown that the sub-nano atomic Au_n clusters (n = 2–20) supported on magnesia are the active in CO oxidation [2]. At the same time, some alloyed nanoparticles, including Au–Pd nanoalloys, $MeAu_n$ (Me = W, Pb, Zr, Sc and n = 12–17), Cu-doped Au nanoparticles [3], are more active than pure gold clusters. The detailed investigation of the cluster structure and electronic properties as well as the possible orientations and activation of O_2 and CO on their surface would allow the further design and modification of the nanoparticles and their application in various processes.

In this theoretical study we have investigated CO oxidation catalyzed by neutral, positively and negatively charged tetrahedral $Au_{20-x}Cu_x$ clusters having the heteroatom on the top, the edge, and the facet of the cluster. All calculations were performed within the spin-polarized relativistic DFT approach using the PBE functional using Priroda program package [4].

The results show that O_2 can be effectively activated upon adsorption on bimetallic clusters. The activation can be further enhanced by the co-adsorption of CO. Molecules of oxygen prefer to adsorb on copper atoms; the nearby gold atoms are more favorable for CO molecule adsorption. As was expected, the charged $Au_{20-x}Cu_x$ cluster can adsorb CO and O_2 more strongly than the neutral counterpart. The apex atoms in the clusters are more active in the binding of O_2 and CO. In general, CO oxidation occurs more readily on the anionic and cationic clusters than on their neutral analogs. Compared with the reaction on gold clusters, CO oxidation on Cu-doping Au occurs easily. The $Au_{19}Cu$ having heteroatom on the top (effective reaction barriers 0.2–0.6 eV) appears to be a good candidate for a CO oxidation catalyst.

Acknowledgement. This research was supported by the Russian Federation Foundation for Fundamental Research through the Project 14-01-00310 and by the Council for Grants of the Russian Federation President Project NSh 8845.2016.3. The reported study was supported by the Supercomputing Center of M.V. Lomonosov Moscow State University.

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Mechanism of the Selective Oxidation of Olefins with Nitrous Oxide

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The development of more efficient and environmentally acceptable methods for producing ketones and aldehydes remains an important task of modern chemistry. It was shown recently that the thermal liquid phase oxidation of various olefins with nitrous oxide (the so-called ketonization reaction) proceeds with selective formation of ketones and aldehydes [1]. The reaction selectivity depends on the olefin structure and often exceeds 90%. This opens a new way to the synthesis of a wide variety of valuable carbonyl compounds. BASF uses this novel method for the large scale production of cyclododecanone and cyclopentanone [2].

In this study the CBS-QB3 quantum-chemical method was applied to reveal the mechanism of alkenes oxidation with N_2O. In particular, it gives detailed information on the way the C=C bond is cleaved and which products are formed. Theory predicts that oxidation is accompanied by aldehydes and diazo- compounds formation. The latter in turn decompose to alkenes. Also, it predicts alkyl shift as one of side reactions. The distribution of all oxidation products was calculated according to Transition State Theory assuming that only chemical kinetics controls the product ratios. A *quantitative* agreement between theory and experiment was achieved for the gas-phase cyclohexene oxidation with N_2O.

The calculation also provides an understanding of the *cis/trans* isomerism effect on the distribution of 3-heptene oxidation products in the liquid phase. The *cis/trans* isomerism of the olefin has a pronounced effect on the reaction route involving the cleavage of the initial C=C bond and, accordingly, on the products ratio. The yield of ketones is lower for the trans-isomer due to higher contribution of the cleavage route [3].

Acknowledgement. This work was supported by the Russian Foundation for Basic Research (Grant No. 14-03-31052 mol_a) and by Russian Academy of Sciences and Federal Agency of Scientific Organizations (project V.44.2.3).

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SOP$_{10}$-06

Propylene Epoxidation over Silver and Bimetallic Gold-Silver Clusters

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Silver catalysts are known to be active in different oxidation catalysts. Alkene epoxidaion is one of the most important reactions in chemistry industry due to widely used of oxidized products. Today, the ethylene epoxide selectivity of the industrial catalysts lies in the range 90%. However, propylene epoxidized over silver catalysts with low selectivity. Recently, it was shown that the range of properties of silver catalysts can be greatly extended by taking mixture of elements such as Au, Pd, Cu and then some. The increase of activity or selectivity od bimetallic systems occurs due to change the cluster's quantized electronic structure.

The goal of this study was to investigated the mechanism of propylene epoxidation over pure silver. The 20-atomic cluster is chosen as a model of catalysts due to two reasons. Firstly, it is well established that a magic number cluster containing 20 silver atoms is a highly stable and chemical inert clusters. The second reason is that Ag_{20} have a structure with Td symmetry and atoms with different coordination number. Thus, the co-existence of the low– and high–coordinated metal atoms in the tetrahedral structure allows us to study the influence of the structural features on the mechanism of propylene epoxidation. The next aim of our study was to examined how will gold inclusion affect the properties of silver catalysts. All calculation were performed within spin-polarized all-electron approach DFT/PBE.

It was shown, that on Ag_{20} and $Ag_{19}Au$ propylene oxide formation proceeds through the formation of a five-membered oxametallacycle consisting of two metal atoms and a −O−C−C− fragment and four-membered oxametallacycle including a single metal atom and −O−C− fragment. Formation of propylene oxide on Ag_{20} is more favorable on 22 kJ/mol than formation of allyl radical, however, reaction goes through high energy barrier. A comparison of pathway on Ag_{20} and $Ag_{19}Au$ shows that the propylene oxide formation barrier of the $Ag_{19}Au$ is 70 kJ/mol lower than that of the Ag_{20} pathway. It should be noted that reaction of allyl radical formation on $Ag_{19}Au$ goes through high activation barrier (184 kJ/mol). Therefore, in silver catalysts the presence of gold atom increases activation energy of allyl radical formation, and decreases activation energy of propylene oxide formation.

Acknowledgement. This research was supported by the Russian Federation Foundation for Fundamental Research through the Projects 13−03−00320, 14-01-00310, and 11−01−00280, and by the Council for Grants of the Russian Federation President Projects NSh−3171.2014.3. The reported study was supported by the Supercomputing Center of M.V. Lomonosov Moscow State University

SOP$_{10}$-07

Theoretical Investigation of Solvent Influence on Catalytic Activity of New di- and tetraNuclear Copper(II) Complexes with Mannich-Base Ligands

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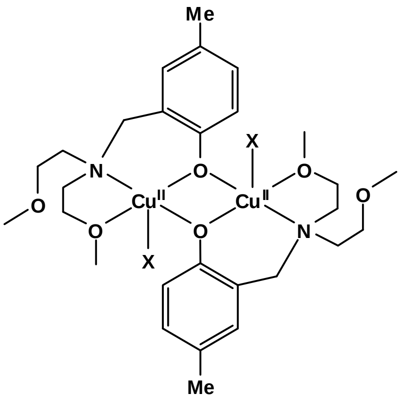
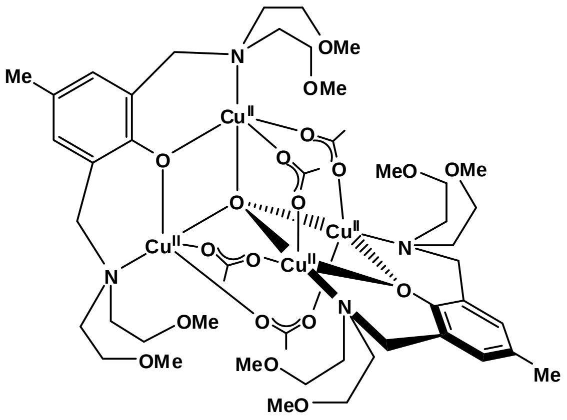
During last two decades considerable interest has been focused on experimental studies of the catechol oxidase synthetic analogues. However, theoretical aspects of the catalytic activity of such complexes were reported occasionally. Two newly synthesized dinuclear and one tetranuclear copper(II) complexes **1**-**3** with Mannich-base ligands reveal catecholase activity by reacting with 3,5-di-*tert*-butylcatechol (3,5-DTBC) in mixtures of acetonitrile and water under completely aerobic conditions. The catalytic efficiency of tetranuclear complex **3** in MeCN/H_2O decreases as the water content is increased from 0 to 25% while complexes **1** and **2** display an opposite trend.



1 X = OAc   2 X = Cl



3

To interpret these effects the interactions between complexes and 3,5-DTBC have been investigated by DFT modeling at the B3LYP/DGDZVP level of theory with the PCM approach for MeCN and H_2O. A neutral catalytic cycle has been proposed for the tetranuclear complex in the presence of water. In addition, the solvation and dissociation of complexes have been analyzed. In pure MeCN alcoholysis of complex **3** by 3,5-DTBC with formation of a dicopper catecholate appears to be energetically favorable (-7.2 kcal/mol). The decrease in the **3** catocholase activity on addition of water is explained by exothermic hydrolysis of the tetramer producing less active dicopper species (-10.0 kcal/mol). On the other hand, the increase of the H_2O content in solution results in the ionic dissociation of the dicopper complexes leading to formation of efficient cationic catalytic systems. These two opposite effects of water provide the different behavior of **1**, **2** and **3**.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research (Project 16-03-01109).

SOP_{10}-08

Study of Adsorption and Diffusion of Atomic Oxygen on the Surface and in Subsurface Region of Pd Nanoparticles and Pd(110) Single Crystal

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Palladium is an active metal of platinum group, widely used in three-way catalysts to remove CO and hydrocarbons from exhaust gas of vehicles and industrial plants.

However, untill now a number of important processes occurring in the catalyst cannot be studied directly through experiments, hence the modelling of the catalytic reaction or individual steps are often used. During the last decade, methods based on the density functional theory (DFT) have been widely developed to have an accurate description of solids and their surfaces at atomistic level. The most of the studies concerning the interaction of oxygen with palladium were devoted to explore high-coverage adsorbed structures, their stability and the conditions of oxide formation. Meanwhile the process of beginning penetration of oxygen in palladium is still unclear.

In spite of intensively discussed subsurface oxygen formation on Pd(110), neither the position of oxygen in the subsurface nor the energetics of the penetration into the bulk have been object of modeling.

This study consists in a multiscale investigation, performed both at PAW and localized basis set levels of theory, and it concerns:

- determination of the binding energy of the oxygen in various adsorption sites of the surface of Pd(110), Pd-nanoparticles;
- simulation of the process of diffusion of oxygen atoms along the surface;
- simulation of the process of diffusion of oxygen atoms in the subsurface layer of Pd(110) single-crystal and Pd nanoparticles.
- the influence of oxygen adsorption on the structure of surface of Pd-catalysts.

Acknowledgement. This work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (project V.44.1.15). Computing resources were provided by Siberian supercomputer centre SB RAS.

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POSTER PRESENTATIONS

PP-01

Conjugation of Carbon Monoxide Steam Conversion with Ethylbenzene to Styrene Dehydrogenation in the Presence of CO_2

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High demand for styrene (St), one of the most important monomers used in the industry requires intensification of its receipt technology. The most optimal solution of this problem is replacing the direct dehydrogenation of ethylbenzene (EB) to St by oxidative dehydrogenation. The search of oxidants showed that using of carbon dioxide for this purpose is possible. Successful transfer of modern industrial process of St from EB obtaining requires the replacement of the nitrogen by CO_2 and utilization of forming carbon monoxide. Using of the steam conversion of carbon monoxide (SCCM) for this purpose allows to create the CO_2 recycling process and an additional hydrogen source.

Thus, the solution of this problem requires a combination of EB dehydrogenation with SCCM. The purpose of this work is studying the effect of CO steam conversion on the EB to St transformation in the presence of CO_2.

Studies of EB to St conversion and SCCM were conducted using the copper and potassium modified model dehydrogenative alumochromium catalyst (AChC), in the flow eactor at atmospheric pressure, 580^0C and WHSV $2h^{-1}$.

It was found that the EB conversion in comparison with nitrogen increases under the influence of CO_2. However, this effect on the EB to St dehydrogenation is complicated. Thus, with increasing of CO_2:EB ratio from 0 to 4 (mol) the EB to St conversion increases more than twice reaching to 65% and retains this value practically constant up to the CO_2: EB ratio equal to 6 (mol). Then, the increase of CO_2:EB ratio results in the reducing of EB conversion and formation of St is accompanied by the formation of CO. Changing the yield of St with the increasing of the CO_2:EB ratio can be explained by the reaction, reverse to SCCM. The released during the EB dehydrogenation hydrogen consumes on the CO_2 reduction and the process shifts to the increasing of the purpose product (St). It was found that under the influence of CO AChC catalyst undergoes to deactivation (Boudoir reaction). Introducing of water vapor has a positive effect on the stability of the EB to St dehydrogenation by accelerating of the conversion products desorption from the catalyst surface. At the same time the water molecules do no affect the process of EB to St conversion. It was also found that in the presence of water vapor the complete absence of carbon monoxide in the products, as well as the increase in the hydrogen yield corresponding to St can be achieved. These results indicate the high activity of AChC catalyst in the SCCM. Determined regularities of the CO conversion over the AChC catalyst confirm the interconnection of the EB to St dehydrogenation and SCCM in the presence CO_2.

Thus, due to the conjugate character of forward and reverse SCCM and oxidative dehydrogenation of EB to St the activity of AChC catalyst significantly increases what permits to consider CO_2 as a cyclic oxygen carrier.

On the basis of the obtained data and taking into account the notions of the mechanism of SCCM for the EB to St conversion in the presence of CO_2, the following scheme can be assumed:

$$\left.\begin{array}{c} EB \leftrightarrow St + 2H_{ads} \\ CO_{2gas} \leftrightarrow C-O-O_{ads} \end{array}\right\} \leftrightarrow \left.\begin{array}{c} Cm - \\ Cu(HCOO)OH \end{array}\right\} \leftrightarrow \begin{array}{c} H_2O+ \\ CO_{ads} \end{array} \leftrightarrow CO_{gas}$$

$$\left.\begin{array}{c} H_{2(gas)} \leftrightarrow 2H_{ads} \\ CO_{2(gas)} \leftrightarrow C-O-O_{ads} \end{array}\right\} \leftrightarrow HCOO_{ads} + H_{ads}\} \leftrightarrow \begin{array}{c} H_2O \\ CO \end{array}$$

PP-02

Eco-friendly High-Octane Petrol Extracting from Straight-run Gasoline by Low Temperature Reforming

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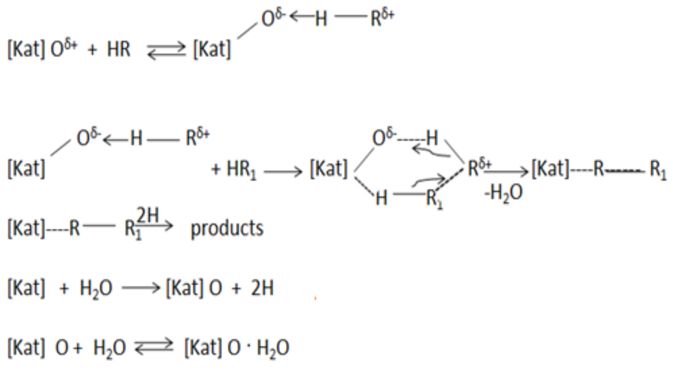
Isomerization of C_{7+} hydrocarbons located in straight-run gasoline (SRG), is limited by that under the isomerization conditions over 30% of these hydrocarbons are converted to side C_1-C_4 hydrocarbons so that involving of C_{7+} hydrocarbons into isomerization processing is not yet carried out properly. This problem may be solved by development of catalytic systems with conjugate isomerizing and disproportionate activity for conversion of C_{7+} SRG components into the valuable ramified C_5-C_6 hydrocarbons [1]. We synthesized Me/H-zeolite/SZ composite catalyst systems (Me = Co, Ni, Pt) and conducted the SRG contacting with these catalysts at 140-220° C, GHSV = 2.5 h^{-1} at atmospheric pressure in a hydrogen flow (20-40 ml/min). The basic observed result consists in a significant change in the distribution of the hydrocarbon composition - amount of C_5-C_6 hydrocarbons, consisting of 56.9wt% of high-isomers, increases by more than fourfold [2].

Through the isomerization - disproportionation processing of normal and slightly ramified alkanes the accumulation of hydrocarbons with average molecular mass with predominant formation of iso-C_5-C_6 alkanes is observed.

For clarifying the mechanism of the SRG conversion the model transformation of n-butane, n-hexane and mixtures thereof (1:1 mol) over $Co/MOR/SO_4^{2-}/ZrO_2$ was studied. N-butane conversion was found to increase significantly under the effect of n-hexane with formation of C_5-C_6 iso-alkanes as main products which was explained by bimolecular synthesis of C_8-C_{12} intermediates with subsequent isomerization-disproportionational decomposition. Therefore, an increase in the C_5-C_6 content in the SRG conversion products may be related to the same mechanism of bimolecular activation.

Taking into account the involvement of the less reactive n-butane by more reactive n-hexane into the process, received reaction products, as well as the published notions on the mechanism of low temperature isomerization over the sulfated zirconia catalytic systems, the following assumption on the mechanism of activation and conversion of n-alkanes mixture can be proposed:



Thus, the initial activation of n-alkanes occurs over sulfated zirconia sites, whereas further stabilization of the resulting intermediates with corresponding thermodynamically favorable skeletal isomerization and subsequent disproportionational decomposition proceeds over both M/H-zeolites and sulfated zirconia.

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PP-03

Catalytic Synthesis of *m*-, *p*-Xylylenediamine Monomers for Heat-Resistant Polymers by Hydrogenating of Isophthalo-, Terephthalonitriles

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An ammoxidation reaction opens up wide possibilities for the synthesis of aromatic dinitriles. A promising and affordable method for the synthesis of aromatic diamines is the hydrogenation of the corresponding dinitriles. For this purpose, as a basic raw material can be used products of deep processing an oil and coal. The basic starting material for heat-resistant polymers serve m- and p-xylylenediamine synthesized by catalytic hydrogenation of isophthalo-, terephthalonitriles, obtained by oxidative ammonolysis of m-and p-xylenes [1, 2].

With the aim of intensifying the catalytic synthesis of m- and p-xylylenediamine from isophthalo- and terephthalonitriles respectively, for the first time we studied in the presence of various alloyed catalysts based in Ni-Raney. Catalytic hydrogenation of isophthalo- and terephthalonitrile was conducted in the liquid phase in the isobaric-isothermal mode to a high-pressure kinetic (KUVD) allowing monitoring the consumption of hydrogen per unit time [3]. Hydrogenation is carried out until the termination of hydrogen uptake from the gas phase. For the analysis of hydrogenation products were applied potentiometric titration, IR-spectroscopy and elemental analysis.

In the catalytic hydrogenation of isophthalo-, terephthalonitriles to the corresponding m- and p-xylylenediamine in the liquid phase under pressure hydrogen were used new theoretical approaches to the catalytic synthesis of aliphatic-aromatic amines with regard to their structure and composition, as well as the influence of other factors (solvent, temperature, hydrogen pressure, the ratio of catalyst:dinitrile, the ratio of ammonia:dinitrile and the ratio of m-dinitrile:n-dinitrile).

Comparative results of the hydrogenation isophthalo-, terephthalonitriles on Ni-Raney catalyst, which is an alloy of Ni:Al = 50:50 and modified with additives Mg, Ti, Nb catalysts based on Ni-Raney in ethanol at 4.0 MPa hydrogen pressure and 80 ^{0}C temperature shows that a characteristic feature of the kinetics of the hydrogenation of isophthalo-, terephthalonitriles that constant and fairly large reducing the reaction rate throughout the experiment. The activity of the catalyst Ni-Nb$_{sk}$ in 2-3 times higher than Ni-Ti$_{sk}$ and Ni-Mg$_{sk}$ and 4-5 times higher activity of Ni-Raney (Ni$_{sk}$). It is shown that the aliphatic alcohols (C$_1$-C$_4$) at a ratio of nitrile:ammonia = 1:3 (g/g), the yield of m- ,p-xylylenediamine are on Ni-catalyst Nb$_{sk}$ 96-98%.

The classic way of getting primary mono- and diamines is hydrogenation process of nitriles and dinitriles in the presence of ammonia. First intermediate compound formed on the surface of the catalyst in the hydrogenation of nitriles and dinitriles is aldimine. The formation of the aminonitrile in the catalytic hydrogenation of aromatic dinitriles indicates sequential recovery of the nitrile groups.

To direct the reaction towards the formation of primary mono- and diamines is necessary to increase the hydrogen concentration on the catalyst surface, for example, using elevated hydrogen pressure and strengthen the adsorption of hydrogen bond with the surface by promoting the skeletal nickel, or the selection of the solvent, in particular, its introduction into the ammonia or additives basic character. The activity and selectivity of studied catalyst under the catalytic synthesis of primary amines can be associated with a high degree of enrichment of the catalyst strongly bound by adsorbed hydrogen. The ammonia prevents reactive aldimines react with a primary amine, which are formed by reacting a Schiff base and further reaction with hydrogen passes to a secondary amine.

The aldimine mechanism of hydrogenation of isophthalonitrile in the presence of ammonia can be depicted by the following figure 1:

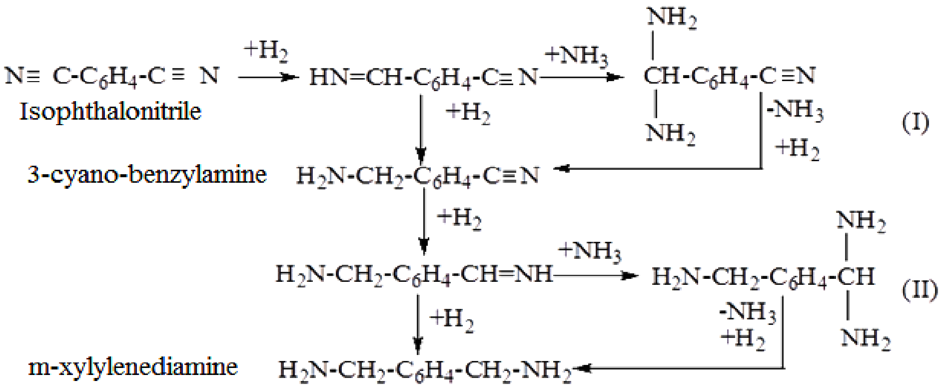

Figure 1. The aldimine mechanism of hydrogenation of isophthalonitrile in the presence of ammonia

General linear flowsheet producing polymers can be represented as follows: Raw material – Oil – Aromatic compounds of oil – p, m-xylene – isophthalo-, terephthalonitriles – m- and p-xylylenediamine – polymers.

Comparative results of the hydrogenation isophthalo-, terephthalonitriles on Ni-Raney catalyst, which is an alloy of Ni:Al = 50:50 and modified with additives Mg, Ti, Nb catalysts based on Ni-Raney in ethanol at 4.0 MPa hydrogen pressure and 80 ^{0}C temperature shows that a characteristic feature of the kinetics of the hydrogenation of isophthalo-, terephthalonitriles that constant and fairly large reducing the reaction rate throughout the experiment. The activity of the catalyst Ni-Nb$_{sk}$ in 2-3 times higher than Ni-Ti$_{sk}$ and Ni-Mg$_{sk}$ and 4-5 times higher activity of Ni-Raney (Ni$_{sk}$). It is shown that the aliphatic alcohols (C$_1$-C$_4$) at a ratio of nitrile:ammonia = 1:3 (g/g), the yield of m- ,p-xylylenediamine are on Ni-catalyst Nb$_{sk}$ 96-98%.

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Nickel Supported on MOF-5 and UiO-66 in Vapor-Phase Hydrodechlorination of Chlorobenzene

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Metal-Organic Framework (MOF) systems attract attention as possible supports for catalytic systems due to high adsorption capacity, high specific surface values and ordered structure. Ni-containing catalysts are widely used in hydrogenation processes due to low cost and high efficiency. In this work UiO-66 and MOF-5 were synthesized according to [1,2] and used as carriers for Ni catalysts. Ni was supported by impregnation method from ethanol solution of Ni(acac)$_2$ as described in [3]. Such produced Ni(acac)$_2$/UiO-66 and Ni(acac)$_2$/MOF-5 were characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD), AAS, scanning electron microscopy (SEM), low-temperature N_2 adsorption-desorption. Catalysts precursors were reduced by H_2 at 300ºC during 3 h to form Ni/MOF-5 or Ni/UiO-66 in the catalytic reactor immediately before the catalytic tests in chlorobenzene (CB) hydrodechlorination (HDC) in vapor-phase in continuous-flow fixed bed catalytic system.

XRD diffraction patterns of UiO-66 and MOF-5 synthesized in our work (Fig. 1a) are similar to those described in literature [1,2]. Therefore, XRD results confirm the formation of UiO-66 and MOF-5. TG and DSC curves of Ni(acac)$_2$/MOF-5 and Ni(acac)$_2$/UiO-66 produced in this work are similar to those for MOF-5 and UiO-66 reported in literature [2,3,4] confirming the presence of MOF-5 and UiO-66 in the samples. Decomposition of MOF-5 structure during TG-DSC proceeds at lower temperature, 400ºC, than decomposition of UiO-66 (545ºC). The S_{BET} values for MOF-5 (759 m^2/g) and Ni(acac)$_2$/MOF-5 (554 m^2/g) are consistent with the values given in literature. S_{BET} value for Ni(acac)$_2$/UiO-66 (230 m^2/g) is lower than the values for UiO-66 presented in literature. However, pore sizes (DFT) were about 6 Å for Ni(acac)$_2$/UiO-66 and 9 Å for Ni(acac)$_2$/MOF-5, that is consistent with well-known values for MOF-5and UiO-66. SEM-EDS method demonstrates the presence and uniform distribution of Ni on the surface of both samples. Exact Ni loading 0.11 wt.% in Ni(acac)$_2$/MOF-5 and 0.28 wt.% in Ni(acac)$_2$/UiO-66 was detected using AAS.

Both samples demonstrated good performance in chlorobenzene HDC to benzene at 100-350 ºC. Stable state CB conversion values are higher on Ni/UiO-66 and grows with temperature increase on both samples (Ni/MOF-5: 39% at 150ºC, 69% at 200ºC, 75% at 250ºC and 82% at 300ºC; on Ni/UiO-66: 57% at 100ºC, 91% at 150ºC, 99% at 200ºC and 100% at 250ºC and 300ºC). This difference can be caused by different Ni loading that is about 2 times higher in Ni/UiO-66. Probably better activity of Ni/UiO-66 is connected also with higher stability of UiO-66 framework structure in severe reaction conditions. Thus effective low-loaded Ni catalysts for HDC were prepared.

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PP-05

Electrochemical Modification of Cellulose on Smooth Platinum in Concentrated Solutions of Methane Sulfonic Acid

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Mesylates are the esters, which are formed at interaction of the functional hydroxyl groups of cellulose with methylsulfogroups. They find their application in medicine and pharmacy [1]. Previously, the authors [2] proposed the electrochemical modification of cellulose in reagent of Schweitzer - $[Cu(NH_3)_4](OH)_2$. Nowadays modification of cellulose carried by chemical methods. The main difficulty lies in the selection of solvent for the cellulose since it is poorly soluble in organic solvents and inorganic [3]. In paper [4], the authors demonstrated the possibility of the formation of cellulose mesylates via its anode modification on a smooth platinum electrode by dissolution in DMSO - 4M CH_3SO_3H.

Anode modifying processes of cellulose pulp in the system DMSO — MSA are studied using a potentiostatic methods and preparative electrolysis. Potentiostatic measurements were carried out using a potentiostat IPC – Pro MF.

When dissolving 0.1 g / ml of cellulose gel formed viscous solution in 10 M MSA solution. As the proportion of the solvent decreases the viscosity and increases the mobility solution. In concentrated solutions of cellulose MSA methylsulfogroups can react with acids to form esters - mesylates of cellulose, highly soluble in water.

In fig. 1 that in stationary conditions in a wide range of polarization potentials of 1.8 - 2.8V oxidation of cellulose current is observed, that indicates the possibility of modifying the electrochemical of cellulose at high anodic potentials.

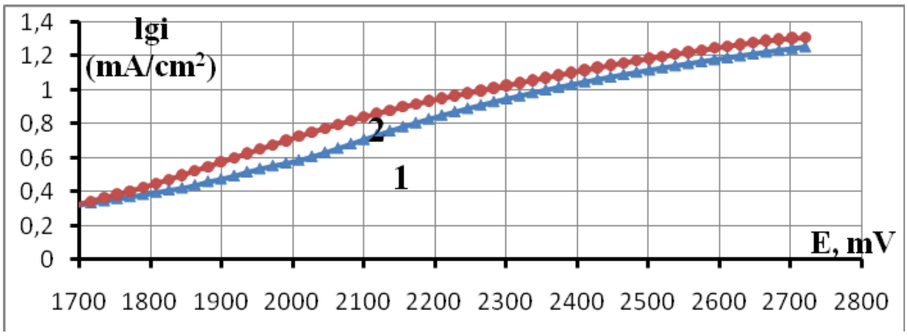


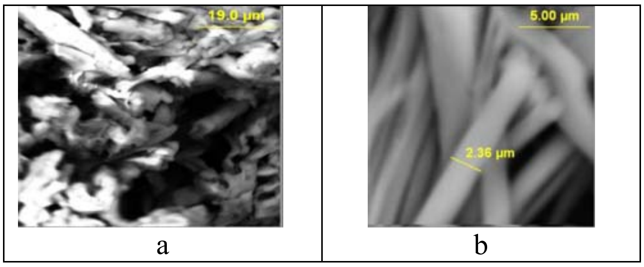
Fig.1. Stationary polarization curves of potentiostatic smooth platinum electrode in a solution of 10 M 10 M CH_3SO_3H (1) and in the presence of cellulose $(C_6H_{10}O_5)$n of 0.1 g /ml (2).

The presence of methylsulfogroups in the product electrochemically modified of cellulose is found by IR spectroscopy (table1).

Table 1. Values of the characteristic absorption bands of functional groups of the product electrochemically modified of cellulose.

The region of absorption, cm^{-1}	Characteristic groups
1480-1450	CH_2–
1280-1230	R–SO_2–R^1
1100-1050	S=O;R–S(O)–OH
850-800	S–O
600-580	C–S

The presence of sulfur atoms in the methylsulfogroups in the resulting product of the modified pulp was found by energy dispersive analysis (EDX). EDX-analysis of data mesylate of indicate shows the presence of of sulfur atoms - 84.1% oxygen - and 13.1% carbon - 2.8%. From the results of obtained by X-ray fluorescence analysis, it is seen that the ratio of sulfur to carbon in the resulting product is 40: 1, which are close to the theoretical values calculated for the molecular level mesylate of cellulose. Such coincidence is observed when complete substitution residues methylsulfogroups three hydroxyl groups of of cellulose monomer. Figures 2 are images structural changes of cellulose (before and after electrolysis) obtained by the scanning electron microscope ACPEX PSEM Express.



a b

Fig. 2. Image of SEM the surface of cellulose before (a) and after (b) electrolysis

The resulting product was identified as a modified cellulose mesylate having a gross formula $[C_6H_7O_2(OH)_{3-x}(SO_3CH_3)_3]_n$ of the following structure (Fig. 3).

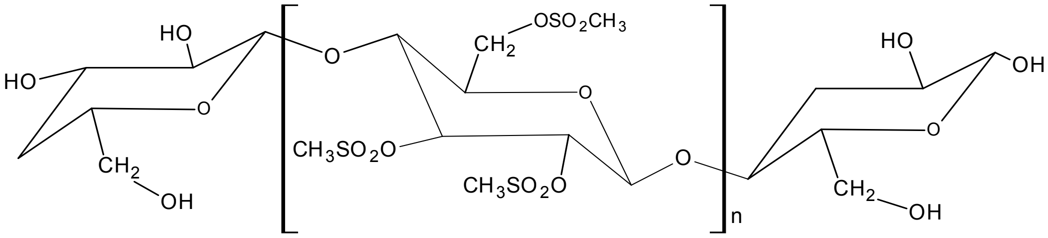


Fig 3. The structural formula of cellulose mesylate

Voltammetric methods studied electrochemical oxidation of the cellulose in a concentrated solution of methane sulfonic acid (MSA). It has been shown in a wide range of anodic potentials of 1.8 -2.8 V. The observed process of electrochemical oxidation of cellulose that can be caused by modification of the OH-groups.

Acknowledgement: This work was supported by the Russian Foundation for assistance to small innovative forms enterprises in scientific and technical area (FASIE) grant № 0016996 (8809ГУ2/2015)

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PP-06

Development of Kinetic Models of Catalytic Reactions with the Use of Parallel Computing

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In this paper we identified and reviewed internal concurrency problems on the example of the reaction hydroaluminizing olefins [1], comprising the steps of the overall reaction scheme includes taking place parallel to the stage, some of them are the same for reactions with organoaluminum compounds and olefins. In the implementation of the computing process of the inverse problem solution is carried out independently for the parallel occurring steps that can significantly reduce the computation time.

For the organization of the computational process is considered a three-level threading model, combining parallelization on experimental basis, in accordance with internal parallelism and task-based decomposition method of the inverse problem solution [2].

The software package that implements the calculations for this model, tested on a computing cluster of the Bashkir State University and the supercomputer MVS-100K RAS Joint Supercomputer Center. When solving the inverse problem for the reaction of olefins hydroaluminizing all the experimental data on the basis of genetic algorithm based on the total time of the supercomputer MVS-100K (with 120 processors) was 15 minutes vs. 360 hours on a personal computer using a standard algorithm [3].

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PP-07

The Oxidation of Petroleum Hydrocarbons in the Presence of Modified with Fe, Mn Fullerene Duda

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The search, selection of new catalysts to improve the technological parameters of industrially important reactions is relevant and the main theme of many researchers working in the field of fundamental and applied catalysis. The fullerene duda containing 8% of fullerene and 92% (by mass) of amorphous carbon was modified with iron ferrocene and manganese naphthenate [1]. The obtained Fe, Mn-containing carbon material was used as a catalyst in oxidation reactions of diesel fractions recovered from the mixture of Azerbaijani oils. The results of catalytic studies are given in Table 1.

Table 1

Name of catalyst	The amount of catalyst		Quantity of aromatic hydro-carbons, %	Duration of reaction, h	Acid number of oxidate mgKOH/g	output of SOA*, %	output of SOOA* %	Acid number of SOA mg KOH/g	Acid number of SOOA mg KOH/g
	mg	%							
Fulleren duda	30	0.025	1.0	3.0	27.0	12.0	3.5	102.6	78.0
Fe-Mn/C_{60} duda	30	0.025	1.0	2.40	29.5	17.0	5.7	104.5	96
Fe-Mn/C_{60} Duda	20	0.017	1.0	5	64.1	18.4	21.8	96.5	77.0

*SOA- synthetic oil acid, SOOA-synthetic oil oxyacid

The data of the table indicate a significant increase in output of SNA in the presence of a catalyst. The phase composition, the content of iron and manganese, the distribution of these catalytically active elements on the surface and in near the surface layers, magnetic properties of the synthesized samples were studied using X-ray diffraction, atomic absorption spectroscopy, X-ray fluorescence microscopy, electron spin resonance methods, respectively. The Fe, Mn - containing magnetic phases were identified, the amount and composition of their as a function of the catalyst preparation, conditions and the duration of the oxidation reaction of the diesel fraction were studied. It was found that the obtained catalyst is the carbon-based Fe, Mn -containing nano-structured material. The nature of the catalytically active centers and mechanism of the reactions with their participation are discussed.

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PP-08

Effect of Support of Ternary KCoMoS Catalysts on the Morphology of Active Phase Species and Their Properties in Selective FCC Gasoline Hydrotreating

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The aim of the work was to study the role of the support nature in designing the selective catalysts for hydrotreating of FCC gasoline.

Catalysts were synthesized by wetness impregnation of the different carriers (Al_2O_3, SiO_2, ZrO_2, TiO_2 and SBA-15) with the joint aqueous solutions of the active components ($H_3PMo_{12}O_{40}$, cobalt citrate and potassium hydroxide as a modifier). All catalysts were dried at 110 °C during 5 h without calcination step with the following liquid-phase sulfidation. The composition of the synthesized catalysts is shown in Table 1.

Table 1 – The composition of synthesized catalysts

Catalyst support	SSA of carrier (m^2/g)	Metal content (%)			Surface concentration of Mo for carriers (at Mo/nm^2)
		Mo	Co	K	
Al_2O_3	220	12.0	3.7	10.0	4.4
SiO_2	356	13.7	4.2	11.2	4.0
SiO_2	356	8.6	2.6	7.0	2.0
TiO_2	153	7.6	2.3	6.2	4.0
ZrO_2	113	6.0	1.8	4.9	4.0
SBA-15	800	10.3	3.2	8.4	1.2
SBA-15	800	14.7	4.5	12.0	2.0

Physical-chemical characteristics of the synthesized catalysts were analyzed with the use of the following techniques: low-temperature nitrogen adsorption, IR Spectroscopy of adsorbed pyridine, X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM), NH_3-TPD, X-ray Diffraction, H_2-TPR.

The catalytic properties of the synthesized samples were determined in a hydrotreating of a model feed containing 1000 ppm of sulfur, 36 % wt. of *n*-hexene-1 and heptane as a solvent. The catalytic tests were carried out in a fixed bed microcatalytic reactor under the following conditions: a H_2 pressure of 1.5-3.0 MPa, the temperature of 220-340 °C with the step of 20 °C, LHSV of 2.5-5 h^{-1}, volume ration hydrogen: feed 100 nL/L. The HDS/HYDO selectivity of the synthesized catalysts was calculated as a ratio of rate constants of the HDS and HYD reactions.

It was found that the nature of using carrier plays one of the key role in the formation of high selective active phase and is promising for the design of catalysts for hydro-upgrading FCC gasolines.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 15-33-20511.

Three-Stage Waste-Free Process of Alkylpetrol Preparation from Methanol on Zeolite Catalysts Base

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Constant toughening of requirements to structure and properties of automobile gasolines results in introduction of the new standards forbidding or limiting use aromatic and olefinic hydrocarbons, O-, S-, N- and metallic connections in structure of gasolines. One of alternative ways of an exit from this situation is the increase in manufacture of a share of non-polluting automobile fuel components motor, such as alkylates and isomerizates. The limiting factor on this way is absence of enough of a source of raw materials and optimum technological decisions.

The method of alkylhetrol preparation by a three-stage catalytic conversion from accessible raw material - methanol with use of heterogeneous catalysts such as SAPO, PdLaCa (Mg) X (Y) - Faujasite and some Al_2O_3-modifications is developed.

The method differs presence of the following stages:

1) Methanol conversion in dimethyl ether (DME) with use of catalysts SAPO and γ-Al_2O_3 at speeds 2÷10h^{-1} and temperatures 300÷400ºC. Thus there is practically 100 %-s' methanol conversion in DME

2) Subsequent conversion DME on zeolite catalysts such as SAPO at speeds 2÷4h^{-1} and temperatures 400÷450ºC in a mix olefinic and iso-/n-parafinic hydrocarbons of the following structure: ethylene - 1÷5 weights of %, propylene - 1÷4 weights of %, isobuthylene - no more than 0,5 weights of %, n-butylene-1 and n- butylenes-2 - no more than 0,5 weights of %, isobutane - 10÷30 weights of %, n-butane - no more than 5 weights of %, the rest a mix of metane, ethane, propane, hydrogen, carbon monooxide and traces of formaldehyde

3) Fluid-phased alkylation of iso-/n-butane by C_2-C_4-olefines in zeolite catalysts presence such as PdLaCa (Mg) X (Y) - Faujasite at speeds 2÷4 h^{-1} and temperatures 50÷100ºC with preparation of alkylpetrol components, mainly, trimethylpentanes and dimethylhexanes with the following characteristics: Total conversion of olefines - about 99 %, the output of liquid products from theoretical counting upon olefines - about 95 %, the contents of fractions C_8 - 80÷85 weights of %, C_{9+} - no more than 8 weights of %, C_5-C_7 - no more than 9 weights of %, trimethylpentanes - 65÷70 weights of %, the mass relation trimethylpentane/dimethyl-hexane - 5÷5,5

PP-10

Isotopic Methods to Study Little-known Catalytic Activity of Solid Alkaline Hydroxides for Energy Conversion and Storage

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Methodology of isotopic exchange by Boreskov-Muzykantov was modified for thermodynamic inequality of hydrogen isotopes. It was necessary because even at highest temperatures (400 K) H/D separation coefficient was 1.6. The main reason to do it is due to the necessity to study the mechanism of chemical reactions used for energy conversion and storage with hydrogen containing compounds in heterogeneous systems. **Why alkaline hydroxides**? Recently new (or little known) combinations of electrolytes and electrodes were found and presented in our papers [1-3]. The main part of them are different forms of solid ALKALINE [4] hydroxides. There are some differences between hydroxide of alkaline and transition metals. First of all thermo-stability anions (OH^-) in KOH up to 800 K contrary e.g. $Ni(OH)_2$.(The latter relates also to alkaline and the alkali-earthy hydroxides.) These hydroxide as electrolytes have not only high protonic conductance, but also they are able to activate molecules of dihydrogen **without any catalytic agents** even at 250 -400 K**.** Moreover, these hydroxides in solid state could form **protonic heterojunction** by from cheap partners like intermetallic TiFe, metallic Sn, semiconducting Si and Ge at room temperatures.

Experimental part was described in detail in [1-4].

The main aspects of experiments were:

i) all of solid samples were prepared from preliminary molten one;

2) electrodes were introduced into the melt under special atmosphere;

3) no experiment in air!

4 Results and discussion

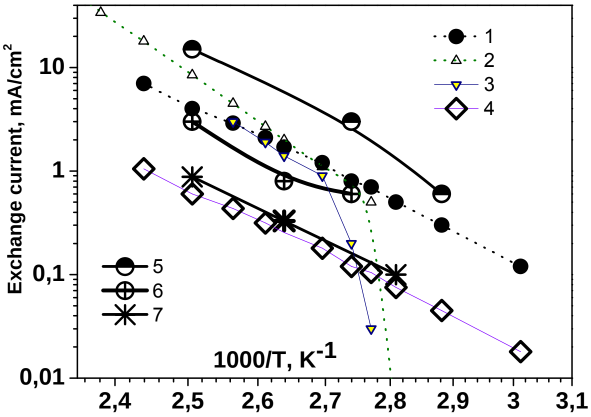

Fig. 1. To demonstrate the catalytic activity of hydroxide compounds under study the electrochemical exchange current on electrode/electrolyte interfaces - (1)- Pd-KOH.H_2O: (2)- Pd-KOH.H_2O; (3)- Pd-KOH.H_2O; (4)- Pd-KOH.H_2O - compared with isotopic exchange between free hydroxides and dihydrogen:
(5) KOH.H_2O and 70 mmHg D_2;
(6) KOH. NaOH and 7 mmHg;
(7) KOH.H_2O and Ti

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Investigation of Activity Supported MoCrGa Catalyst at Oxidative Conversion of Methane of Natural Gas

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Currently, light alkanes are the largest inexpensive and available source of raw materials for the chemical industry. However, as a class they belong to the least reactive organic substances due to the high strength of the C-H and C-C bonds, low polarity, absence of the lone electron pairs of the carbon and hydrogen atoms, the low electron affinity and high ionization potential. Direction on functionalization of hydrocarbons, especially the saturated hydrocarbons, which are the main component of the oil and gas, becomes relevance.

Results of research of the efficiency of developed catalyst systems in oxidation of methane of natural gas to the target products are presented in this paper.

Mono-, bi- and three-component catalyst systems for the oxidation of linear hydrocarbons have been developed. Pretreatment of carrier for preparation of catalysts on the base of EKR clay was carried out. EKR clay was dried at T = 473 K for 2 h, calcined at T = 773 K for 2 h, treated with a solution of 10% HCl and then calcined again at T = 773 K for 2 h.

Catalysts based on Mo, Cr and Ga were prepared by incipient wetness impregnation of the mixed solutions of nitrate salts supported on EKR clay, followed by drying at T = 473 K for 2 h. Calcination of samples at T = 773 K for 2 h in air was carried out for decomposition of supported metal salts and volatilization of nitrates from the catalyst surface. Research the activity of developed catalysts was conducted on a flow installation at atmospheric pressure in a quartz tubular reactor with a fixed catalyst bed.

Activity of the developed Mo-Cr-Ga catalysts supported on EKR clay was investigated in oxidation of methane under conditions: $CH_4 : O_2 = 2 : 1$ (67 % : 33 %), T = 300-900°C and a GHSV = 500 - 2000 h^{-1}. It has been found that the reaction products are formed both in liquid and gaseous phases at varying temperature and GHSV. The formation of ethanol, propanol, ethanol and acetaldehyde occurs at temperatures from 400 to 700°C. H_2 and CO are formed in gas phase at temperatures from 600 to 900°C.

Thus, the supported mono-, bi- and three-component catalysts for oxidation of methane of natural gas into the target products have been developed. Varying the composition of active phase of catalyst was conducted. It was found that supported three-component MoCrGa catalyst is optimal for yield of target products.

Acknowledgement. This work was supported by the Ministry of Education and Science of the Republic of Kazakhstan, grant 0330/GF4.

PP-12

Oxidative Conversion of Light Alkanes for Catalytic Synthesis of Hydrogen

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At present, changes in the structure of production and consumption of hydrocarbons show a steady increase in the role of natural gas as energy and raw materials. The two most important reasons demonstrate this fact:

- significant reserves of natural gas, which are significantly higher than the oil reserves;
- more higher ecological safety of gaseous hydrocarbons.

One-, two- or multicomponent catalysts based on metals of the III and VI groups as well as elements of the I and VIII groups supported on natural and synthetic carriers have been developed to rational selection of catalysts. The developed compositions of catalysts were prepared by incipient wetness impregnation the mixed aqueous solutions of nitrate salts, supported on natural and synthetic carriers, followed by drying at T = 473 K for 2 h. Calcination of the samples at T = 773 K for 2 h in air was carried out for decomposition of supported metal salts and volatilization of nitrates from the catalyst surface.

Activity of developed catalysts was investigated in catalytic oxidation of the C_1 and C_3-C_4 alkanes into hydrogen. Studies on the effect of varying the process parameters and composition of reaction mixture on oxidative conversion of alkanes were carried out.

Oxidative conversion of the methane of natural gas into hydrogen at reaction temperatures varying from 700 to 900°C on the catalysts Ni/ZSM-5+Al_2O_3, Ni-K/ZSM-5+Al_2O_3, Ni-La/ZSM-5+Al_2O_3, Cu-La/ZSM-5+Al_2O_3 and Ni-Cu-Nd/ZSM-5+Al_2O_3 have been studied. It was found that T = 750-900°C and GHSV = 6000 h^{-1} are the optimum conditions for obtaining of 65-69 % hydrogen in the conversion of methane at $CH_4 : O_2 : Ar = 7.0 : 1.0 : 92.0$ (36.0 : 5.0 : 59.0 %) on the developed bimetallic 5.0 % Cu-La/ZSM-5 + Al_2O_3 catalyst.

Three-component supported 1 % MoCrGa catalyst is most suitable catalyst composition for oxidative conversion of C_3-C_4 mixture in hydrogen at C_3-$C_4 : O_2 : N_2 : Ar = 0.95 : 1 : 3.76 : 0.95$, T = 550°C, GHSV = 3150 h^{-1}. 70 % hydrogen was obtained as a result of the tests.

Thus, supported mono-, bi- and multicomponent catalysts for oxidation of light alkanes into hydrogen have been developed. It was determined that the three- and bimetallic catalyst systems are optimal for the conversion of initial reaction mixture into hydrogen.

Acknowledgement. This work was supported by the Ministry of Education and Science of the Republic of Kazakhstan, grant 0075/PF.

PP-13

Enhancement of TiO_2 Photocatalytic Efficiency towards Ethanol Oxidation by Surface F-Doping

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F-doped TiO_2, obtained by treatment commercial TiO_2 Hombifine N (100% anatase, S_{BET} = 300 m^2/g) with acidic NaF solution (pH = 3) was tested in photocatalytic oxidation of ethanol vapor. The choice of substrate is associated with essential drawback of photocatalysis application for air treatment. It is possible generation of toxic (relative to primary contaminants) intermediates – formaldehyde and acetaldehyde. Photocatalytic ethanol oxidation is a good model for the process of intermediate generation since the formation of volatile aldehydes proceeds primarily via oxidation of alcohols [1].

Some results are shown at Fig. 1. As it seen, doped samples demonstrate substantially higher activity towards EtOH oxidation with two-fold less times required for complete acetaldehyde elimination and approximately three fold less times for complete mineralization (not shown)

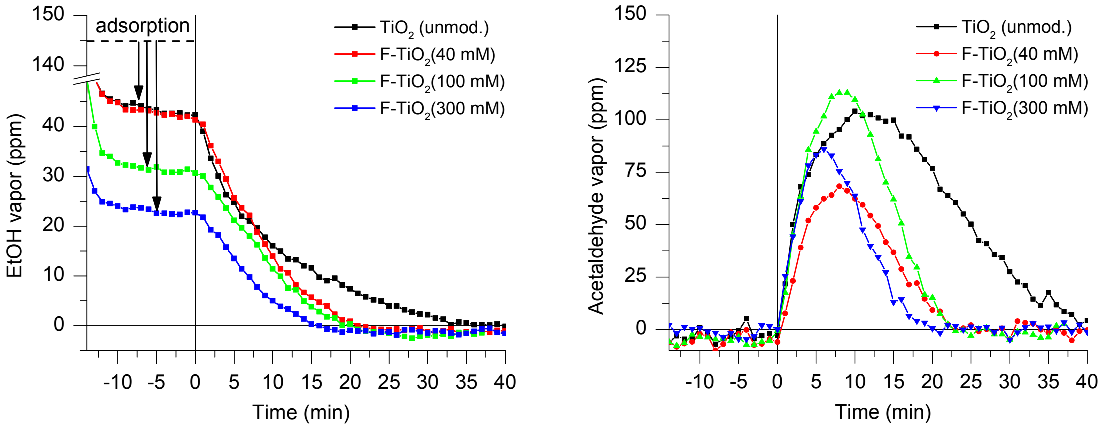

Figure 1. Effect of surface fluorination on ethanol (left) and acetaldehyde (right) concentration during ethanol photocatalytic oxidation over TiO_2. Concentration of modifying NaF solution is in brackets. Start of UV-irradiation is at 0 minute.

With respect to previously published data [2] concerning with acetaldehyde vapor oxidation on F-doped TiO_2 our samples demonstrate much more significant enhancement of reaction rate. We assume that higher concentration of surface terminal OH-groups of used TiO_2 sample which provide deeper (OH- for F-) replacement and as a consequence better charge transfer from TiO_2 to oxidizable molecule.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, research project 16-03-00956 a.

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Surface Oxygen Radicals as Active Sites of Propane Oxidative Dehydrogenation on Supported Vanadia Catalysts

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Oxidative dehydrogenation (ODH) of light alkanes over transition metal oxides is of great interest for synthesis of light olefins as a practicable alternative to non-oxidative dehydrogenation. Supported vanadia catalysts are among the most promising materials for this reaction. Propene ODH over VO_x/TiO_2 catalysts is characterized by low activation energies about 60 kJ/mol. Despite so low activation energy, the propane ODH on VO_x/TiO_2 catalysts typically takes place at 450°C or higher temperatures. This fact seems to indicate that the reaction is initiated on few very active sites rather.

We have recently shown by DFT calculations that oxygen isotopic exchange on titania-supported vanadia might be initiated on surface oxygen radicals. The main objective of this study was to analyze possible role of the oxygen radicals in oxidative dehydrogenation of propane to propene on VO_x/TiO_2, VO_x/SiO_2 and VO_x/MgO catalysts using DFT calculations.

Our computations prove that the surface oxygen radical species forming on the supported vanadium oxide catalyst VO_x/TiO_2 are very reactive and can abstract hydrogen atoms from propane with low activation energy $E^* = 0.56$ eV (54 kJ/mol). In our calculation the energetic barrier of the second stage was slightly lower. The obtained results demonstrate that oxidative dehydrogenation of propane can proceed over oxygen radicals stabilized on the surface of VO_x/TiO_2 catalysts with low activation energies matching the experimentally observed values. The obtained data suggest that oxygen radical species can be the active sites in this and other heterogeneous selective oxidation reactions.

Generally similar results were obtained for propane dehydrogenation on oxygen radical sites of VO_x/SiO_2 and VO_x/MgO catalysts. In both cases the activation energy of hydrogen abstraction from propane was close to the one observed over VO_x/TiO_2. Meanwhile, abstraction of the second hydrogen atom was more difficult accounting for higher activation energies experimentally observed over these catalysts.

It is important that the concentration of oxygen radical sites on the surface is low. So, the released propene, which is more susceptible to oxidation than propane, should not be immediately involved in further oxidation, unless it reaches another radical site after migrating on the surface. All these factors combined suggest that propene oxidative dehydrogenation on the oxygen radical species on the surface of supported vanadia catalysts simulated in this study should be a selective process. On the contrary, if conventional vanadyl groups commonly believed to be the active sites were the places where this reaction takes place, propene molecules would be involved in further oxidation processes immediately upon migrating to any adjacent V^{5+} site present in high concentration on the surface.

Acknowledgement. This study was supported in part by Russian Foundation for Basic Research (Grant 14-03-01110).

The Nature of Surface Electron-Acceptor Sites and Their Role in Catalytic and Solid-State Reactions

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One of the most intriguing properties of many heterogeneous acid catalysts is their ability to generate organic radical cations upon adsorption of aromatic electron donor molecules. Earlier it was suggested that such strong acceptor sites might be responsible for skeletal isomerization and cracking of light alkanes over sulfated zirconia. It was also reported that the catalytic activity of doped alumina catalysts in such conventional acid-catalyzed reaction as ethanol dehydration correlated with the concentration of weaker acceptor sites. In the current communication the properties of electron-acceptor sites of acid catalysts will be explored and their possible structure will be analyzed using DFT quantum chemical simulations. The concentrations of electron-acceptor sites of different strengths measured during catalytic and solid-state reactions were compared with the activity.

The electron-acceptor strength of conventional acid sites usually believed to exist in acid zeolites is below 1 eV. We simulated stronger acid/electron-acceptor sites by increasing the distance between the acidic proton and its counter ion. Our simulations show that such polarization sites are stronger than the conventional sites, but their electron affinity does not exceed ~ 6 eV. This value was obtained for sites where the proton is moved far away from the compensating framework ion sufficiently far that it no longer feels the presence of the counter ion. Their acidity is comparable with those of hydronium ions and conventional strong liquid acids. The acidity of such sites is just right for protonating ethanol.

Stronger acceptor sites with electron affinity approaching the experimental value for the strongest electron-acceptor sites (~ 9 eV) could be simulated only as superelectrophilic sites containing two adjacent extra protons solvated by the oxide matrix. Their acidity is sufficient for protonation of light alkanes similar to the one observed in liquid superacids.

Weak electron acceptor sites were found to be formed on the surface of nanocrystalline MgO destructive adsorbents during their solid-state reactions with CF_2Cl_2. This reaction is characterized by an unusual long induction period. Their activity was observed to correlate with the concentration of weak electron-acceptor sites tested by anthracene or perylene.

The catalytic activity of nanocrystalline MgO was found to increase significantly during the 1-chlorobutane dehydrochlorination reaction, which is accompanied by modification of the MgO surface and bulk with chloride ions. Electron-acceptor sites in this system appeared only during the reaction due to the surface chlorination. A good correlation was observed between the catalytic activity and the concentration of weak electron-acceptor sites.

Acknowledgement. This study was supported in part by Russian Foundation for Basic Research (Grant 15-03-08070-a).

PP-16

Ring-opening Metathesis Polymerization of Fullerene-containing α,ω-bis-Norbornenes by Catalyst Grubbs 1’st Generation

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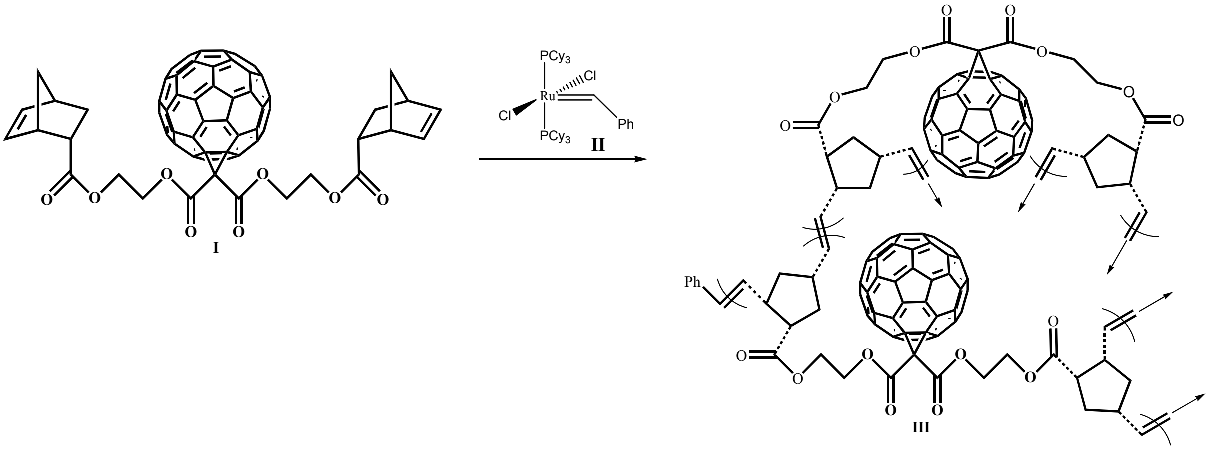
Ring-opening metathesis polymerization of norbornenes is an effective method for synthesis of polymers with cyclopentane core in the main chain. Ring-opening metathesis of α,ω-bisnorbornene systems by analogy with similar di- or polyenes in the construction of fused and spiro-fused ring systems, ‘bird cage’ type structures, molecular gyrotops and gyroscopes, catenanes, and other types gives interesting possibilities in terms of finding new topology of polymers. In this study, we describe the polymerization of fullerene-containing bis-norbornene monomer **I** under metathesis ring-opening conditions. Synthesis of **I** was executed in three steps by us before [1].



During experimental testing, the polymerization of **I** proceeded smoothly at 200 °C for 2–3 h on using Grubbs I catalyst **II** (Scheme). In the course of polymerization the precipitation of polymer **III** was observed. After monomer **I** was consumed, the polymer product was separated, washed with MeOH and dried *in vacuo*. Apparently, due to the presence of bulky fullerene substituent in the structure of compound **I**, intramolecular cyclization, dimerization and cross-linkage should less likely to occur. In a first approximation, **III** is taken as a resulting polymer structure. The polymer is insoluble in organic solvents. Its IR spectrum contained absorption bands of *trans*-double bonds (970 cm^{-1}), carbonyl ester groups (1732 cm^{-1}) and fullerene core (520 cm^{-1}); the absorption of norbornene bonds was not detected.

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

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PP-17

Metathesis Homopolymerization of Fullerene-containing 7-thia-bicyclo[2.2.1]hept-2-ene by Catalyst Grubbs 1’st Generation

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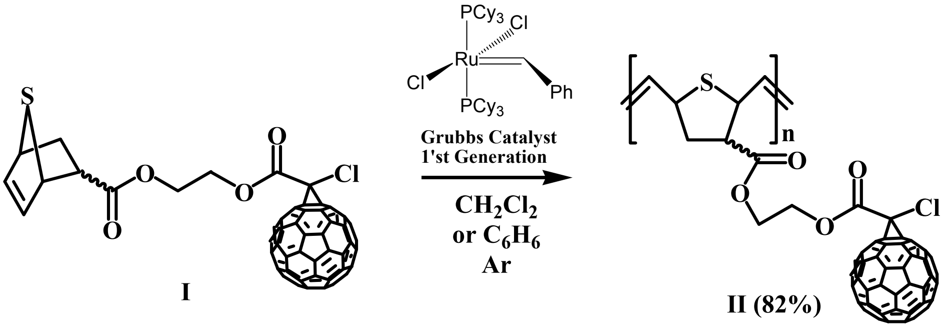
New norbornene derivative with the covalently bonded fullerene C_{60} have been prepared as monomer for ring-opening metathesis polymerization. The fullerene monomer **I** was synthesized by cycloaddition of dichloroacetic acid derivative to C_{60}, purified by column chromatography, and characterized by ^1H, ^{13}C - NMR, IR, UF- spectrum, mass spectrometry (MALDI-TOF) [1].



Homopolymerization of monomer **II** was carried out under inert atmosphere at the presence of the Grubbs 1’st generation catalyst at room temperature in the CH_2Cl_2 (or C_6H_6) solution. During the first 6 hours consumption of the initial monomer (TLC control) and precipitation were observed. The polymer **II** is insoluble in $CHCl_3$, C_6H_6, $C_6H_5CH_3$, THF and EtOAc and is partially plumped at keeping in DMSO, so the molecular weight of polymer was impossible to estimate.

The thermal degradation of synthetic homopolymer (**II**) was studied. Parameters of the thermal degradation demonstrate the following: the temperature of intensive thermal degradation start (T_i) was 384°C, the final temperature of the mass loss (T_f) (calculated by the method of tangents) – 429°C, the temperature corresponding to the reduction of the weight of the polymer thermal destruction at 1% ($T_{1\%}$) – 283°C and temperature of maximum rate of thermal degradation (T_{max}) – 402°C.

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

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PP-18

Influence of the Electronic Properties of Palladium Particles Deposited on Alumina on the Reaction Mechanism of Hydrogenation of 1,3-Butadiene

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The influence of the structural and electronic characteristics of supported Pd catalysts on their adsorption and catalytic properties was studied. The supports of the catalysts were unmodified and modified γ-Al_2O_3. The modifying compounds were acetic acid and ammonium fluoride, which were mixed with pseudoboehmite. Then, the unmodified and modified aluminum hydroxides were calcined at 550 ^{0}C. For palladium precursor was used complex of acetylacetonate for all catalysts.

It was shown that the catalysts have different dispersion of palladium particles. The support with acetic acid has more amount acid centers and corresponding catalyst has largest dispersion of active component. It promotes high values of conversion of 1,3-butadiene. Also, this catalyst has more amount of palladium particles with higher electron density on the 3d-orbital in comparison with other samples. This results to high selectivity of 1-butene. The catalyst prepared with fluorinated support also demonstrate good performance.

Parahydrogen-induced Polarization for Mechanistic Investigation of Heterogeneous Hydrogenation Reactions

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Parahydrogen-induced polarization (PHIP) effect can be observed in conditions of pairwise hydrogen addition to an unsaturated substrate molecule followed by ^{1}H NMR detection of the reaction products. If both atoms from the one molecule of parahydrogen are added to the same substrate molecule and they end up in magnetically non-equivalent positions in the product molecule, the NMR signals of the reaction intermediates and product molecule become significantly enhanced. Accordingly signal enhancing capabilities, PHIP is a very promising technique for studying kinetics and mechanisms of reactions with molecular hydrogen in homogeneous and heterogeneous catalysis.

Herein, PHIP technique was applied for mechanistic study of heterogeneous hydrogenation of C6-cyclic hydrocarbons (benzene, cyclohexene, 1,3-cyclohexadiene, 1,4-cyclohexadiene) over Rh/TiO_2 catalyst. In case of cyclohexene hydrogenation the satellite PHIP signals of cyclohexane were observed in despite of symmetry of cyclohexane molecule. This fact is explained by presence of ^{13}C nuclei in natural abundance which led to breaking of molecular symmetry. Also in experiments with cyclohexene the reactant's NMR signals were polarized, demonstrating that hydrogen exchange is possible. Possible reaction pathways of this pairwise replacement were analyzed using ^{1}H NMR spectral simulations. In hydrogenation of 1,3-cyclohexadiene and 1,4-cyclohexadiene all NMR signals of cyclohexene exhibited PHIP effects, implying isomerization of C=C bonds in these compounds. At the same time, in benzene and toluene hydrogenation only cyclohexane and methylcyclohexane respectively were observed and their NMR signals were not polarized. This fact can be explained by either differences in reaction mechanism.

Farther, in this work hydrogenation of furan compounds (furan, 2,3-dihydrofuran, 2,5-dihydrofuran) over Rh/TiO_2 catalyst was studied both in liquid and gas phases by means of PHIP technique. It was shown that for furan and 2,3-dihydrofuran hydrogenation over Rh/TiO_2 catalyst polarized signal of CH-group of 2,3-dihydrofuran was observed. This observation can be explain in terms of pairwise replacement. So we proposed the next mechanism of pairwise replacement involving sequential 2,3-dihydrofuran pairwise hydrogenation followed by dehydrogenation.

Acknowledgement. This work was supported by the RFBR (grants 14-03-93183 MCX_a and 16-03-00407-a) and MK-4498-2016-3.

PP-20

Mechanistic Aspects of the Activation of Silica-supported Iron Catalysts for Fischer–Tropsch Synthesis in Carbon Monoxide and Syngas

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Fischer–Tropsch (FT) synthesis is the catalytic conversion of syngas (H_2+CO) into hydrocarbons and oxygenates that can be used for the production of synthetic fuels and chemicals [1]. Fe-containing catalysts currently represent special interest for several reasons. Most of the experimental evidence obtained so far has indicated that iron carbides of different composition could constitute the active phase for FT synthesis. It was also found that activity and selectivity of iron catalysts strongly depend on the conditions of catalyst activation [2]. However, very little information is available in the literature about the kinetics of activation and carbidization of iron oxide catalysts with carbon monoxide or syngas.

In present work the mechanism of activation of silica-supported iron catalysts for Fischer–Tropsch synthesis was investigated in syngas or carbon monoxide under transient and isothermal conditions using the in situ magnetic method.

The catalyst activation proceeds in two steps and involves reduction of hematite into magnetite and magnetite carbidization into Hägg carbide. Smaller supported iron particles exhibit higher rates of hematite reduction and magnetite carbidization than the larger counterparts. The reduction of hematite to magnetite proceeds with similar rates in syngas and pure carbon monoxide, while magnetite can be carbided more rapidly in carbon monoxide. The concentration of iron carbide was approximately 3 times higher after activation in CO relative to the activation in syngas.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research (Grant №16-03-00215a).

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The Direct Condensation of Supercritical Ethanol into Higher Linear α-Alcohols over Heterogeneous Catalysts

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Heterogeneous $CuO_x/Au/Al_2O_3$ and $NiO_x/Au/Al_2O_3$ catalysts with different metal loadings and monometallic analogues (Au/Al_2O_3, NiO_x/Al_2O_3, $CuOx/Al_2O_3$) were applied for the direct ethanol conversion into linear α-alcohols in the supercritical regime in batch reactor. $CuO_x/Au/Al_2O_3$ catalyst was found to provide ethanol conversion into 1-butanol, 1-hexanol and 1-octanol with 77.6% selectivity of 1-butanol or total selectivity of linear α-alcohols of 99.8 at 45 % conversion of ethanol. The supercritical conditions allow increasing catalysts productivity in comparison with subcritical regime. Kinetics measurements showed the difference of n-butanol formation activation parameters (E_a) of mono- and bimetallic catalysts and preexponential factor (A) difference between sub- and supercritical regimes. During long-term experiments optimal reaction time was found during that ethanol stayed in supercritical regime. The exceeding of this time leads to ethanol phase change from supercritical state into gaseous phase and results in sharp decrease of selectivity. The reason of observed in our work beneficial catalytic activity increase under supercritical conditions may be caused by several factors: the decrease of hydrogen bonds of ethanol, diffusion barrier lowering and O-H bonds acidity increase.

The high activity and selectivity of bimetallic Au-Cu and Au-Ni catalysts compared with monometallic ones presumably is a result of its specific surface and higher concentration of $Au^{\delta+}$ cations comparative with monometallic Au-containing catalysts. An interaction between Au and MO species (M= Cu, Ni) leads to an increase of dispersion of gold clusters from 10 to 5 nm, so with equal gold content bimetallic catalyst should have larger gold surface area. One more reason is the formation of gold cations Au^{n+} (where $1 \leq n \leq 3$). Ethanol self-aldolization passes through the dehydrogenation-hydrogenation steps. These processes for metal-containing catalysts are accompanied by a change in oxidation state from M^0 to M^{+2}. For monometallic catalyst Au/Al_2O_3 this changes may be described with the next equation: $Au^0 \rightarrow Au^{+2} \rightarrow Au^0$, that includes uncharacteristic for gold oxidation state +2. That may be a reason of low selectivity of Au clusters in Au/Al_2O_3 catalyst. In case of bimetallic system gold is mainly presented as cations with charge state close to +1, that makes possible activation of hydrogenation-dehydrogenation cycle with typically charge states of gold: $Au^{+1} \rightarrow Au^{+3} \rightarrow Au^{+1}$.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 15-13-30034.

PP-22

The Paramagnetic Nature of Rare Earth Containing Polyoxometallates Catalysts

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A number of Polyoxymetallates catalysts, mainly in molybdenum and tungsten-based containing rare-earth elements Gd^{3+}, La^{3+}, Nd^{3+} have been studied by EPR spectroscopy. The EPR spectra of the investigated catalysts were recorded on radio-spectrometer Bruker-BioSpin at 25°C. The adjustment on internal standard of field was defined by the etalon of UDD (ultradispersed diamond, g-2,0036) [1].

The main objective was to determine the EPR spectra of the synthesized catalysts in order to identify them in the paramagnetic centers, radical formation and to determine their nature, concentration and etc.

It was investigated that in the spectra of EPR Gd lines in HBr и H_3PO_4 matrices unlike matrices of oxalate widened that can probably be resulted in spin-spin interactions of Gd from its medium(matrices). The signals from Mo in the present case do not defined.

In the EPR spectra of catalysts containing rare earth elements La and Nd is observed ultrafine structure of EPR spectra, presenting superposition of two radicals: triplet (ΔH_{wide}=15,0 mT) and singlet in the central part of spectrum (ΔH_{wide}=3,0 mT) with g-factors of 1,89867; 1,9250 accordingly [2]. We consider that availability of positively charged ion of hydrogen (NH_4^+) in molybdenum base can promote detachment of Cl atom from $LaCl_3 \times 6H_2O$ by formation of $\dot{La}Cl_2$ radical.

For finding out what amount of La to introduce during the synthesis of catalyst we have conducted additional EPR researches of synthesized catalysts with various ratios $LaCl_3 \times 6H_2O$ (3:1), (2:1), (1:1) with respect to the base $(NH_4)_6Mo_7O_{24} \times 4H_2O$. It was found that when the ratio (3: 1) on the EPR spectrum appears hyperfine structure due to radicals ultrafine structure caused by $\dot{La}Cl_2$ radicals, but the concentration of Mo ions considerably decreases. Thus is established that, in the spectra of catalysts with elements of the amount of La and Nd observed hyperfine structure of the EPR lines indicating the formation of these radical catalysts of sustainable complex.

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PP-23

Electrocatalysis on Bimetallic Nanoobjects

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The aim: correlation between the origin of adsorption sites and their reactivity for nitrate electroreduction on Pt single crystals: Pt(111), Pt(100), stepped surfaces Pt(610), Pt(410), Pt(210) (6,4,2-atomic width (100) terraces with monoatomic height (110) steps), Pt nanoparticles with (100) preferable orientation and Cu-modified electrodes.

Perchloric and sulfuric acid solutions, cyclic voltammetry.

The Cu_{ad} accumulation was carried out by the potential cycling between 50 and 350 mV at 50 mV/s, then anodic limit of the cycling was increased and the amount of deposited Cu was estimated by integration of Cu desorption peaks between 550 and 950 mV. Rough estimation shows that although similar amounts of Cu_{ad} was accumulated on the electrodes (ca. 0.2-0.4 ML), the rate of the nitrate reduction is maximal for wide terraces of Pt(610) and minimal (ca. 20 times lower) for narrow terraces of Pt(210).

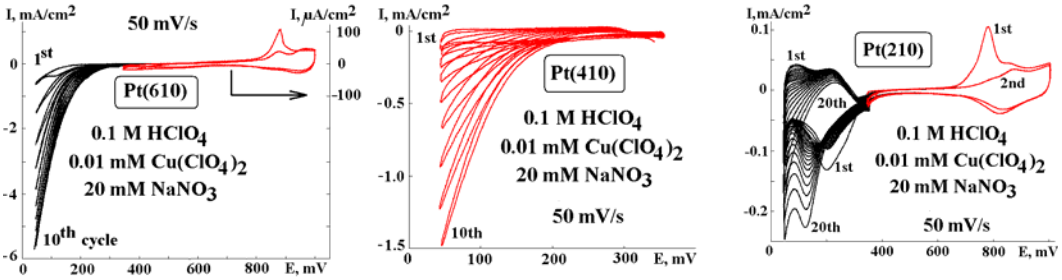

Fig. Nitrate reduction (50-350 mV) and Cu desorption (350-950 mV) at the stepped surfaces.

The rate of nitrate reduction in perchloric acid solutions is much higher (by 2-4 orders of magnitude) on Cu-modified electrodes as compared with bare platinum ones, this process takes place **mainly on the terraces** (100) of the stepped surfaces. The catalytic effect of copper adatoms is largely caused by the facilitation of nitrate adsorption on the platinum surface near Cu_{ad} and/or on the islands of the Cu(1×1) monolayer (induced nitrate adsorption). The rate of the process is determined not only by the amount of Cu adatoms but also in a great extent by the **structure of the adlayer** on the Pt(hkl)+Cu_{ad} surfaces.

It has been found that nitrate reduction on Cu-modified electrodes in sulphuric acid solutions is hindered as compared with bare platinum due to induced sulfate adsorption. Sulfate blocks the adsorption sites on the platinum surface and/or islands of epitaxial Cu(1×1) monolayer thus hindering the adsorption of nitrate anions and their reduction.

Acknowledgement. This work was supported by the RFBR, grant 14-03-00530.

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PP-24

Nickel Based Catalysts for Combined Steam and Carbon Dioxide Reforming of Methane

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The combined steam and carbon dioxide reforming (SCDR) of methane to synthesis gas attracts much attention. In comparison with dry reforming of methane, the use of steam in the feed for CO_2-reforming reduces the formation of carbon. By changing the H_2O/CO_2 ratio in the reaction feed, the H_2/CO product ratio can be controlled, and this makes it possible to produce synthesis gas with the H_2/CO ratio of about 2, which is suitable for the methanol and Fisher-Tropsch syntheses.

The major problem encountered towards the application of this process is carbonization of catalysts. The aim of this work was to study the catalytic properties of the nickel catalysts supported on a porous nickel ribbon (pNirb) with a MgO underlayer in the SCDR of methane to synthesis gas.

The method of preparation of nickel catalysts consisted in supporting of the MgO underlayer (6 wt. %) by impregnation with solution of $Mg(NO_3)_2$ of 0.1mm thick pNirb ($S_{sp} \sim 0.15$ m^2/g, $V_\Sigma \sim 0.1$ cm^3/g, $r_{preval} \sim 5$-60 μm); additional supporting of nickel (1-4 wt. %) was performed by impregnation of the support (pNirb + 6.0 wt. % MgO) with a mixture of solutions of $Ni(NO_3)_2$ and $Mg(NO_3)_2$. The catalysts were characterized by XRD, low-temperature adsorption of nitrogen, XPS, SEM and TEM in combination with EDX analysis. Catalyst activity in SCDR of methane was evaluated by the flow method (1 atm., 750°C, $CH_4/CO_2/H_2O/N_2 = 35/23/39/3$, GHSV= 62.5 L/gh). Prior to testing the catalysts were reduced at 750-900°C for 1 hour in H_2 flow.

TEM data indicate that in the reduced catalysts the supported nickel crystallites are highly dispersed (3–7 nm) and epitaxially bound to the MgO. After testing in the catalysts most of supported nickel crystallites remain in the stable state of dispersed crystallites epitaxially bound to MgO. The activity of catalyst with low content of MgO (6.7 wt. %) decreased during testing. After reaction in this catalyst no carbon deposits were found on dispersed nickel crystallites epitaxially bound to MgO, but the islet formation of graphite-like carbon was observed on the large crystallites of nickel ribbon. The catalysts with high content of MgO (8.6- 2.2 wt. %) in which the MgO underlayer completely covering the nickel ribbon showed stable activity throughout the test period (18 h) and contained no carbon deposits.

The resistance of these catalysts to carbonization was attributed both to the formation of nickel crystallites epitaxially bound to MgO and the formation of the MgO underlayer, that completely covers the nickel ribbon and prevents its contact with the reaction medium. The H_2/CO ratio in the reaction products over these catalysts was 2.1-2.2.

The work was supported by the Russian Foundation for Basic Research (grant №15-03-04001).

PP-25

Selective Carvone Hydrogenation to Dihydrocarvone over Au Catalyst

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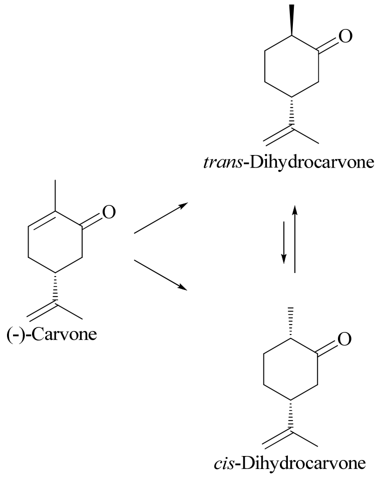
Carvone is one of the most widespread natural monoterpenoids, which is widely used in food and perfumery industry as well as in the synthesis of fine chemicals. Carvone hydrogenation is of great practical interest giving a range of valuable products, including dihydrocarvone, which is formed as a mixture of two stereoisomers, has spearmint-like odor and is used as a flavoring additive in various foods. At the same time carvone is an interesting substrate to explore catalyst activity in stereo- and chemoselective hydrogenation, because it contains an asymmetric center with a specific configuration as well as three types of functional groups. In general, selective hydrogenation of multifunctional organic molecules is one of the main challenges in catalytic fine organics synthesis.



In this work the aim was to study carvone hydrogenation regularities over a gold catalyst with the general idea to investigate both gold catalysts activity in competitive hydrogenation of different functional groups and to develop an approach to the synthesis of valuable carvone derivatives such as dihydricarvone. Selective hydrogenation of natural carvone to industrially valuable dihydrocarvone was carried out at 100°C under hydrogen pressure over 1.9 wt. % Au/TiO_2 catalyst [1]. This catalyst was found to promote stereo- and chemoselective carvone hydrogenation to dihydrocarvone with predominant formation of the *trans*-isomer, which generally is a novel synthetic method for an industrially valuable dihydrocarvone. The obtained results demonstrate a possibility of gold catalysts utilization for preferential hydrogenation of C=C bond conjugated with a carbonyl group even when another C=C group is present in the substrate. Effect of the solvent on catalytic activity as well as on the ratio between *trans*- and *cis*-dihydrocarvone was observed. A range of C_1-C_3 alcohol solvents was applied for carvone hydrogenation with the highest yield of dihydrocarvone achieved in the case of methanol. Based on the transition state theory the quantitative description of the *trans*-/*cis*-dihydrocarvone ratio variations in different solvents was made.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 15-33-20198.

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PP-26

Electrocatalytic Mechanisms of Hydrogen Production at Low pH in the Presence Iron(II) Clathrochelates

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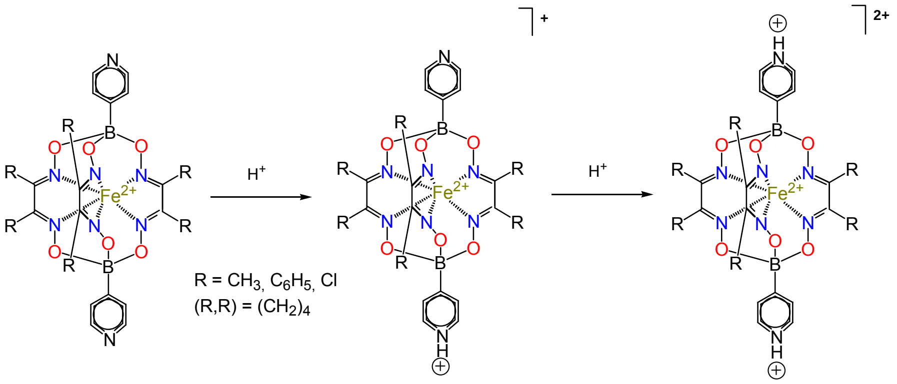
Increasing energy demands of an ever-growing population calls for new energy sources, one of them being molecular hydrogen. To make hydrogen-based economics a reality, highly efficient and chemically stable catalysts for hydrogen production that do not contain precious platinum group metals need to be designed. For this purpose, we suggest to use iron(II) clathrochelate complexes with functionalizing pyridinyl substituents, which emerged as effective homogeneous electrocatalysts for hydrogen evolution at low pH; we expected the protonation of these complexes to increase their solubility in water due to the formation of salts (Scheme 1).



R = CH_3, C_6H_5, Cl
(R,R) = $(CH_2)_4$

The complexes obtained efficiently electrocatalyze hydrogen evolution from an acid solution in acetonitrile as well as from aqueous buffers with low pH (1 – 4). NMR spectroscopy data confirmed that protonation of both the pyridine moieties occurred, thus giving protonated species that were stable in these conditions. Titration of an acetonitrile solution of a clathrochelate with an acid resulted in a significant increase of the current assigned to the $Fe^{2+/+}$ pair, while the peak of the reverse process vanished. Kinetic parameters and overall efficiency of the catalytic process depended greatly on the nature of ribbed substituents in chelate fragments of these clathrochelates. Based on the dependence of the rate of the electrocatalytic process $2H^+/H_2$ on the pH value of the aqueous solution, a limiting step was identified and a catalytic mechanism elucidated experimentally. All proton reduction reactions were first order in the catalyst's concentration and second order in the acid's concentration; for all of them, rate constants and activation energies have been obtained.

Thus pyridinyl-functionilized iron(II) clathrochelates emerge as first homogeneous electrocatalysts of hydrogen evolution at low pH; varying their ribbed substituents allows designing electrocatalysts with better performance and stability in harsh near-industrial conditions.

On a Mechanism of Catalytic Combustion of Soot: Evaluating "Extra-Tight" Catalyst-Soot Contact Condition

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Intro. Since 1990's, catalytic combustion of soot is of great interest mainly due to strong demand for solutions to decrease vehicular exhaust soot emissions [1]. Catalysts were implemented to lower the temperature of diesel particulate filters (DPF) regeneration [2].

Standard method of kinetic studies of soot combustion consists in burning mixture of soot and catalyst along the temperature ramp (TPO), measuring rates of CO_X evolution or carbon disappearance. Contact condition between catalyst and soot is very important. Uncertainty in the definitions of commonly used "loose" and "tight" conditions may cause significant deviations in the results. Another important parameter is soot-to-catalyst mass ratio (SCMR). In most cases, SCMR used in the lab experiments is 1/20 to 1/5, being much lower than the real soot-to-catalyst ratios observed within DPF.

The purpose of the present work was to evaluate "extra-tight" catalyst-soot contact condition, together with more realistic ratio between catalyst and soot.

Experimental. Samples representing extra-tight catalyst-soot contact condition were prepared according to [3]. Activated carbon (AC) was impregnated with solution of the Pt pre-cursor, followed by drying and reduction. SCMR corresponded to the Pt loading of the sample. SCMR of 10/1 (10% wt. Pt on AC) was investigated. Pure support material (AC) was characterized as well as a reference sample.

Samples were characterized for a reactivity in $C+O_2$ reaction using TPO in O_2-He flow, with CO_2 and O_2 measured with MS. Texture properties, PGM sites availability, PGM particles size were characterized with N_2 BET, pulse chemisorption, HRTEM and XRD.

Results. For the sample 10%Pt-AC representing extra-tight catalyst-soot contact condition, the following soot combustion characteristics were measured in TPO run in dry O_2-He mixture: $T_{10\%} \sim 400^oC$, $T_{50\%} \sim 493^oC$, $T_{90\%} \sim 575^oC$. The low-temperature shift vs. reference sample was: $\Delta T_{10\%} \sim 210^oC$, $\Delta T_{50\%} \sim 193^oC$, $T_{90\%} \sim 217^oC$. Main kinetic parameters were obtained by fitting a simplified kinetic model to experimental data.

Conclusion. Extra-tight catalyst-soot contact condition allows measuring real potential of the given catalyst, including correct comparison of catalysts and using intrinsic kinetic parameters in different soot combustion/DPF regeneration models.

Acknowledgement. Many thanks to Scientific-Educational Centre of the Energy-Effective Catalysis (Novosibirsk, Russia) for borrowing their ChemBET Pulsar TPR/TPD and Cirrus 2 machines to us.

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PP-28

Effect of Pore Size of Zeolites on Olefin Oligomerization

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Oligomerization of light alkenes represents an important route to the production of environmentally friendly synthetic liquid fuels, free of sulfur and aromatics. Zeolites are used as catalysts for the oligomerization of olefins. The oligomerization over zeolites BEA and MOR is accompanied with fast deactivation due to formation of heavy products, which block the pores of zeolites. On zeolite MFI having narrower pores the coke formation is suppressed because of steric hindrance of polyalkylaromatics (coke precursors) formation. However, the peculiarities of olefin transformation over zeolites with small pore size (less than size in MFI structure) are not well studied.

The zeolites with pore diameter 3.5-5.6 Å were studied in oligomerization of light alkenes. Zeolites had similar crystal size and Si/Al ratio. The concentration and strength of acid sites on zeolites were studied by IR spectroscopy of adsorbed CO. The reaction was carried out in fix-bed reactor at 300°C and 15 atm.

FER and TON with narrow pores were found to be more selective to dimers or trimers in comparison to MFI. Yield-Conversion relations obtained for the zeolites showed that dimers are primary stable products for FER and TON unlike MFI structure. Thus the further transformation of dimers is sterically hindered in small pores. Among studied zeolites TON showed higher stability compared to FER and MFI. This was attributed to one dimensional structure of TON with no intersections or cavities where coke precursors could be formed.

Eventually, the change of pore size is an effective tool for increasing selectivity into desired products.

Acknowledgement. This work was supported by the Russian Science Foundation, grant №14-23-00094.

Metal-Carbon Nanocomposites Based on Activated IR Pyrolized Polyacrylonitrile

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Activated carbon (AC) takes a special place among advanced materials due to a set of physical-chemical properties. The main feature of activated carbon is high surface area which can provide high adsorption capacity for adsorbent or uniform distribution of catalytic active sites for catalyst. At present time the quest for effective methods of preparation of metal-carbon nanocomposites based on AC and catalytic active metal nanoparticles with prescribed properties is an important mission. The new AC synthesis method applying IR pyrolysis with low-dose activating agent was proposed.

For the first time the metal-carbon nanocomposites based on activated IR pyrolized PAN were prepared. The major feature of this method is simultaneous carbon matrix formation and its activation during IR pyrolysis which allows to reduce the time of heat treatment significantly.

AC samples were obtained under the conditions of infrared (IR) annealing of a precursor based on PAN pyrolyzed at 200 °C and potassium hydroxide. Molar ratio was C:KOH=5:1. The metal-carbon nanocomposites were prepared from KOH-treated pre-carbonized precursor based on PAN and $Pd(CH_3COO)_2$ or $RuCl_3$ solution in N,N-dimethylformamide. The activation process took 2 min at heat treatment temperature which was varied from 600 to 900 °C. After activation step the samples were washed out with distil water up to neutral pH and dried to constant weight.

The samples with BET surface area of 2068 and 1091 m^2/g were obtained at the same activation conditions: C:KOH ratio was 5:1 and activation temperature was 800 °C. The difference between those two samples was a temperature of preliminary heat treatment, 200 and 700 °C, respectively. All metal-carbon nanocomposite samples based on activated IR pyrolized PAN were synthesized via IR annealing of the precursors at 800 °C in inert atmosphere in the presence of KOH. In the case of bimetallic system the alloy formation is observed. Specific surface area varies depending on the presence of the metal.

Metal-carbon nanocomposites IR-PAN-a/Pd-Ru were tested as heterogeneous catalysts in the reaction of steam reforming of ethanol.

Acknowledgement. This work was supported by Russian Federation President Grant for Government Support of Young Russian Scientists, project MK-7364.2015.

PP-30

Evaluating the Possibility of Nonadiabatic Crossing in Selenium-substituted [NiFe]-Hydrogenase

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Spin-forbidden crossing, or nonadiabatic transitions between electronic states with different spin multiplicities, plays an important role in different areas of molecular sciences. For example, in photochemistry and photophysics, the intersystem crossing, spontaneous emission and internal conversion which are nonadiabatic transitions between states with the same spin, determine the decay rate and lifetime of electronic excited states [1]. Many thermally activated chemical reactions can proceed through so-called multistate spin-forbidden mechanisms where reaction rate can strongly depend on the efficiency of intersystem crossings [2, 3]. However, the catalytic reaction mechanisms are usually assumed to involve only a single electronic state. Even when a crossing between different spin-states along the reaction path is identified, often the transition between two spin states is treated as either completely spin-forbidden or spin-allowed. Our work on biological NiFe clusters indicates that such nonadiabatic transitions mediated by spin-orbit coupling can play a critical role in catalysis, and therefore, must be taken into account to gain a detailed understanding in the mechanisms and dynamics of reactions catalyzed by transition metal clusters [4]. In large complex systems the nonadiabatic transitions between electronic states with different spin multiplicities can be modelled using computationally efficient time independent methods. Arguably the most successful of these methods is nonadiabatic transition state theory (NA - TST). We follow with one example of application of NA-TST to intersystem crossings in the active site of the metal-sulphur proteins [NiFe]-hydrogenase. One or two sulfur atoms in this model were replaced by selenium atoms. It is assumed that substituting sulfur with selenium is capable of enhancing spin-orbital coupling which, in turn, can change the probability of nonadiabatic transition. Hydrogenases are enzymes that catalyze both the proton reduction and oxidation of molecular hydrogen: $2H^{+}+2e^{-} \rightleftharpoons H_2$, reactions relevant to clean energy storage and utilization. The reaction mechanism is not completely understood. Further insight into the H_2 binding on the active site is needed to understand the catalytic properties of [NiFe]-hydrogenase and aid into the creation of a functioning synthetic counterpart.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-13-00139.

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Exchange H_2-D_2 Reaction and Protium Ortho-Para Conversion for Characteristics of Catalytic and Adsorptive Properties of Iron Nanoparticles

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The adsorption and catalytic properties of iron nanoparticles with an average size of 0.6 nm, supported on γ-Al_2O_3 have been studied. The nanoparticles obtained in reverse micellar solutions [1]. The size of the nanoparticles is estimated on EnviroScope 5.30 atomic force microscope. The iron content in the sample is calculated based on the spectrophotometric measurements, and was 1.9% by weight. Hydrogen adsorption in a wide temperature range of 77 ÷ 500 K is observed on the sample. The amount of adsorbed gas sharply decreases with increasing of adsorption temperature. The whole adsorbed hydrogen on the surface is weakly bound, and can be easily removed by pumping at the temperature of adsorption. The active surface of the sample is determined by the value of hydrogen adsorption at temperature 77 K.

For the carrying of the reaction H2-D2 exchange in the negative temperature field it requires the presence of the dissociated hydrogen on the surface (mechanisms Ridila). Iron nanoparticles showed no catalytic activity in this reaction. Therefore, under these conditions, the hydrogen is adsorbed only in molecular form on the surface of the catalyst.

It is known that the reaction of the protium ortho-para conversion can occur as on dissociative and on the magnetic mechanisms. Iron nanoparticles showed high catalytic activity in the conversion reaction of hydrogen at temperatures of 77-110 K, which can be explained by the occurrence of the reaction on magnetic mechanism under the influence of the magnetic field of the iron particles.

The magnetic moment can possess both metal atoms and ions of iron. With decreasing the size of the particle, magnetic properties can increase significantly. The presence of the molecular adsorption of hydrogen on the surface is enough for the course of the protium ortho-para conversion.

Thus, using the selected reactions we can characterize hydrogen state on the surface of the nanoparticles, and by varying the dimensions of the nanoparticles - vary the speed of the reactions.

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PP-32

Tri-Reforming of Methane to Synthesis Gas over Porous Nickel Based Catalysts

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In recent years the catalytic processes of the tri-reforming – mixed CO_2-H_2O-O_2-reforming of methane to synthesis gas have been developed. It gives the possibility to use renewable energy sources, for example, biogas for generation of synthesis gas. The major problems encountered towards the application of these processes are local overheatings, sintering and oxidation of the active component in the inlet part of the catalyst bed and the carbonization of the catalyst in the catalyst bed region, where steam and carbon dioxide reforming of methane occurs. To enhance heat transfer efficiency of the catalyst it is reasonable to use high thermal conductive metallic support of catalyst. The aim of this work was to study the peculiarities of the formation of the phase composition, structure of MgO, phase composition, morphology of the nickel catalysts supported on porous nickel ribbon and epitaxial binding of nickel particles to MgO.

To prepare supported nickel catalysts, 0.1 mm-thick ribbon porous nickel prepared by rolling ($S_{sp} \sim 0.15$ m^2/g, $V_\Sigma \sim 0.1$ cm^3/g) was used as a support. The MgO underlayer (10-12 wt.%) was supported by impregnation of the nickel support with solution of $Mg(NO_3)_2$ (support I) or $Mg(CH_3COO)_2$ (support II) followed by calcination at 750°C in H_2. Nickel (1-2 wt.%) was supported by impregnation of support with MgO underlayer with a mixture of $Ni(NO_3)_2$ and $Mg(NO_3)_2$ solutions followed by calcination at 500°C in N_2 or He. The catalysts were characterized by XRD, low-temperature adsorption of nitrogen, XPS, SEM and TEM in combination with EDX analysis. Catalytic activity in TRM was evaluated by the flow method (1 atm.,750°C, $CH_4/CO_2/H_2O/O_2/N_2$ = 1/0.75/0.75/0.14/1.4, feed rate of the reaction mixture 25.0 l/h, m_{cat}= 0.40g). The catalysts were reduced at 900°C in H_2 flow.

XRD data showed that supports I and II contained phases of nickel and MgO. The specific surface area of support I was 7.9 m^2/g and of support II was 2.5 m^2/g. The MgO underlayer in support I had fine pores with an average diameter of 6-9 nm. In the support II the contribution of fine pores was lower. XRD data showed that reduced catalysts obtained by calcinations of precursor in N_2 contained the solid solution of NiO in MgO. According to TEM data the crystallites of supported nickel were dispersed (3-5 nm) and epitaxially bound to MgO, the nickel crystallites didn't have an oxide layer. The catalysts obtained by calcination of precursor in He didn't contain the solid solution of NiO in MgO; epitaxially bound crystallites of supported nickel were very rare, these crystallites were oxidized and their surface contained a layer of NiO.

The catalytic activity tests showed that the catalyst obtained by calcination in N_2 was more active (initial conversion degree was about 75 %, the decrease in the activity was about 4 %) than the catalyst obtained by calcination in He (initial conversion degree was about 61 %, the decrease in the activity was about 7 %) that can be attributed to the interaction of NiO and MgO in catalyst obtained in N_2 with the formation of solid solution, from which dispersed nickel crystallites were formed.

Thus, the nickel catalysts supported on the ribbon porous nickel with MgO underlayer were active in the tri-reforming of CH_4 to synthesis gas.

This work was supported by the Russian Foundation of Basic Research (grant **15-03-04001**).

A Study of Adsorption Substances on Catalysts by the Response Method

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Consider adsorption substance A on the catalyst in the form of step

$$dA + (a + b)Z = aIZ + bJZ\ , \qquad (1)$$

where Z – free active centers; IZ and JZ – forms of substance adsorbed on the catalyst surface; $a,\ b,\ d$ – stoichiometric coefficients ($a+b \geq d>0$). Dynamic of adsorption process under isothermal conditions in gradientless reactor described by a system of differential equations:

$$x'_t = a(r_1 - r_2), \quad C'_t = d(r_2 - r_1)L/N+(C_0 - C)V/N, \qquad (2)$$

$r_1 = k_1C^dz^{a+b}$ and $r_2 = k_2x^ay^b$ – the rates of adsorption and desorption; k_1 and k_2 – the rate constants of adsorption and desorption; x and $y = bx/a$ – parts of the catalyst surface of JZ and IZ substances; $z=1-x-y$ – part of vacancy centers Z; C_0 and C – concentrations of A at the inlet and outlet of the reactor; t – time; L – the number of centers on the entire surface of the sample of the catalyst; N – number of molecules in the gas volume of reactor; V – velocity of the gas stream. In regime of adsorption reactor previously washed with an inert gas. Then, at some moment of time (accept it as the beginning of start $t = 0$) instead of the inert gas in the reactor starts to be supplied with a constant flow rate of a mixture of inert gas with a small amount of substance A. After reaching steady state (when the concentration of substance A reactor outlet stops changing) the first experiment (regime 1) ends. After that immediately follows the desorption regime: inert gas stream with a pure substance A is replaced with an inert gas, there is a drop at the outlet of reactor A to zero concentration. These experiments were applied to the system (2), the following initial conditions (the second subscript indicates the number regime:

$$\text{adsorption regime: } x(0) = 0,\ C(0) = 0; \text{ desorption regime: } x(0) = x_{\infty1},\ C(0) = C_{\infty1}, \qquad (3)$$

where $x_{\infty1}$, $C_{\infty1}$ – steady state values IZ and A in adsorption regime:

$$x_{\infty1} = 1/\{[k_2\,(b/a)^b/(k_1C_{\infty1}{}^d)]^{1/(a+b)} +1+b/a\},\ C_{\infty1} = C_{01}, \qquad (4)$$

is C_{01} – concentration of A at the reactor inlet in the adsorption regime. The stationary value of IZ in the desorption regime

$$x_{\infty2} = 0,\ C_{\infty2} = 0. \qquad (5)$$

Found in a general form for the model (2) of linear relaxation time

$$\tau = 2/\left|\sigma_\infty-(\sigma_\infty{}^2-4\Delta_\infty)^{1/2}\right|, \qquad (6)$$

where (following expressions for σ_∞ and Δ_∞ taken steady state values $C=C_\infty$ and $x=x_\infty$)

$$\sigma_\infty = a(-k_1C^dz^{a+b}(a+b)(1+b/a)/(1-z) +k_2(b/a)^bx^{a+b}(a+b)/x) -d^2k_1C^d/Cz^{a+b}L/N-V/N, \qquad (7)$$

$$\Delta_\infty = a(k_1C^dz^{a+b}(a+b)(1+b/a)/z-k_2(b/a)^bx^{a+b}(a+b)/x)(d^2k_1C^d/Cz^{a+b}L/N+V/N)+$$
$$d^2(-k_1C^dz^{a+b}(a+b)(1+b/a)/z+k_2(b/a)^bx^{a+b}(a+b)/x)L/Nak_1C^d/Cz^{a+b} \qquad (8)$$

Relationships (6)-(8) connect the rate constants of adsorption and desorption with linear relaxation times τ_1 and τ_2, which can be determined from the experimental data in the above two modes according to the formula:

$$\tau = (t_2 - t_1)/\ln[(C_1 - C_\infty)/(C_2 - C_\infty)], \qquad (9)$$

where C_1 and C_2 – concentration of substance A at times t_1 and t_2. To determine the constants k_1 and k_2 enough to write the equation (6) for regimes of adsorption and desorption with the determination of relaxation times τ_1 and τ_2. Using the above method the mechanisms of adsorption benzene and acetic acid on alumina-platinum catalysts and carbon dioxide deposited on chromium oxide and gallium oxide catalysts were identified. For these mechanisms constants adsorption and desorption were calculated.

PP-34

Different Activity of Zn^{2+} and ZnO Species for Methane Activation and Conversion at Zn-modified Zeolites

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Zeolites modified with zinc are considered to be promising catalysts for rational methane utilization by its conversion to higher hydrocarbons. One of the important issues for further improvement of the catalysts performance is the activity of different zinc species. Being introduced into zeolite, zinc can form isolated cations attached to the framework oxygens [1] or small oxide clusters located either inside zeolite pores or on the external surface [2]. According to existing data, these species could have different properties regarding methane activation and conversion.

To address this issue, two samples of zeolite beta containing exclusively either Zn^{2+} (Zn^{2+}/H-BEA) or ZnO (ZnO/H-BEA) species have been prepared and studied in this work. A well-known method of zeolite interaction with zinc vapour has been applied to obtain Zn^{2+}/H-BEA sample with Zn^{2+}-sites [3]. On the other hand, original procedure has been developed and used for the preparation of ZnO/H-BEA sample with zinc in the form of oxide clusters only. The state of zinc species has been investigated and confirmed by the set of various spectroscopic methods: NMR, FTIR, UV-vis., EXAFS, and XPS. Most importantly, the behavior of these species regarding methane activation and conversion has been monitored *in situ* with NMR spectroscopy.

Remarkably different performance has been observed for methane activation at Zn^{2+}/H-BEA and ZnO/H-BEA samples by studying the kinetics of H/D exchange between Brønsted acid sites of the zeolites and methane (CD_4) with ^1H MAS NMR spectroscopy *in situ*. Additionally, ^{13}C MAS NMR method has been used to reveal weather any surface intermediates are formed from methane-^{13}C on Zn^{2+} or ZnO sites. The reactivity of detected intermediates towards various reagents has been investigated.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 14-03-00040.

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Electrochemical Synthesis, Electrochemical Properties and Reactivity of Organonickel Sigma-Complexes of Type [NiBr(aryl)(bpy)], Where aryl is *ortho*-Substituted Phenyl, bpy - 2,2'-bipyridine

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The combination of nickel complexes with the principles of homogeneous redox catalysis allows obtaining in a simple way various products of homo- and cross-coupling of organic halides, chlorophosphines, and elemental (white) phosphorus [1]. The catalytic cycles involves *in situ* formation of organonickel sigma-complexes by oxidative addition of electrochemically generated nickel(0) complexes to aryl-halogen bond of the used organic halides [2]. The stability of these intermediates is very low due to the presence of very reactive metal-carbon sigma-bond and only a limited number of such type complexes has been stabilized and isolated as the free stable species [3].

In this work we describe the synthesis and structure of new organonickel sigma-complexes of type [NiBr(aryl)(bpy)], where aryl is 2,4,6-tricyclohexylphenyl (Tchp), 2,3,5,6-tetramethylphenyl (Tmp) and 2,6-diisopropylphenyl (Dipp), bpy = 2,2'-bipyridine.

The organonickel complexes have been synthesized according to the elaborated procedure by the reaction of oxidative addition of electrochemically generated [Ni^0(bpy)] complex to the corresponding aryl bromides in undivided electrochemical cell supplied with sacrificial nickel anodes used as the nickel source for preparation of organonickel complexes [4,5]. These species were isolated and characterized by various physico-chemical methods including NMR, mass-spectrometry and X-ray crystal structure analysis.

Acknowledgement. This work is financially supported by the Russian Foundation for Basic Research (project 15-43-02667).

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PP-36

Mechanism of n-Hexane Isomerization over Palladium Catalysts

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Nowadays emission standards for gasoline require the reduction of benzene, aromatic hydrocarbons, olefins and sulphur. Catalytic isomerization of light alkanes to corresponding isoparaffins considers as an alternative for octane boosters instead of aromatic compounds and allows increasing octane number. The reaction of C_5-C_6-alkanes isomerization is generally carried out over bifunctional catalysts, containing small amounts of Pt and Pd, dispersed on an acidic support. The works devoted to the study of n-paraffins isomerization on supported platinum catalysts are much more, than on palladium ones, also possessing high activity. These catalysts can be more low-cost alternative to platinum catalysts. Earlier by us it has been shown that the catalyst 0.8%Pd/HZSM-5 exhibited comparable activity with 0.35 % Pt/HZSM-5 in n-hexane isomerization. Introduction of promoters in this catalyst allow increasing its activity, selectivity and stability. Designing new catalysts requires depth knowledge of the reaction mechanism. In this work mechanism of n-hexane isomerisation over Pd catalysts with promoters (Co or Ni) and without them was investigated by unstationary and stationary kinetic methods. Concentration of Co and Ni was 1.0%. Physico-chemical characteristics of catalysts were studied by various methods: BET, XRD, TEM, TPD-NH_3, TPR-H_2, HPC, IR-spectroscopy and TGA. The kinetic experiments were carried out in a gradientless flow circulating system at atmospheric pressure and the temperature range from 215 to 260°C. The initial partial pressures of n-hexane (P^o_{n-C6}), hydrogen (P^o_{H2}) and isohexanes (P^o_{i-C6}) varied in the ranges of 33.3–137; 307-718 and 0–19.2 hPa, respectively. The following kinetic equation describes the obtained data over promoted catalysts:

$$r = \frac{kP_{n-C6}P_{H_2}^{0.5}\gamma}{1 + k_1P_{n-C_6} + k_2P_{H_2}^{0.5} + k_3P_{i-C_6}}$$ (r-reaction rate, k-k_3-constants, γ-accounts reversed reaction).

Unstationary response method was used for studying of process mechanism and adsorption characteristics of catalysts. It was shown, that mechanism of n-hexane isomerization is the same over studied catalysts but adsorption characteristics are different. The introduction of Ni and Co results in an increase of bond strength of isohexanes and n-hexane and their amounts on catalyst surface. It was also shown that hydrogen takes participation in the isomerization reaction increasing the yield of isohexanes. Step-scheme of the reaction was proposed: isomerization of n-hexane proceeds through the step of dissociative adsorption of n-hexane with formation of n-C_6H_{13} over Pd. This species interacts with boundary acid centers of HZSM-5 and suffers skeleton intramolecular rearrengement with transfer of H-atom to acid center (the slow step), breaking the second hydrogen atom from acid center and its addition to another carbon atom. Obtained kinetic equation can be derived from this step-scheme at proposition of proceeding the reaction in the middle surface coverage.

Substituted Anthraquinones: New Way of a Production via Diene Synthesis in the Presence of Mo-V-P Heteropoly Acid Solution as a Bifunctional Catalyst

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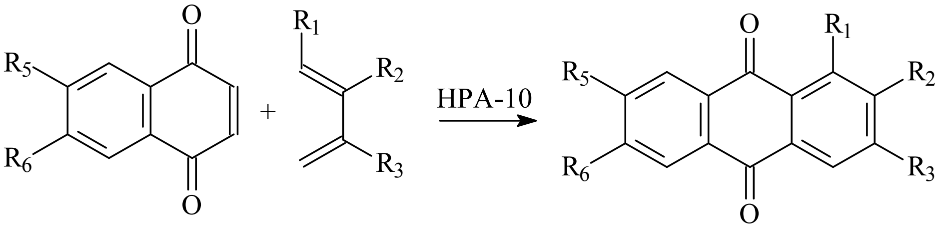
In the present work we develop one-pot processes for the preparation of substituted anthraquinones (AQ) via diene synthesis in the presence of heteropoly acid solution of the general formula $H_{17}P_3Mo_{16}V_{10}O_{89}$ (HPA-10) as a bifunctional catalyst, i.e., acidic catalyst for diene synthesis and catalyst for the oxidation of the obtained adducts. The general scheme of such processes is shown below:



After product filtration the HPA-10 solution is regenerated by oxygen in separate stage [1] following which this catalyst can be used many times.

Experimental results [1,2] are presented in the Table.

№	Substituents	Yield of AQ, %	Content of main product, %
1	$R_1=R_2=R_3=R_5=R_6=H$	67	97
2	$R_1= R_3=R_5=R_6=H, R_2=CH_3$	72	98
3	$R_2= R_3=R_5=R_6=H, R_1=CH_3$	91	99
4	$R_1=R_5=R_6=H, R_2= R_3= CH_3$	78	98
5	$R_1= R_3=R_5=R_6=H, R_2=Cl$	30	95
6	$R_2= R_3=R_5=R_6= CH_3, R_1= H$	70	94
Conditions: 0,2 M water HPA-10 solution, volume ratio HPA-10:1,4-dioxane 1:1, reaction time 7 h, temperature 80 °C. Conversion of naphthoquinones $\geq 99\%$.			

The obtained results open a prospect for the low-waste one-pot processes of substituted AQ production from substituted 1,3-butadienes and 1,4-naphthoquinone.

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PP-38

Mechanisms of Ethanol-Water Mixtures Oxidation in Electrochemical System with Proton-Exchange Membrane

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The purpose of this communication is to report on low-temperature electrochemical reforming of ethanol water solutions in electrochemical cell based on proton-exchange membrane (PEM). In comparison with conventional PEM water electrolysis, this competitive electrolysis process demonstrates reduced (up to 2-3 times [1]) power costs for hydrogen production and simplified cold-start of electrolysis system at sub-zero temperatures [2].

In this study, specific electrocatalytic, electrode and membrane materials intended for decomposition of ethanol-water solutions have been developed and tested. The mechanisms of reactions of ethanol-water mixtures oxidation in PEM-based electrochemical system on different electrocatalysts (on the basis of Pt, Ru and non-platinum metals) in wide range of potentials including simultaneous oxidation of water and ethanol are discussed. Mechanism of electrochemical oxidation of alcohols on electrocatalysts involves formation of adsorbed alcoholic species on the metallic surface. The oxidation takes place through a series of reaction steps involving successive electron transfer from alcohols to electrocatalysts. In acid solution, Pt/Ru is the most effective bimetallic catalyst used for alcohols oxidation. The Ru-containing catalysts shifted the onset potential for alcohols oxidation to more negative values. Both potentiodynamic, quasi-stationary and current-voltage performances have been recorded and analyzed.

Acknowledgement. The reported study was financially supported by the Russian Foundation for Basic Research within the framework of research project No. 16-08-01070 A.

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PP-39

Kinetics of Cross-Metathesis between Polynorbornene and Polyoctename in the Presence of 1st and 2nd Generation Grubbs' Catalysts

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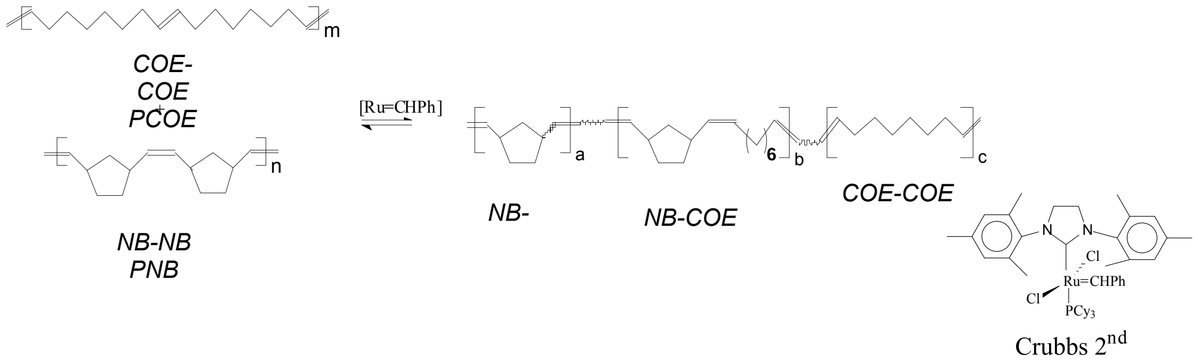
Metathesis reactions are well known in organic chemistry. Cross-metathesis is a reaction between two unsaturated compounds that exchange their substituents near C=C double bonds. Previously, we synthesized for the first time copolymers of norbornene and cyclooctene by the cross-metathesis of polynorbornene (PNB) with polyoctenamer (PCOE) using the 1st generation Grubbs' catalyst $Cl_2(PCy_3)_2Ru=CHPh$ (Gr-1) [1], studied the reaction kinetics [2] and gained some insights into its mechanism [3].

In this paper we present a study of this reaction in the presence of the 2nd generation Grubbs' catalyst (Gr-2) and compare the results obtained with Gr-1 and Gr-2. In situ 1H NMR spectroscopy is used for monitoring the kinetics of carbenes transformation. Evolution of the dyad composition of polymer chains was studied by 13C NMR.



Cross-metathesis of PNB with PCOE was performed in chloroform solution at room temperature, the initial PNB/PCOE and polymers/catalyst ratios were respectively 1/1 and 20/1 (mol/mol). The synthesized copolymers were characterized by NMR spectroscopy, GPC and DSC methods. The degree of crystallinity was calculated from the DSC thermogram.

We observed that after 24 h of interaction with Gr-2 the initial homopolymer mixture transformed into a completely random (the degree of blockiness is equal to unity), fully amorphous copolymer of norbornene and cyclooctene. Interaction with Gr-1 under identical conditions led to a crystalline copolymer with the degree of blockiness of 0.53 [2, 3]. Surprisingly, using more active Gr-2 catalyst resulted in a higher molecular mass of the copolymer, whereas the glass transition temperature only weakly depended on the catalyst type.

Acknowledgement. This work was supported by the RFBR, grant 14-03-00665.

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PP-40

Synthesis of (Me)$_3$Si-Norbornene–Cyclooctene Multiblock Copolymers with the Cross-Metathesis of Poly(Me$_3$Si-Norbornene) and Polyoctenamer Using Grubbs 1st Catalyst

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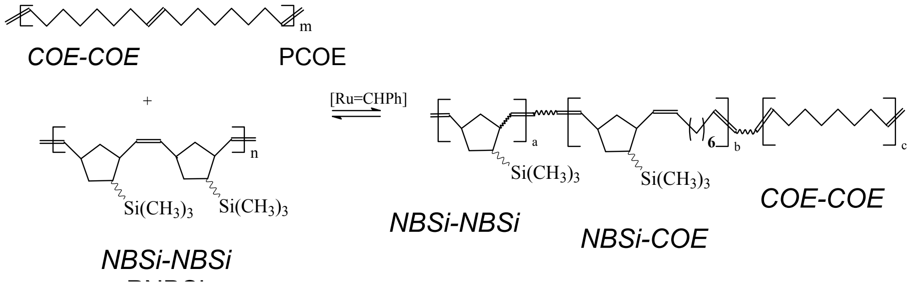
Recently we proposed a new approach to multiblock copolymer synthesis based on cross-metathesis reactions and obtained a copolymer of norbornene and cyclooctene starting from homopolymers polynorbornene (PNB) and polyoctenamer (PCOE) [1,2]. It is of interest to involve substituted polynorbornenes into the reaction of polymer cross-metathesis. The main idea of the present study is to explore the possibility of copolymer synthesis by interchain exchange of poly(trimethylsilyl norbornene) (PNBSi) with PCOE through the cross-metathesis reaction. It is known that introducing the Me$_3$Si pendant groups is capable of improving gas separation properties of polymers.



The initial homopolymers were synthesized by the ring-opening metathesis polymerization of the corresponding monomers (5-trimethylsilylnorbornene and cis-cyclooctene) in the presence of the first generation Grubbs catalyst $Cl_2(PCy_3)_2Ru{=}CHPh$. Then t**he** cross-metathesis reaction was performed in chloroform at room temperature under the action of the same catalyst. Novel multiblock copolymers were characterized by 1H, 13C, and 29Si NMR spectroscopy, DSC and GPC. Using *in situ* 1H NMR spectroscopy enabled monitoring the conversion of the reaction active centers – Ru-carbene complexes - directly in the course of the cross-metathesis between PNBSi and PCOE. By combining the data of above *in situ* measurements and *ex situ* 13C NMR data on the copolymer dyad structure, it was possible to compare the reactivity of different carbenes and predict the dependence of the copolymer degree of blockiness on the reaction conditions, such as time, PNB/PCOE and polymers/catalyst ratios.

Acknowledgement. This work was supported by the RF President grant for young Russian scientists (MK-7525.2015.3)

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Catalysis of Hydrogen Atom Transfer in KBr Matrix

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The present work introduces a new experimental approach, which allows to reveal the water intermediates and study their transformation in condensed phase at ambient temperature by IR spectra. We have taken the regular technique of spectra registration for solid species in KBr matrix as the ground of our method and have extended it for the gas and liquid compounds.

The sample preparation of potassium bromide matrix was described in our paper [1]. Briefly, on the first stage the KBr powder is saturated by gas under consideration (ammonia or carbon dioxide) during two – three hours in a reactor elaborated for these experiments either together with the water vapour, or by the gas passed through water layer. After trituration the KBr powder, prepared in such a way, is pressed, and the obtained pallet is situated in FTIR spectrometer.

Ammonia-Water System. New bands at 3240 and 1401 cm^{-1}, having the expected for heavy water isotopic shift, were observed. These data indicate on the formation of water intermediate and hydrogen atom transfer from water to ammonia molecule.

Carbon Dioxide-Water System. For this system new bands at 3120, 2925 cm^{-1}, having isotopic shift, as well as the bands at 2140, 2108, 1395 and 1380 cm^{-1} having no isotopic shift for heavy water, were found. These data manifest, on one hand, the formation of water intermediate with carbon dioxide and, on the other one, on the transfer of water hydrogen atom within complex to CO_2 molecule.

Theoretical study. *Ab initio* calculation was carried out in terms of DFT theory. It shows that distances between KBr molecule and fragments of ammonia-water intermediate are considerably longer than the distance between the fragments in the complex. At the same time the calculation predicts the almost barrierless H-transfer from water to NH_3 molecule and big shift of OH-stretching in the presence of KBr. The optimized geometry of ($CO_2/2H_2O$/KBr) system shows that all distances between fragments in a cluster are about the same. The hydrogen atom transfers to another water molecule and then the tri - molecular system ($OH^-/H3O^+/CO_2$) transforms with the arising of (H_2CO_3)-fragment.

Thus in considered cases KBr molecule is not neutral to the components disposed in matrix, but may provide the stabilisation of intermediates as well as catalyse the hydrogen atom transfer between fragments in complexes.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-08-00898

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PP-42

Influence of Electric Field on the Chemical Properties of Nanoparticles

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Our purpose was to experimentally demonstrate the controllability of the adsorption properties of deposited nanoparticles of different chemical composition by providing them with the electric potential of different polarity and value from an external voltage source.

Experiments were performed in the ultrahigh vacuum setup equipped with a scanning tunneling microscope, Auger and mass spectrometer, additional accessories. The residual gas pressure in the setup chamber didn't exceed $P = 2 \times 10^{-10}$ mbar. The Au, Pt and organoboron (OBN) nanoparticles were deposited on HOPG surface using corresponding impregnation techniques. All reactions were studied at 300 or 700 K under 10^{-6} Torr. Due to low amount of nanoparticles their state and results of adsorption were determined by means of scanning tunnelling spectroscopy.

It is shown that the rate of decomposition of ammonia by platinum and organoboron $(C_2B_{10}H_4)_n$ nanoparticles is strongly depended on electric potential. At 300 K for Pt the rate increases by 44% under negative potential – 6 V and by 70% under the positive potential of 6V. A similar effect was found for organoboron nanoparticles. At 700 K the positive potential +6 V on the particles increased decomposition rate by 26%, while the negative potential -6 V reduced it by 37%, compared to the rate of decomposition of ammonia at the ground potential of the particles.

Au nanoparticles show change in their adsorption properties towards molecular hydrogen. At 300 K the hydrogen adsorption on gold nanoparticles is not observed under potentials of $\varphi_1 = +5$V and $\varphi_2 = +1$V, and in case of nonpositive potential ($\varphi_3 = 0$ and $\varphi_4 = -1$) the hydrogen adsorption takes place.

So the controllability of adsorption properties of gold nanoparticles and platinum and catalytic properties of organoboron nanoparticles deposited on HOPG by the electric potential of different polarity and value was experimentally proved. These experiments simulate charge transfer between nanoparticles and supporter in catalytic systems.

Acknowledgement. This work was supported by the Russian Science Foundation, grants 14-03-00156, 15-03-00515, 15-03-02523, 15-33-20831, 16-03-00046.

Modeling of the Electrochemical Impedance in Anodic Dissolution of Iron Using a Heuristic Algoritms

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Impedance techniques are nowdays widely applied for investigating the mechanism and rate of corroding system. Essential electrochemical impedance techniques provide more or less time resolved and surface averaged information on the interface phenomenon. It must be a priory a difficult task to deduce from this kind of experiment an accurate interpretation of localized corrosion. In the present work, we used model with three absorbed species it was possible to explain the iron.

In this paper, we will focus on the relations between the impedance spectra and the reaction mechanism, and interpret the physical meaning of the low frequency inductive and capacitive loops. It was recently found that impedance diagrams reveal at least three time constants concerning the faradaic process in the iron-sulphate systems was proposed by Keddam [1].

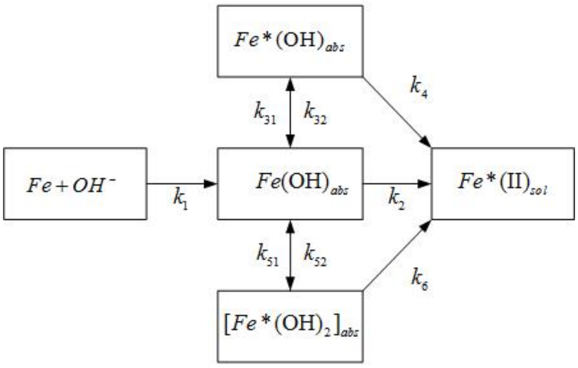

Figure 1 Model of dissolution of iron

The reaction kinetic parameters were calculated by heuristic algorithms such as genetic algorithm, swarm optimization, simulated annealing [2]. In our researches the best results were shown by genetic algorithm. The experimental impedance diagrams showed one high-frequency capacitive are and three time constant at lower frequencies appearing or capacitive loops.

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PP-44

Identification of Corrosion Processes by Morphology of Metal Surface Using Computer Vision

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Many physical-chemical problems connected with the resolving of chemical technologies fundamental issues require considerable calculations. The subject of this paper is identification of corrosion processes using morphology of metal surface researches [1].

A fractal dimension (FD) is a ratio providing a statistical index of complexity comparing how detail in a pattern changes with the scale at which it is measured. FD is one of the most important features of images. Metal surface is scale-invariant as well as in the condition of corrosion process. FD in our experiments estimated by visual (optical microscopy) and electrochemical (impedance electrochemical spectroscopy and hronoamperometriya) methods. The main objective of pilot phase was obtained different images of single sample during the reaction. System is corrosion cracking of stainless steels.

Fig. 1. Entrance data for pipe X70 steel.

This research work is directed on application of methods of computer sight in a problem of studying of corrosion cracking [2] (Fig. 1). The approach offered in work allows to determine by images (Fig. 1) of object of research dependence of structural changes of a crack with chemical and mechanical impact on it (Fig. 2).

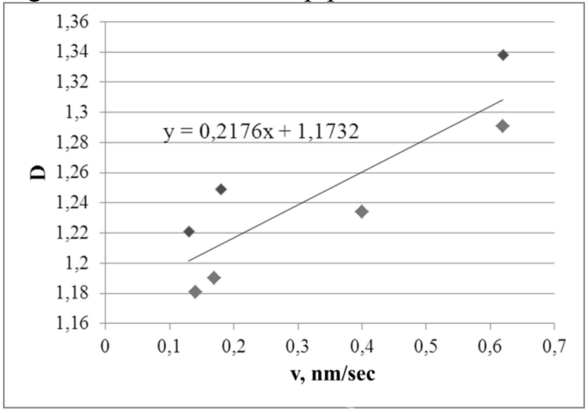

Fig. 2. Interrelation of growth rate of a corrosion crack and its fractal dimension

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-13-12345.

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PP-45

Study of the Mechanism of the Catalytic Reaction of Alcohols with Dimethyl Carbonate

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In last years, methods of "green chemistry" is improved greatly. They reduced the harmful effects of chemical processes on the environment. An important tool of "Green Chemistry" is using non-toxic environmental agents. One of such reagent is dimethyl carbonate (DMC) - an effective substitute toxic methyl halides (MeX, X = I, Br, Cl) and phosgene. Reactivity DMC, so the reaction is conducted in the presence of catalyst [1].

$$ROH + (MeO)_2CO \xrightarrow{Co_2(CO)_8} ROMe + ROCO_2Me + CO_2 + MeOH$$

In this paper, the mechanism of complex chemical reaction is studied by constructing kinetic models, which based on inverse problems of chemical kinetics solutions [2 - 4]. Submitted analysis and comparison of the two mechanisms proposed by the catalytic reaction of alcohols with DMC.

Kinetic models for the possible schemes of chemical transformations at various initial concentrations of the catalyst. Comparative analysis of the activation energies of possible chemical transformation steps allowed determining the flow routes and choosing the adequate mechanism.

Acknowledgement. This work was supported of part by the RFBI, grant 15-07-01764 A.

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PP-46

Catalytic Activity and Charge State of Supported Metal Nanoparticles

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We report on the essential relation between specific catalytic activity of supported metal nanoparticles (NPs) and their charge state determined by particle surface density on a support.

Laser electrodispersion (LED) technique has been used for the preparation of Pd/C and Pt/C catalysts. The key feature of LED is that metal NPs of *fixed size* are formed in laser plasma *prior* to deposition on the support surface. Thus, the particle surface density is preset by the time of deposition and the dependence of catalytic activity vs. particle surface density appears without admixture of common particle size effect. The effect of particle surface density is illustrated by two vapor- and liquid phase processes: chlorobenzene hydrodechlorination (CB HDC) at 150°C on Pd/C and oxygen reduction reaction (ORR) in 0.1 M H_2SO_4 at 20°C on Pt/C. In CB HDC maximum specific activity was found at the lowest Pd load (less than 0.1 ML covering) [1], while in ORR maximum activity was detected at Pt NPs surface density about 0.5 ML.

It would appear reasonable that the observed effects of particle density are related to some sort of particle interaction. For this Coulomb interaction of particle charges is the main candidate. In favour of this proposition, Kelvin probe force microscopy (KPFM) experiments have shown that Pt and Pd NPs are positively charged when positioned on carbon (HOPG) support and a fraction of charged NPs is density dependent. It is adopted that the origin of particle charging is electron transfer between NPs and support, which is caused by the difference of particle and support work functions. To gain a better understanding of particle density effects in catalysis a theoretical model was developed describing the charge state of supported NPs with consideration of inter-particle polarization effects and the presence of strong (~1 V/nm) electric field at the surface of charged NPs. The results of simulations performed on the basis of this model are in good agreement with the results of KPFM experiments. Using this model one can explain, on a common basis, the observed different dependencies of catalytic activity vs. the NPs density. The explanation is given regarding the particle density dependencies of the energy levels of charged NPs and accessibility of field areas by the reacting species. These considerations should be taken into account in optimization of the catalyst structures.

Acknowledgement. This work was supported by the RFBR grant 14-29-04050.

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PP-47

Catalytic Decomposition of Hydroperoxides in the Interface between LDPE Film and ZnO Thin Coating: The Role of Oxygen Vacancies in the ZnO

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At the last MCR conference, we reported that the suppression of photo-initiated oxidation of LDPE film with thin ZnO coating takes place not only because of the UV-screen effect and of the barrier for oxygen permeation, but also due to the dissociative adsorption of hydroperoxides on ZnO surface and their catalytic decomposition [1].

Further investigation showed that this occurs only under the following conditions:

- when the sputtered coatings had the sufficiently high relative content of the crystalline phase, oriented in the normal direction to polymer surface (in accordance to the c-axis of wurtzite-type ZnO) in the few first layers (<7 nm), which are directly adjacent to the polymer, and also when the subsequent growth of ZnO coating occurs mainly in the [0001] crystallographic direction.
- if the above conditions of the ZnO crystal growth have been met, one more factor of influence in the rate of the hydroperoxide accumulation - it is vacancies of oxygen in the ZnO structure reveals oneself. (See Fig. 1.)

The intensity ratio for (002) plane in the few first layers was determined by the following formula: $i(002)=I_{(002)}/(I_{(100)}+I_{(002)}+I_{(101)})$, where I(100), I(002) and I(101) represent the intensities of (100), (002) and (101) x-ray diffraction peaks, respectively [2]. The relative content of oxygen vacancies $RC(V_O)$ in the structure of zinc oxide was evaluated by ratio of optical densities of bands at 505 cm^{-1} (corresponds to the oxygen vacancy defect complex in ZnO [3]) and at 447 cm^{-1} (corresponds to the hexagonal ZnO) in FTIR spectra.

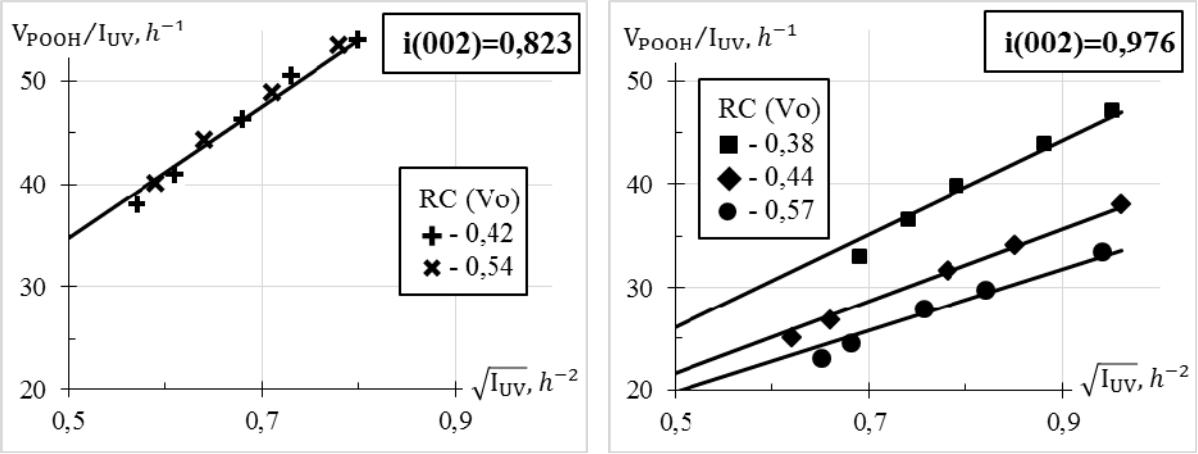

Fig. 1. The ratio of the rate of the hydroperoxides accumulation to the UV radiation relative intensity vs. square root of the UV radiation relative intensity.

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PP-48

Selective Oxidation of Alcohols to Aldehydes over Pt-Sb/C Catalysts

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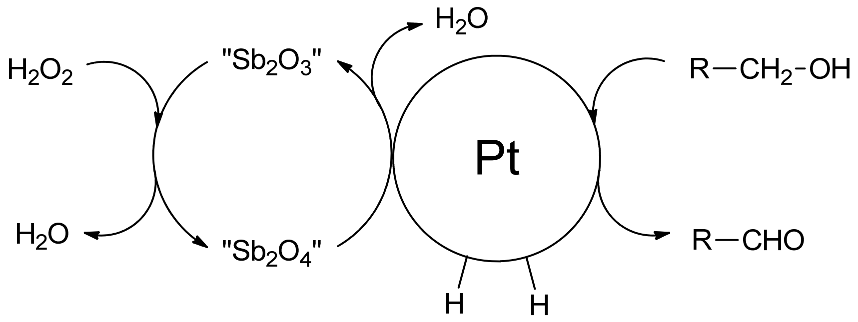
The selective oxidation of alcohols to aldehydes is a reaction of great industrial importance for the manufacturing of organic intermediates and fine chemicals.[1] Although platinum is an effective catalyst for alcohol oxidation when used alone, significant stability and selectivity improvements are observed upon incorporation of bismuth as a second metal compound.[2] The exact role of bismuth has been an unresolved debate for a long time. We recently reported that this reaction greatly benefits from replacing bismuth with antimony.[3]

Pt-Sb and Pt-Bi catalysts supported on activated carbon were prepared by various methods. The materials were characterized by N_2 physisorption, XRD and HRTEM. The samples were tested as catalysts for the selective oxidation of cinnamyl alcohol to cinnamaldehyde, using H_2O_2 as the oxidant. 5%Pt-5%Sb/C largely suppresses over-oxidation to carboxylic acid, and shows selectivities to the aldehyde in excess of 98% in both water and toluene as the reaction medium. In comparison, bismuth catalysts give selectivities of 73-95% (in water) and 84% (in toluene).

On the active catalyst, antimony is present as an oxide (XRD), and our results support an oxidative dehydrogenation mechanism (Scheme 1), similar to that previously proposed for the the oxidation of D-glucopyranose to δ-D-gluconolactone over a Pd-Bi/C catalyst.[2]



Scheme 2. Proposed mechanism for the selective oxidation of cinnamyl alcohol to cinnamaldehyde over a Pt-Sb/C catalyst.

Interestingly, the further conversion of the aldehyde to the acid appears to be a parallel, rather than a consecutive reaction. A refined mechanism will be suggested to account for this.

Acknowledgement. This work was supported by the Nat. Res. Found. of South Africa, grant 63266.

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PP-49

Pt_{24} Subnanoparticle as a Prospective Nanocatalyst for Regioselective Hydrogenation. DFT Study of Its Structural, Thermodynamic and Adsorption Properties

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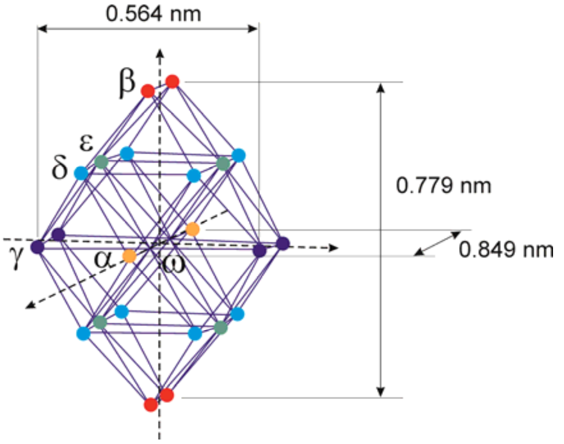
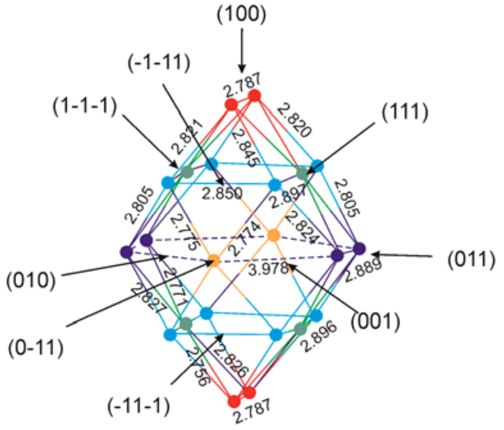
Platinum and platinum based materials are of fundamental importance for modern and developed catalysts, fuel cells, sensors, hydrogen production and storage systems, nanoelectronic devices. The sub-nanosize cluster Pt_{24} was considered as a model of the prospective catalytic system based on supported size-selected Pt nanoparticles (Pt NPs) or Pt NPs which can be synthesized by modern sol-gel methods or within the zeolite pores. Structural, electronic, thermodynamic and spectral properties of the the Pt_{24} cluster as well as its adsorption complexes of molecular and atomic hydrogen on the sub-nanosize Pt_{24} cluster (see Figure below) have been studied using the DFT method (BLYP functional with the 6-31G(p) basis for H and the CRENBS pseudopotential for Pt atoms). The structural, spectral and thermodynamic parameters of Pt_{24} in various spin states (M = 1, 3, 5, 7, 9, 11, 13, 15) were predicted. It was found that the ground state of the cluster is quintet, and the considered structure is more favorable in energy than the Pt_{24} global minimum found earlier [1] with the Sutton-Chen potential. The considered structure is very symmetric (close to D_{2d} symmetry point group) and has only five types of surface atoms (α, β,γ, δ, ε in Figure). On this basis, the full maps of possible adsorption modes, free valences and atomic charges on its surface were obtained and the conclusions were made about the possibility to use this cluster as a base for the prospective nanocatalysts in the reactions of regio- or stereoselective aldehyde hydrogenation and simulation of Pt NPs catalysts.





Acknowledgement. This work was supported by the Russian Foundation for Basic research, grant 14-03-00585.

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PP-50

DFT Study of Pt Catalyzed Hydrogenation: Adsorption, Surface Diffusion, and Subsurface Migration of Molecular and Atomic Hydrogen on the Pt_{24} Subnanoparticle

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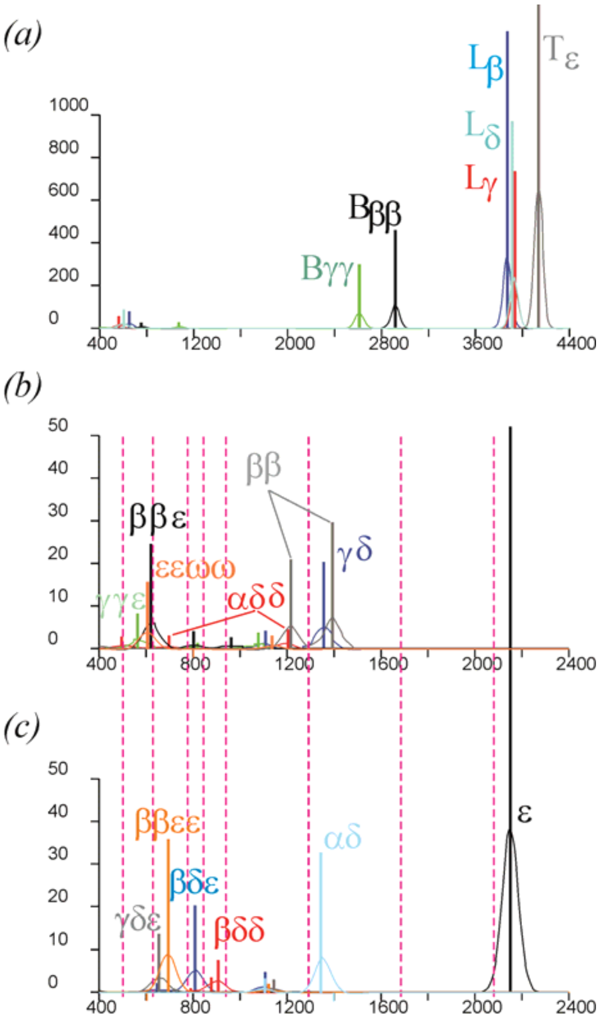
The sub-nanosize cluster Pt_{24} was considered as a model of the prospective catalytic system based on the oxide and carbide supported size-selected Pt nanoparticles (Pt NPs) or Pt NPs for prospective and highly demanding regio- and stereoselective catalysts. Structural, electronic, thermodynamic and spectral properties of the adsorption complexes of molecular and atomic hydrogen on the Pt_{24} cluster have been studied using the DFT method (BLYP functional with the 6-31G(p) basis for H and the CRENBS pseudopotential for Pt atoms) in the quintet (for H_2 complexes) and quartet (for H complexes) spin states. In the case of molecular complexes, only three kinds of adsorption complexes were found – one on top complex T, three two-fold coordinated (lateral) ones L, and two kinds of bridge-like complexes B. The energies of adsorption are varied from 1.4 to 6.7 kcal/mol (bridge-like complexes are more favourable). In the case of adsorption of H atoms, 10 different adsorption complexes were found (marked with Greek letters) with the most stable FCC-coordinated structure (11.4/kcal/mol). The coordination energies are in a good agreement with the available experimental data. The simulated IR and Raman spectra of the adsorption complexes were compared with corresponding data on the Raman and neutron scattering (see Figure where the bars marked with Latin and Greek letters designates the calculated Raman activities of H_2 and H complexes and the dashed lines show the experimental band positions).



Acknowledgement. This work was supported by the Russian Foundation for Basic research, grant 14-03-00585.

Effect of Reaction Conditions on Ethane Oxidative Conversion over MoVTeNbO Catalyst

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Oxidative dehydrogenation of C2-C3 alkanes is an interesting alternative to the current industrial processes (steam cracking or catalytic dehydrogenation) for the olefins production. At present, the most promising results are obtained for transformation of ethane to ethylene [1] due to its lower reactivity as compared to propylene. The goal of the present study is reveal of the reaction condition effects on the performance of MoVTeNbO catalyst in oxidative conversion of ethane.

Oxide catalyst with the ratio Mo:V:Te:Nb = 1:0.3:0.23:0.12 have been prepared according [2] by stepwise thermal decomposition of mixed slurry with formation of the so-called M1 and M2 phases, the first being an active one [3]. Catalytic activity has been carried out at 340-480°C and varied mole ratio $O_2/C_2H_6 = 10.0 \div 0.2$ in flow and flow circulating set-ups with on-line chromatographic analysis.

Formation of reaction products is described by triangular scheme with ethylene and carbon oxides forming by parallel path from ethane and carbon oxides forming by consecutive route from ethylene as well. Under $O_2/C_2H_6 \geq 1$ within 340-460°C temperature was determined does not affect the part of parallel and consecutive routes of reaction products formation, therefore at equal ethane conversion selectivity to ethylene and COx are independent of temperature. When ratio O_2/C_2H_6 decreases up to 0.2 and reaction temperature becomes higher then 470°C catalyst deactivation is observed. Decline in catalytic activity and ethylene selectivity is conditioned by decomposition of M1 and M2 phases owing to partial elimination of Te and Mo and formation of Te-free phases – $Mo_{5-x}(V,Nb)_xO_{14}$ and $(Mo,V)O_2$ possessing insufficient catalytic properties. On the basis of the dependencies of the rates of particular reactions on reaction conditions kinetic model was proposed and kinetic parameters were estimated with the maximal deviation of the calculated and experimental reaction mixture concentrations of no more than 5.3%.

Acknowledgement. This work was supported by the Ministry of Education and Science of the Russian Federation, unique descriptor of application study no. RFMEFI60714X0053.

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PP-52

K_x-CoMoS/Al_2O_3 Catalysts with Low Metal Loadings for Selective Hydrotreating of FCC Gasoline

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The aim of the work was to investigate the effect of decrease of active metals amount on the active phase morphology and catalytic activity and selectivity of KCoMoS/Al_2O_3 catalysts synthesized with the use of heteropolycompounds in hydrotreating of model and real FCC gasoline.

Two series of K-CoMo/Al_2O_3 catalysts (MoO_3 content of 12 wt. % and 9 wt. % and various K/Mo ratios) were synthesized by means of the incipient wetness technique via impregnation of the alumina with the aqueous solutions of precursors with following drying and liquid-phase sulfidation. As the reference group it was used a series of K-CoMo/Al_2O_3 catalysts with the amount of MoO_3 about 18 wt % and the same K/Mo ratios.

Physical-chemical characteristics of the catalysts were analyzed with the use of the following techniques: low-temperature nitrogen adsorption, X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM).

Catalytic activity examination was carried out in a bench-scale flow reactor in hydrotreating of both model and real feed. The model feed contained 1000 ppm of sulphur from thiophene and 36 wt. % of n-hexene-1. The performance of synthesized catalysts was estimated with conversions of sulfur and olefinic compounds and HDS/HYDO selectivity that calculated as a ratio of HDS and HYD rate constants.

It was found that when passing from typical active metal loadings to the low metal loadings the essential dependences of physical-chemical characteristics on the activity and selectivity of synthesized catalysts were preserved. Using potassium favored the growth of average slab length and the sulfidation degree of metals with selective formation of CoMoS active phase. Modifying catalysts with potassium led to the partial poisoning of the active sites what resulted in decrease of both HDS and HYD activities in comparison with the sample without alkali metal. Olefin HYD was more sensitive to potassium than HDS reactions what resulted in the growth of the dependence of selectivity factor on potassium content in the catalysts of all studying series.

Thus it was managed to form the (K)$CoMoS_2$ species with the similar geometrical, promotion and catalytic properties from the fewer active metals than in reference series.

Acknowledgement. This work was supported by The Ministry of education and science of Russian Federation, project No 14.577.21.0152 (Unique identifier of applied scientific researches and experimental developments (project number) is RFMEFI57714X0152).

PP-53

DFT Study on MAO Effect in Alkene Hydrometalation as Stage of Ziegler-Natta Type Catalytic Processes

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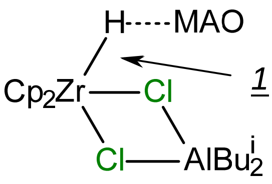
Hypothesis that hydrometalation, controlled by hydride metal complexes, is the one of the key steps in alkene di-, oligo- and polymerization process in Ziegler-Natta type catalytic systems has repeatedly mentioned in the literature [1]. Previously, we have shown that bimetallic Zr,Al-hydride intermediates work as the active centers in alkene hydroalumination, in which intra- and intermolecular exchange, influenced by the steric factor of the η^5-ligand and organoaluminum compound nature, determines the activity of the whole catalytic system [2].
In order to elucidate the role of MAO at the hydrometalation stage we carried out quantum-chemical study of possible ways of propene insertion (reactions *1*-*4*) into the Zr,Al-hydride clusters [2-4], associated with MAO (complexes **1**-**3**), using DFT/PBE/3ζ. The interaction provides corresponding alkyl chloride zirconocene.



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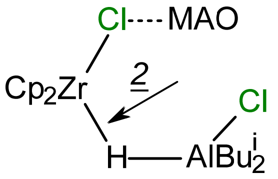

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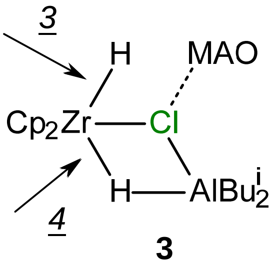

3

Calculations of thermodynamic and activation parameters showed that reactions *3* and *4* are not realized due to high energy barriers (≥56 kcal/mol). Moreover, we were unable to locate the transition state on the PES of reaction *1*. The alkene insertion is possible via reaction *2*, but this way is more energy-consuming than the interaction with known Zr,Al-hydride complexes [2-4].

Acknowledgement. This work was supported by the Russian Foundation of Basic Research, grant 16-33-60203mol_a_dk.

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PP-54

$La_{1-x}Ca_xCoO_3$ Perovskites for Methane Oxidation

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Due to high catalytic activity in oxidative processes at elevated temperatures Ca substituted $LaCoO_3$ perovskites are very promising as materials for oxidation catalysts. Preparation route may play a very important role in their properties due to influence not only on microstructure and defect structure of perovskites but on a phase composition as well because they are key factors of active sites formation. At that final formation of active cites may occur under reaction conditions. Pechini route is a waste less method for preparation of mixed oxides and is of great interest for preparation of supported catalysts especially.

The goal of the paper is preparation of $La_{1-x}Ca_xCoO_3$ perovskite oxide systems via Pechini route and investigation of their physical and chemical properties and catalytic activity in methane oxidation that is very important for design of advanced catalytic system for oxidation processes.

$La_{1-x}Ca_xCoO_3$ perovskites were prepared by Pechini route from appropriate nitrates taken in needed proportions. Samples were calcined at 900 °C during 4 h. Catalytic activity in deep methane oxidation was studied in flow reactor in the range of 250-600 °C. Samples before and after tests were studied with XRD, TEM, TA, TPR, BET.

XRD show the formation of single-phase solid solutions in the range of $0 \leq x \leq 0.4$ although HRTEM revealed presence of simple oxides admixtures as well. At $x>0.4$ the brownmillerite phase is additionally appeared. After catalytic tests in CH_4 oxidation phase composition not change significantly, but HRTEM indicates formation of nanoheterogeneous states on the surface of the perovskite particles. So $LaCoO_3$ is characterized by formation of cluster of orthorhombic structure in rhombohedral perovskite matrix. In the samples with $x = 0.2$ and $x= 0.4$ formation of planar defects in the direction of the crystallographic planes (101) was revealed. As a result in $La_{0.6}Ca_{0.4}CoO_3$ perovskite particles the alternating layers of the perovskite and brownmillerite structure are formed.

Catalytic activity in methane oxidation nonmonotonic depends on the samples composition. Ca adding up to $x=0.3$ leads to increase and then at $x \geq 0.4$ to decrease the activity. Probably that formation of vacancy ordered structures with substitution degree during preparation or under reaction medium leads to decrease activity. Obtained activity row versus x: $0.2=0.3>0.4=0.6>0>0.8=1$ differ from prepared via ceramic route samples in which the highest activity possess the sample with $x=0$. The reasons are discussed in terms of samples microstructure and reducibility.

Acknowledgement. This work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (project V.44.2.5).

The Role of Cs Promoters on N_2O Decomposition over Ni-Co-Spinel Catalyst

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Nitrous oxide is a contributor to the destruction of ozone in the stratosphere and a strong greenhouse gas. A reduction of N_2O emission from industrial sources is indispensable. Cobalt based spinels $M_xCo_{3-x}O_4$ (M = Mg, Ni, Zn, Cu) were found to be highly active catalysts for N_2O decomposition from tail gases in HNO_3 production [1].

The mechanism of the reaction proposes N_2O dissociative adsorption on the active centre (oxygen vacancies or metal centers) whereby N_2 is desorbed while an adsorbed oxygen species stays at the surface of the catalyst. Desorption of adsorbed O species can occur via a Langmuir–Hinshelwood or a Eley–Rideal mechanism being the rate-determining step of the N_2O decomposition reaction. The addition of alkali metal dopants was found to increase the catalyst activity in the reaction. It was proposed that the alkali metal itself could act as an active site and due to its low ionization potential form bonds with surface oxygen [2]. From the other point of view, the doping increases the electron density of Co and weakens the Co–O bond, which facilitates the desorption of oxygen [3].

In this work we studied the effect of Cs addition (1-6%) and preparation conditions (impregnation or polymerizable complex method) on the activity of $Ni_{0.74}Co_{2.26}O_4$ catalyst in N_2O decomposition reaction at 200-300 ^oC under ideal (1500 ppm N_2O + He) and real (1500 ppm N_2O, 55 ppm NO, 700 ppm NH_3, 2.5% O_2, 3% H_2O in He) conditions. Prepared catalysts were studied with XRD, XPS, BET, TPR and TPD-O_2 methods to clarify the influence of the catalyst composition on the catalyst activity and oxygen vacancies content to elucidate the nature of active sites.

It was found that the Cs-modified catalyst exhibited higher activity for N_2O decomposition as compared with undoped Ni-Co-spinel. TPR and TPD measurements indicate that the presence of Cs facilitates the reduction of Co^{3+} and Co^{2+} and O_2 desorption from the catalyst surface. The increase of Cs cations dispersion on the catalysts surface due to varying of preparation conditions results in additional increase of catalytic activity. The catalysts with cesium content in the range of 2-2.5% demonstrates 100% N_2O conversion at 300 ^oC even under real testing conditions. However a partial catalyst deactivation in the presence of ammonia was revealed during testing.

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PP-56

Theoretical and Experimental Aspects of Zirconocene-catalyzed α-Olefin Dimerization and Oligomerization

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Zirconocene-catalyzed selective dimerization of α-olefins in the presence of a *minor* excess of methylaluminoxane (MAO) is traditionally considered as a specific case of coordination polymerization. In accordance with the Bergman concept [1, 2], the reaction mechanism involves zirconocene-hydride catalytic species and includes two stages of α-olefin coordination insertion and β-hydride transfer to Zr atom.

It has been experimentally proven [1, 2] that a Cl atom must be present at the catalytic center of the selective dimerization. Combining these consideration with the presumed nature of the catalytic species, a zirconium-aluminium hydride complexes, we were able to create an effective experimental method for α-olefin dimerization. This method includes a two-stage activation of zirconocene dichloride by triisobutylaluminium (TIBA) and MAO. Using this method, we performed a comparative study of catalytic activity for a series of 30 bridged and/or substituted zirconocenes and determined the formula of the most productive and selective dimerization catalyst.

Various concepts of the selective dimerization mechanism have been discussed. A DFT calculations for zirconocenes of various structural types allowed to make the conclusion that plausible mechanisms involves cationic or cation-likezirconium-aluminium hydride-chloride complexes. The results of DFT calculations correlate with the catalytic experimental data.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 15-13-00053.

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Oxidation of Propane over Pd(111): *In Situ* XPS and Mass Spectrometry Study

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The catalytic oxidation of propane over a Pd(111) single crystal were examined in the temperature range between 300 and 700 K using *in situ* X-ray photoelectron spectroscopy (XPS) and temperature-programmed reaction spectroscopy (TPRS). The experiments were performed at the synchrotron facility BESSY II, Berlin, using the ISISS beamline equipped with an on-line quadrupole mass spectrometer Prizma QMS-200 [1]. The experiments were carried out in a flow regime at 0.5 mbar.

In accordance with the TPRS experiments, both in excess and in deficiency of oxygen H_2, CO, H_2O, and CO_2 were detected as the products in the gas phase. Propylene, acetone, acetaldehyde, and acetic acid were not observed. TPR spectra for the molar ratios $C_3H_8:O_2 = 1:5$ and 1:25 showed that the reaction starts at approximately 650-700 K, the main product is CO. In the excess of oxygen the conversion of propane is lower, and the partial oxidation of H_2 to H_2O takes place. The *in situ* XPS spectra indicated that the surface palladium oxide forms under reaction conditions. The mechanism for the catalytic oxidation of propane over palladium is discussed.

Acknowledgement. The authors thank A.Yu. Kluyshin and M. Hävecker for their assistance in carrying out the XPS experiments.

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PP-58

XPS and STM Study of Model Au/C and Pt/C Samples Oxidation by Nitrogen Dioxide

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Gold and platinum catalysts demonstrate high activity in number of oxidation processes. In this work we study the samples prepared by vacuum deposition of the gold or platinum onto the surface of highly oriented pyrolytic graphite (HOPG) in the extreme oxidative treatment. All the work on the preparation and oxidation of samples were conducted on X-ray photoelectron spectrometer SPECS. The STM images were obtained on high vacuum scanning tunneling microscopes (RHK Technology and GPI-300.02, Russia). We used nitrogen dioxide as effective oxidant in this study. The samples were treated with nitrogen dioxide in the preparation chamber of the XPS spectrometer using an NO2 original vacuum source, whose operating principle is based on the thermal lead nitrate decomposition. Experimental details and main results are described in our reports [1, 2].

Pt/HOPG. A mixture of nitrogen oxides, NO_x, with a prevailing contribution of nitric oxide, NO, is the main noxious component in the exhaust gas of modern internal-combustion engines operating under the lean conditions. The key stage of catalytic neutralization of nitrogen oxides by NO_x storage-reduction (NSR) systems is oxidation of NO to NO_2 on platinum particles. It is supposed that a possible reason of deactivation of high-dispersed NSR catalysts could be oxidation of platinum particles by nitrogen dioxide; the oxidation rate being dependent on the size of the particles. In this work we study two samples with average Pt particle size, D, is equal to 2.5 and 5.5 nm. It was found that there was a size effect in the room temperature reaction of Pt/HOPG samples with NO_2. Indeed, based on changes observed in the Pt 4f region, small platinum particles of $D \approx 2.5$ nm in size were readily oxidized to produce particles of Pt(II) and Pt(IV) oxides. In contrast, relatively big Pt particles of $D \approx 5.5$ nm retained the metallic state in these conditions. Our results can explain cause of the size effect in Pt_based catalytic systems neutralizing harmful exhaust from automobile engines operating under lean fuel conditions.

Au/HOPG. Gold catalysts exhibit high activity in a number of oxidative processes. Nevertheless, it is believed that gold cannot adsorb an oxidant from the gas phase without its specific activation (atomization, microwave discharge, etc.). As a result, the mechanism of action of gold catalysts is currently the subject of debate. We studied Au/HOPG samples consist of 3D particles and individual atoms on graphite surface. The 3D gold particles are resistant to oxidation with nitrogen dioxide at a pressure $3 \cdot 10^{-5}$ torr. The isolated atoms of gold under these conditions are oxidized to form the state Au(III) stabilized on the surface of graphite. The stabilized gold atoms may act as active sites of gold catalysts.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-23-00146.

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X-ray-induced Reduction of $H_2Pt(OH)_6$ and K_2PtCl_6 Studied by XPS

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Pt(IV) compounds are used usually as precursors for preparation of different supported platinum-based catalysts. X-ray Photoelectron Spectroscopy (XPS) is the most effective method for determination of Pt state in these systems. It is known that X-ray radiation is able to reduce some Pt group metals compounds in vacuum conditions. If this occurs, it is likely to make mistake conclusion in the interpretation of XPS data concerning Pt contained catalysts. In this work we studied the effect of X-ray radiation on reduction of powder samples $H_2Pt(OH)_6$ and K_2PtCl_6 under XP spectra registration. The investigation of the Pt state in the samples were carried out in SPECS photoelectron spectrometer at the residual pressure of 5×10^{-9} Torr in the analyzer chamber. For each sample, spectra were recorded using non-monochromatic Mg Kα radiation ($h\nu$ = 1253.6 eV) and 200 W power at X-ray tube. According to the changes occurred in the Pt 4f region, platinum (IV) was reduced in all the samples studied. For the case of K_2PtCl_6, Pt(II) was the only state formed at all steps of reduction; the binding energy (BE) of Pt $4f_{7/2}$ line being equal to those for K_2PtCl_4. For the case of $H_2Pt(OH)_6$, PtO was formed at the initial step of X-ray treatment as result of simultaneous reduction and dehydration processes. PtO_2 was additionally formed at the final step. Possible mechanisms of X-ray induced reduction of the studied compounds are discussed. Our results can be used for interpretation of XPS data obtained on supported catalysts that contains platinum.

Acknowledgement. This work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (project V.44.1.15).

CO Oxidation on $Ce_xZr_{(1-x)}O_2$ and $CuO/Ce_xZr_{(1-x)}O_2$ Catalysts Prepared Using CTAB and Sawdust as a Template

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Ceria is an attractive component of three-way catalysts (TWCs) because of its unique redox and oxygen storage properties. The addition of ZrO_2 to ceria to form a mixed oxide provides both the thermal resistance of the catalyst and the deformation of the crystal lattice, which improves oxygen storage capacity and redox properties [1]. Oxygen mobility is a very important factor in CO oxidation on metal oxide catalysts which proceeds via Mars-van Krevelen mechanism. It involves CO oxidation by oxygen atoms from the surface of oxide crystal lattice and subsequent reoxidation of the surface by O_2 from the reaction mixture.

In this work the catalytic activity of Ce/Zr systems prepared by two different template methods was investigated in CO oxidation. Organic surfactant (cetyltrimethylammonium bromide, CTAB) and pine sawdust (SD) were used as a template.

The increase of Ce:Zr ratio in biomorphic samples from 1 to 4 led to a significant increase of CO conversion at low temperature. $Ce_{0.8}Zr_{0.2}O_2$ (SD) provided 25% CO conversion at 100°C, while $Ce_{0.5}Zr_{0.5}O_2$ (SD) was inactive up to 200°C. $Ce_{0.8}Zr_{0.2}O_2$ (CTAB) exhibited lower activity than $Ce_{0.8}Zr_{0.2}O_2$ (SD) at 100–300°C in spite of its relatively high S_{BET} (75 vs 35 m^2/g). Such discrepancy can be caused by the difference in oxygen mobility and the presence of Ca in biomorphic samples. According to Raman spectroscopy data oxygen mobility in $Ce_{0.8}Zr_{0.2}O_2$ (SD) is higher in comparison with CTAB analogue. The presence of Ca and K in the biomorphic samples was found by SEM-EDX. The addition of small amount of CaO to CeO_2 or Ce/Zr binary oxides is known to facilitate the formation of oxygen vacancies [2–3]. Calcium ions are coordinated with cations of cerium, which provides the transfer of electrons to oxygen, contributing to the reduction of Ce^{4+} to Ce^{3+}. Furthermore, the addition of Ca promotes the activation and dissociation of oxygen molecules.

Modification of CTAB-templated $Ce_{0.8}Zr_{0.2}O_2$ with CuO led to a significant decrease of CO oxidation temperature, in contrast with the biomorphic sample. In the latter case significant increase of catalytic activity was achieved by decreasing the calcination temperature from 600 to 500°C. As a result the highest and similar values of CO conversion at 150–350°C were found on $CuO/Ce_{0.8}Zr_{0.2}O_2$ (CTAB) and $CuO/Ce_{0.8}Zr_{0.2}O_2$ (SD) calcined at 500°C.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 13-03-00613.

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Influence of Potassium on the Activation Process of Silica-Supported Iron Catalysts for Fischer–Tropsch Synthesis in Carbon Monoxide and Syngas

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Fischer–Tropsch synthesis (FTS) is the more preferable method for producing liquid fuel and other chemicals from renewable sources [1]. Fe-containing catalysts currently represent special interest for several reasons. Most of the experimental evidence obtained so far has indicated that iron carbides of different composition could constitute the active phase for FTS. It was also found that activity and selectivity of iron catalysts strongly depend on the conditions of catalyst activation [2]. However, a very little information is available in the literature about the kinetics of activation and carbidization of supported iron oxide catalysts with carbon monoxide or syngas.

In present work influence of potassium on the mechanism of activation of silica-supported iron catalysts for Fischer–Tropsch synthesis was investigated in syngas or carbon monoxide under transient and isothermal conditions using the *in situ* magnetic method.

The catalyst activation proceeds in two steps and involves reduction of hematite into magnetite and magnetite carbidization into Hägg carbide. Effect of potassium on mechanistic aspects of activation was connected with formation of potassium ferrate $KFeO_x$ and lattice defects which formed due to incorporation of potassium ion.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research (Grant №16-03-00215a).

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PP-62

Autothermal Reforming of Ethanol over Ni Catalysts Supported on Ceria-based Mixed Oxides

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Autothermal reforming of bio-ethanol (ATR of C_2H_5OH) is a promising process for hydrogen production from renewable sources. This reaction is characterized by advantageous thermal balance, high yield of H_2 and stability against coke formation. The mono-functional or bi-functional mechanism of catalytic reaction can be realized depending on the nature of the metal and the support selected [1]. The support can take part in the intermediate steps of C_2H_5OH conversion, as well as it can regulate the crystal size, reducibility and electron structure of active metal species. So the control of the reaction pathways through the tuning of support properties is quite a challenging issue [2].

In this work, the ATR of C_2H_5OH reaction has been comparatively studied over Ni catalysts supported on $Ce_{1-x}M_xO_y$ mixed oxides. The effect of $Ce_{1-x}M_xO_y$ preparation mode (Pechini method, sol-gel route using a template Pluronic F127), type (M = Gd, La, Mg) and molar fraction (x = 0-0.5) of a doping cation on the characteristics of Ni catalysts and their activity in the ATR of C_2H_5OH was studied. The composition-dependent changes of catalyst properties were analyzed by means of N_2 adsorption, XRD, XPS, TEM, H_2-TPR and thermal analysis.

The results indicate that the Ni particle size decreases i) with a decrease of crystallite size of $Ce_{1-x}M_xO_y$ support, ii) an increase of M/Ce molar ratio and iii) in the following sequence of the doping cations Mg<Gd<La. The stability of Ni active component against sintering is promoted at doping of the ceria-based support by La or Mg. It is established that reducibility of Ni cations is strongly modified by support composition. The particularities of ATR of C_2H_5OH reaction over Ni/$Ce_{1-x}M_xO_y$ are revealed and correlated with the type of the doping cation; and structural and redox properties of the catalysts.

Acknowledgement. The authors gratefully acknowledge financial support from DST and RFBR under joint project "Principles of formation of the nanostructured oxide materials and nanodimensional catalysts on their basis for hydrogen power engineering" (DST# INT/RUS/RFBR/P-189 and RFBR # 15-53-45039). The authors are thankful to Dr. V.A. Ushakov, Dr. O.A. Stonkus, T.Ya. Efimenko and G.S. Litvak for their help with catalyst characterization.

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Quantum-chemical Modeling of the Active Center of MnNaW/SiO_2 Catalyst for Oxidative Coupling of Methane

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The production of ethylene through the oxidative coupling of methane (OCM) over MnNaW/SiO_2 catalyst is an attractive direct way of natural gas utilization into value added products [1]. It was shown that high activity of MnNaW/SiO_2 catalysts was caused by the presence of all three elements -W, Mn and Na, but the composition and structure of active centers are still matters of debates. Due to the nature of the molecular orbitals it was suggested that tetrahedral WO_4 species with single bridging oxygen may be active sites for methane activation [2]. In the present work, quantum-chemical modeling of the active center of MnNaW/SiO_2 catalyst for OCM has been performed at the B3LYP level using the LANL2TZ(F) and 6-311G** basis sets for tungsten and lighter atoms, respectively.

To get an insight into the origin of the strong synergetic effect for MnNaW/SiO_2 catalyst, mononuclear as well as polynuclear centers were comparatively considered. Stable Mn^{+5} and Mn^{+3} species were predicted, coupled to support by three bridging oxygens in the neighborhood of the W^{+6} complex, that are consistent with the two metal site model of active centers.

On the proposed model active centers, the cleavage of the first C-H bond in methane was considered. The barriers of the hydrogen abstraction at terminal "yl"-oxo centers provided by the W^{+4} and W^{+6} species on α-cristobalite appear to be as high as 40-70 kcal/mol, the fact which is to be likely explained by the closed-shell character of this center. In contrast to tungsten case, the barrier of the C-H activation at the terminal oxo-ligand of Mn^{+5} (in the complex having spin $S=1$) drops down to about 5 kcal/mol. Such a high reactivity is connected with a distinct radical oxyl character of the terminal oxo-ligand of Mn^{+5} cation.

The computational results confirm the important role of surface radical oxo-centers in methane activation and predict that Mn species are responsible for hydrogen abstraction from methane while the W species (i) stabilize the isolated Mn center; (ii) trap the intermediate methyl species (which are not coupled by the surface of cristobalite) in the form of the methoxy ligand. The latter finding in fact indicates the next steps toward oxidative dimerization of methane via the coupling of the second methyl group by methoxy ligand. On the whole, the W species impede the route of deep oxidation.

Acknowledgement. This work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (projects V.45.1.10 and V.44.2.2).

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PP-64

Interpretation of Electronic Promotion of Iron-Oxide Catalysts by the Alkali Oxide Metals M_2O (M = K, Rb, Cs)

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The results of determining a catalytic activity of the $M_2O - mFe_3O_{4-\delta}$ (M = K, Rb, Cs) contacts, obtained for reaction of steam reforming CO on a flow reactor with a fixed bed of catalyst, are presented together with the mass spectrometric measurements of the vapor pressure of alkali metal atoms M of systems studied (see Fig. 1). In accordance with an electron theory catalysis, the decrease E_{act} depending on the nature of the metal M can be explained by lowering of the electron work function (rising Fermi energy level) when the promoter concentration increases and by increasing polarization effects of the atom M in the transition from potassium to cesium which leads to weakening the Fe—O covalent bonds formed by locally ionized M^+ center. In conformity with the proposed N.V. Kulkova and M.I. Temkin mechanism of conversion of CO with water vapor (Fig. 2), the formation of V_{23} vacancies on the surface of the crystal in an oxygen position O_{23}, allows explain the significant reduction E_{act} by weakening of bonding energy O_{23} with the main atom Fe_2^+, performing the role of catalytic center. In turn, a such interpretation allows us to formulate a common approach to the selection of electronic promoters, the essence of which is as follows: decrease E_{act} of catalytic act of redox reaction is achieved by increasing the energy of the interaction of structural electron acceptor (anion sublattice element) with an electron donor (atom M), which leads to a lowering the transition energy of the valence electron of an active atom Fe_2^+ on the free-2p orbital of the acceptor of CO and formation of a bond with oxygen.

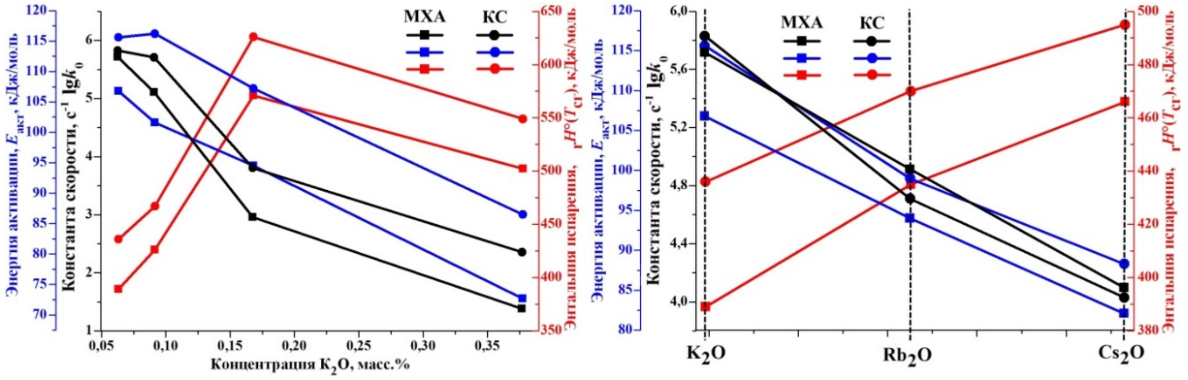

Fig. 1. Correlation between kinetic properties ($E_{акт}$ и k_0) of catalyst and $\Delta_rH°(T)$ of alkaline metals M from kinetically active system $M_2O - mFe_3O_{4-\delta}$

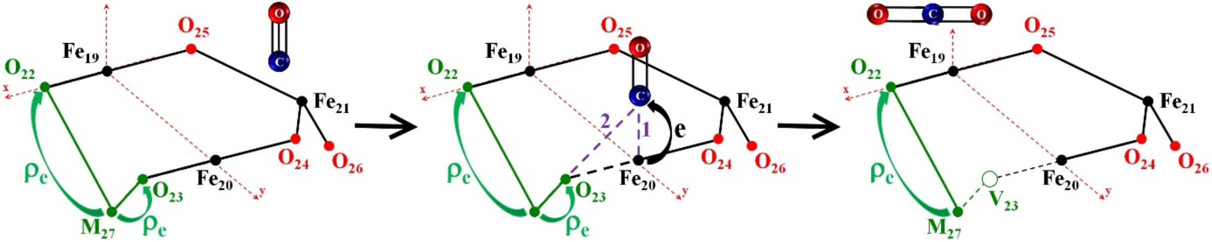

Fig. 2. Scheme of electronic promotion of atom Fe^{2+} in active center composition

This work was supported by the Russian Foundation for Basic Research (Project №14-03-31545) and the Ministry of Education and Science of the Russian Federation (in framework of Government order, project №4.1385.2014/K).

PP-65

Hydrodechlorination of Chlorobenzene on PdCo/C Catalyst Produced by Pyrolysis of Sawdust Impregnated with a Solution of $Pd(NO_3)_2$ and $Co(NO_3)_2$

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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. Pd/C catalysts are very effective in this process.

In [1] a new shortened method including the pyrolysis of sawdust impregnated with $Pd(NO_3)_2$ solution was suggested, and two catalysts were prepared in different pyrolysis conditions. Both of them demonstrated high efficiency in gas-phase chlorobenzene (CB) HDC. Both samples comprise only Pd^0 nanoparticles, some of them are covered with carbon. To increase activity in HDC it was proposed to add Co to Pd/C, because alloy formation could prevent carbidization of metal surface and decrease carbon shell formation. In this work PdCo/C catalysts was prepared by similar method, tested in CB HDC and compared with monometallic Pd/C and Co/C catalysts.

According to TEM data 1Pd/C comprises both carbon coated and naked Pd particles; in bimetallic catalysts the share of Pd particles without carbon shell is greater in comparison with 1Pd/C. According to XPS only Pd^0 was found both in Pd/C and bimetallic samples, but Co-containing catalysts comprise only oxidized Co. No PdCo alloys were found. TEM and XPS data confirm that 2Co/C contains only CoO. It seems that reducing gases (H_2, CO) and carbon formed during pyrolysis effectively reduce palladium but not cobalt.

Catalysts were tested in HDC of CB in a fixed bed continuous flow reactor for 18-20 h. All catalysts were active in CB transformation to benzene (90-95% at 150-200ºC). Conversion of CB at low temperatures (150-200ºC) is higher on Co-containing catalysts than on 1Pd/C possibly due to partial decoration of Pd with carbon. Partial oxidation of Pd during HDC found by XPS was twice lower for 1Pd1Co/C (11%) than for other samples (more than 20%). Good performance of 2Co/C catalyst that comprises only cobalt oxides needs further investigation.

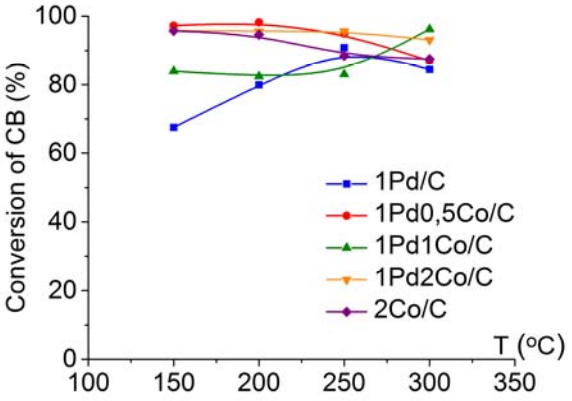

Fig. 1. Conversion of CB vs temperature in the presence PdCo/C catalysts, 2Co/C and 1Pd/C

Acknowledgement. This work was maintained by Russian Science Foundation (14-33-00018).

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PP-66

Transition Metal Sulfide Catalysts for Synthesis Gas Conversion into Alcohols and Other Oxygenates

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Studying the mechanism of syngas conversion on the sulphidized KCoMo catalysts, we obtained the general regularities governing the action of the AC of transition metal sulphides in the hydrogenolysis of sulphur containing organic compounds and syngas conversion. The role of Co is the activation of a CO molecule. It was shown that with the temperature rise the hydrogenolysis of the C-O bond and hydrogenation of alkyl fragment to hydrocarbon becomes more favorable than formation of alcohols. Potassium stabilizes the C-O bond, favouring alcohol formation.

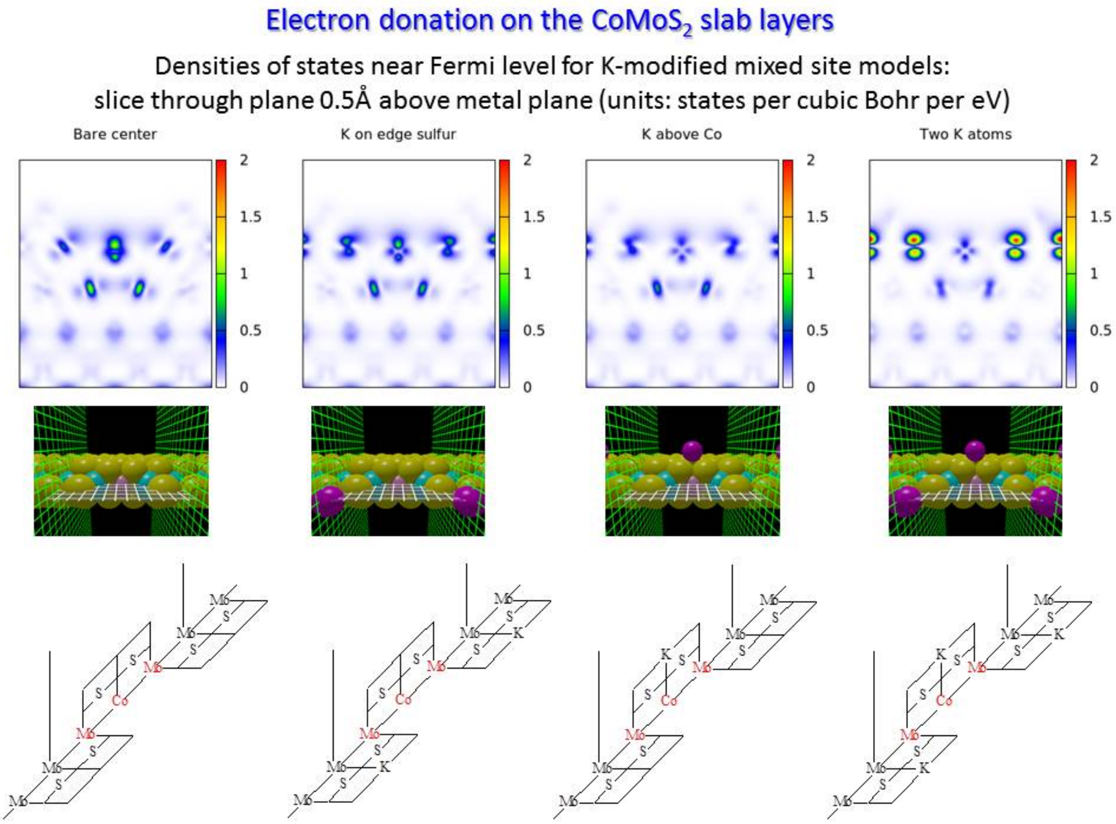

Fig.1. Graphical results of DFT calculations of the Mo and Co atoms *d*-electron densities depending on K atoms amount (1 or 2) and position in KMoCoS supercell (upper row – *d*-electron densities near Fermi level, middle and bottom rows – ball and structural models of the supercells respectively).

DFT calculations support this statement, because as it has been shown, that presence of potassium leads to decrease in Lewis acidity, promoting oxygenate desorption, lowering C-O bond polarization and inhibiting its cleavage. Increased electronic population on Co d-orbitals favors back-donation and stabilizes oxidative addition products.

Selective CO Methanation in the Presence of CO_2 over Nickel-Ceria Catalysts: from Mechanistic Studies to Catalyst Design

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There is an increasing interest to the process of selective CO methanation in H_2-rich gas mixtures in the presence of CO_2, as a fundamental problem of substrate-selective hydrogenation and as a promising way for deep CO removal in H_2-rich streams. 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. This work reports our new results on mechanistic study of the influence of chlorine additives on the CO and CO_2 methanation reactions kinetics over Ni/CeO_2 catalysts.

The properties of catalysts prepared by nitrate (Ni/CeO_2) and chloride (Ni(Cl)/CeO_2) precursors were compared. Catalysts were studied by BET, XRD, TEM, EDX, XPS, FTIR and CO chemisorption techniques. It was shown, that Ni/CeO_2 is active in both CO and CO_2 methanation, exhibiting low selectivity. In contrast to Ni/CeO_2, Ni(Cl)/CeO_2 is active in CO and inactive in CO_2 methanation at T < 300 °C, providing highly selective operation.

The kinetic and FTIR in situ study showed that for both Ni/CeO_2 and Ni(Cl)/CeO_2 catalysts the CO methanation reaction proceeds similarly over the Ni surface via CO and H_2 chemisorption. The CO_2 methanation kinetics was different for Ni/CeO_2 and Ni(Cl)/CeO_2 catalysts. Also the big differences were found in the nature of surface species during CO_2 methanation (Fig. 1): ceria carbonate and formate species take part in CO_2 methanation over Ni/CeO_2. However, chlorine addition dramatically inhibits the formation of such species due to ceria surface blockage. Thus it could be concluded, that for Ni/CeO_2 CO_2 methanation reaction proceeds via CO_2 adsorption over ceria surface and stepwise hydrogenation to hydrocarbonates and formates by the hydrogen spilled over from Ni. While for Ni(Cl)/CeO_2 this reaction pathway is locked by chlorine, providing inactivity in CO_2 methanation and therefore high efficiency in selective CO methanation. If so, for highly efficient selective CO methanation catalyst, high Ni dispersion over chlorine-containing ceria support should be reached. And it has been successfully done by optimizing the preparation procedure.

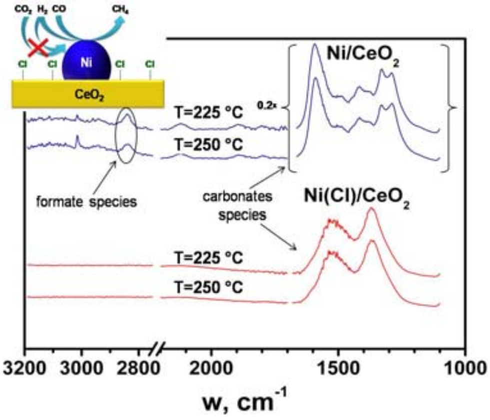

Fig. 1. FTIR spectra for CO_2 methanation over Ni/CeO_2 and Ni(Cl)/CeO_2 catalysts.

Acknowledgement. The work was supported by Grant 14-03-00457a and project V.44.2.9.

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PP-68

Understanding the Key Intermediate of Aromatic Nitration Mechanism Catalyzed by Lewis Acids

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The aromatics nitration in industry is carried out in liquid phase with mixture containing nitric and sulphuric acids. A sulphuric acid has two functions: it acts as homogeneous nitration catalyst and as a dehydrating agent. A major problem for this technology is diluting of the acids mixture by water formed as one of the reaction products (0.9 ton acid wastes per 1 ton of commercial product). Therefore, lots of efforts had been directed to seek environmentally friendly and reusable alternatives in recent years using acid catalysts.

We have prepared two kinds of the catalytic systems for the aromatic nitration. MX_n (homogeneous Lewis acids) [1] and MX_n deposited on the carbon nanofibers or silica support (heterogeneous Lewis acids) (M=Bi, Sc, Tm, Y, Yb; X= triflate (OTf); $C_8F_{17}SO_3$ (OPf) or sulphated perfluoropolymer (Nafion) anions, subsequently). For all studied catalytic systems HRTEM, XRD, XPS, FTIR, NH_3-TPD, base titration (for acidity measurements) and low-temperature nitrogen adsorption (for texture properties)) methods were applied for the materials characterization. Their performance was tested in the gas-phase and liquid-phase catalytic aromatic nitration (benzene, toluene and o-xylene nitration reactions) [2]. The highest catalyst productivity (3.5-4.1 $g_{NB}/(g_{cat}*h)$) were achieved over ytterbium systems ($Yb(OTf)_3$, $Yb(OPf)_3/SiO_2$). The best catalyst exhibits 99.9% selectivity to nitroproduct with concentration of by-products (mainly nitrophenols) less than 300 ppm. The use of supported lanthanide perfluorooctanoic acid salts is the first attempt for these systems as a heterogeneous nitration of aromatic compounds catalysts.

The mechanism of triflate (perfluorooctanoic sulphate) salts catalytic action was studied in detail using DFT calculations. It is shown that nitric acid binds to the metal ions via displacement of water from its inner co-ordination sphere ($H^+[MX_nNO_3]^-$). Coordination of the nitrate ion to metal cation promotes nitric acid dissociation, which in turn increases the equilibrium concentration of the nitrating agent: NO_2^+. A possibility of the nitronium cation to form an ionic pair with triphlate is considered to have an impact for transportation of NO_2^+ to the organic phase.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 16-29-10740.

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Mechanistic Insights in Aldol Condensation of n-Butanal over ZrBEA Catalyst

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Aldol condensation of n-butanal leads to 2-ethylhexenal, which is further hydrogenated with formation of 2-ethylhexanol, one of the most important industrial plasticizer, solvent and perspective diesel additive.[1] Aqueous alkali is typically used as catalyst for aldol condensation of butanal in industry. This leads to large quantities of by-products, corrosion of the equipment and the necessity of additional purification of 2-ethylhexenal. Although basic catalysts are the most frequently used catalysts for aldol condensation. It has been demonstrated this process can be also performed on Lewis acids.[2] Recently, Zr-containing zeolites was shown to be efficient catalysts of aldol condensation.[3] These material possess unique Lewis acidic properties associated with partially hydrolyzed «open» $Zr(OH)(OSi)_3$ and fully condensed «closed» $Zr(OSi)_4$ Lewis acid sites isolated in siliceous framework.[3]

The purpose of this study was to elucidate the mechanism of the aldol condensation of butanal over ZrBEA catalysts. The reaction was studied both in integral and differential regimes. *In situ* FTIR spectroscopy was applied in order to establish the main forms of surface species under operating conditions. Pyridine, 2,6-ditertbutyl-pyridine and CO_2 were used as probe molecules for *in situ* specific poisoning experiments for investigation of reactivity of «open» and «closed» sites of ZrBEA.

The analysis of reaction network pointed that the main reaction pathway involves aldol condensation with formation of 2-ethylhexenal, the side reactions involved Cannizzaro disproportionation of butanal leading to butyl butyrate and 4-heptanone, butanol and butyric acid formation via ether hydrolysis. Kinetic data suggested that butanal condensation obeys monomolecular Langmuir-Hinshelwood mechanism with butanal enolization as rate-limiting step. The *in situ* studies showed that enolic form of butanal is the most abundant on the catalyst surface. The experiments on active sites poisoning showed that pyridine deactivates all Lewis acid sites unselectively, while 2,6-ditertbutyl-pyridine selectively poisons «open» sites. Impact of «open» sites on overall activity was found to be approx. 70% form total reaction rate. Besides that, open sites were shown to interact with CO_2 used as acidic poison.

In conclusion, the results reveal that a both acidic and basic poison prevents enolization. To account for this observation, the bifunctional acid-base mechanism is proposed.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-23-00094.

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PP-70

Mechanistic Studies of Heterogeneous Reaction and NMR Imaging of Catalytic Hydrogenation by Using Parahydrogen

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For a long time the observation of parahydrogen-induced polarization (PHIP) effects in hydrogenation reactions was considered to be a signature of the "homogeneous" mechanism of hydrogenation with H_2. Indeed, observation of PHIP imposes the requirement of the pairwise addition of H_2 to a substrate by a catalyst, which can be achieved in homogeneous hydrogenations with dissolved transition metal complexes but may be incompatible with the classical heterogeneous hydrogenation mechanisms. But it was shown that is also possible to observed PHIP over supported metal catalysts.[1] After these results several supported metal catalysts were synthesized, characterized and tested in heterogeneous hydrogenation of propene with parahydrogen to maximize nuclear spin hyperpolarization of propane gas. 3D ^1H magnetic resonance imaging (MRI) of 1% hyperpolarized flowing gas with micro-scale spatial resolution ($625\times625\times625$ μm^3) was demonstrated using pre-clinical 4.7 T scanner and 17.4 s imaging scan time.[2] Moreover, propene-d_6 gas was efficiently hyperpolarized using PHIP technique and Rh/TiO_2 catalyst allowing for preparation of pure HP propane-d_6 gas. PHIP of propane-d_6 provides significant advantages for the mechanistic studies of the catalytic hydrogenation reaction, showing in particular that propene gas is hydrogenated to yield propane, which can be subsequently dehydrogenated by the catalyst studied.[3] In the case of mechanism evaluation very recent results show that PHIP may be succesfully utilized for studying strong metal-support interaction (SMSI) effect for palladium supported on titania catalysts.[4] However, despite a substantial body of research performed in the field of heterogeneous PHIP, efficient heterogeneous catalysts for PHIP production are yet to be identified and demonstrated. But nowadays PHIP technique can be successfully utilized for mechanistic studies of heterogeneous processes and reactor imaging.

Acknowledgement. This work was supported by RFBR (14-03-00374-a, 14-03-93183 MCX_a and 16-03-00407) and MK-4498.2016.3.

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Effect of Activated Carbon Fibers Modification by Fe on Electron States and Structure of Pt/C Catalysts for CO Oxidation

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This work is devoted to study of activated carbon fibers Busofit modified by Fe effect on the electronic state and structure of the supported platinum and its catalytic properties. Woven activated carbon fabric modified with thermally stable acid groups was used for preparation of supported metal catalysts. Fe^{3+} ion introduction into carbon was carried out by treating of Busofit in Na-form with $Fe(NO_3)_3$ aqueous solution, modification of support with Fe oxides was conducted by Busofit in Fe-form treatment with NH_4OH aqueous solution. Pt in Na- and Fe-forms of Busofit was introduced from $Pt(NH_3)_4Cl_2$ aqueous solution by ion-exchange, in modified with Fe oxides form - by impregnation. Prepared catalysts (Pt-1.0 wt.%; Fe-0.9, 2.2 wt.%) were calcined (He, 200°C, 2h) and reduced (H_2, 450°C, 2h). All prepared samples were studied by XPS, HRTEM, XANES/EXAFS. HRTEM images were obtained by JEM-2010 at a 0.14 nm resolution. The XANES/EXAFS spectra (Pt-L_3) were measured on an EXAFS spectrometer at the SSTRC (Novosibirsk). XPS studies were carried out on a SPECS spectrometer (AlKα). Catalytic activities for Pt/C systems were determined in the CO oxidation reaction: dry reaction mixture (0.3 vol.% CO in air), 5.5 mg of Pt in catalyst loading, 400 ml/min, 3300 h^{-1}.

Introduction of 2.2 wt. % of Fe into Busofit Na-form lead to a drastic increase of catalytic activity of the supported platinum (50 % CO conversion temperature (T_{50}) shifts from 110°C to 45°C). Analysis the XPS spectra of Pt containing samples has shown almost all the platinum in the prepared catalysts to be in a metallic state; this fact was confirmed by XANES data. According to the XPS data, the aforementioned samples contain significant quantity of the surface oxygen bound with Fe^{3+} similarly to supports modified with Fe oxides. According to the EXAFS data, the Pt-Me length in the discussed sample was ~0.2A shorter than Pt-Pt of the Pt foil. On the other hand, these data indicate presence of a highly dispersed metallic Fe, while in supports iron is present mainly in oxide forms. One can assume formation of Pt-Fe intermetallic compound (nano-alloy). Apparently, the electron state and structure features of sample determine its high catalytic activity. As for Pt/C catalysts (with significantly lower activity), only Pt^0 nanoparticles were found. All possible structural models were discussed.

Acknowledgement. This work was supported by the Belarusian Republican Foundation for Fundamental Research, project № X14P-090, RFBR (140301066, 160301139).

PP-72

Effect of the Preparation Method of $GdFeO_3$ Perovskites on Their Catalytic Properties

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The interest in oxides with mixed oxygen-ionic and electronic conductivity is associated with the possibility of their wide application as a stable, active and selective catalysts for high temperature processes.

The study objects of catalytic properties in carbon-dioxide reforming of methane were ferrites $GdFeO_3$ and were obtained by the high temperature solid state reactions and by sol-gel technology with glycine and citric acid are as stabilizers. X-ray powder diffraction (XRD) confirmed the presence of single phase with perovskite-type layered structure for all investigated samples. XRD, scanning electron microscopy (SEM), photon correlation spectroscopy show that the samples of ferrites obtained by high temperature ceramic synthesis are in submicrocrystalline state (d= 10 µm) and oxides prepared by sol-gel technology are nanocrystalline state and theese oxides have a porous structure (d_{citric}=50-60 nm, d_{gl}=30-50nm). A study of the complex oxides prepareted using ceramic technology by Mössbauer spectroscopy showed that the iron atoms of this samples are founed in one state Fe^{+3}, which is magnetically ordered. As in the case of the synthesis by sol-gel technology with glycine-nitrate metod using and in the case of synthesis by sol-gel technology with citric acid the iron atoms of complex ferrites are found in one state - Fe^{+3}, but in two fields of different symmetry, where one iron atom has a magnetic splitting and the other has only quadrupole and is not magnetically ordered.

The catalytic properties of ferrites in dry reforming of methane (DRM) were studied in a flow apparatus at atmospheric pressure. Analyses of the products were performed by chromatography. It was found that the preparation method has no significantly effect on the CH_4 and CO_2 conversion. But in regard to the formation of products the catalysts activity was increased in the row: $GdFeO_3$*(ceramic)* < $GdFeO_3$*(sol-gel, gl)* < $GdFeO_3$*(sol-gel citric)*. At the same row the hydrogen selectivity was increased. Higher catalytic activity of ferrites synthesized by sol-gel technology may be related to differences in the iron atoms state and particles morphology of the crystallites, which obtained by two different methods. In addition, the more porous sol-gel-citric samples structure is favorable for the intermediates transport from one active site to another.

Acknowledgement. This work was supported by the Russian Science Foundation, grant № 14-03-00940 A.

PP-73

The Quantum-chemical Research of Catalytic Elementary Processes on the Silica Surface

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The structure of surface's chemical compounds are defined not only the chemisorption's peculiarities, but the modifying surface transformation too. It does refer not to many layer surface structure formations, but to the chemical and thermal transformations of the new functional groups immobilizing on the surface. The nature of bonding between adsorbat and surface is still subject to some interpretation. It is naturally difficult to know how molecules desorbed: molecularly or dissociatively, because it is hard to investigate by experimentally. In such case the quantum-chemical calculation can be very useful instrument for clarification and explanation of the elementary processes on the surfaces during chemisorption.

The quantum-chemical calculations have been provided by the *ab initio* method in the 6-31 G basis set to investigate the chemical way to destruct of organic molecules immobilizing on the silica surface. Point defects, stabilized on the activated silica surface have the high reactivity, and they have been used as "foundation" for immobilized on the surface intermediates both diamagnetic and paramagnetic nature. This method is founded effective for obtaining of different chemical structure intermediates. The subject of research was organic and inorganic radicals of fire inhibiting agents. It was showed before [1], at the application of fire extinguishing substances they are inhibiting by radicals, which could appear during thermal destruction of inhibitor molecules. The destruction products could be immobilized on the silica surface as catalytic support.

Calculations have been provided for the immobilizing inhibitor agents on the silica surface. The calculation results have presented in the table.

№	Elementary steps of reactions	Abstraction energy, E, kcal/mole
1.	$Si(OH)_3Br \rightarrow Si(OH)_3^\bullet + Br^\bullet$	71,21
2.	$Si(OH)_3Cl \rightarrow Si(OH)_3^\bullet + Cl^\bullet$	162,14
3.	$Si(OH)_3F \rightarrow Si(OH)_3^\bullet + F^\bullet$	199,47
4.	$Si(OH)_3CCl_3 \rightarrow Si(OH)_3^\bullet + CCl_3^\bullet$	129,44
5.	$Si(OH)_3CFHCl \rightarrow Si(OH)_3^\bullet + CFHCl^\bullet$	185,24
6.	$(OH)_3Si\text{-}PO \rightarrow (OH)_3Si^\bullet + PO^\bullet$	21,3
7.	$(OH)_3Si\text{-}NH_2 \rightarrow (OH)_3Si^\bullet + NH_2^\bullet$	87,8
8.	$(OH)_3Si\text{-}PH_2 \rightarrow (OH)_3Si^\bullet + PH_2^\bullet$	50,1

As we can see from the table, the more preferable destruction way from the silica surfaces is the abstraction PO-radical. Among the organic substrates only Br abstracted with reasonable energy. But it is well known that bromine containing substances destroy of the stratosphere Ozone layer. Therefore we can make a conclusion about silica surface as suitable catalytic support for mono phosphorus oxide fire inhibiting agent.

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PP-74

Epoxidation of Fatty Acid Methyl Esters of Vegetable Oils by Air Oxygen

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Current chemical industry is characterized by the tendency of increasing the share of environmentally friendly methods for producing different substances, including the group of technologies based on applying vegetable renewable raw materials. In this work the kinetic regularities and mechanism of the process of epoxidation of fatty acid methyl esters (FAME) of vegetable oils were investigated. Obtained epoxide compounds could be used, for example, as polymer plasticizers. In addition, it is of current interest to use epoxidized FAME as the monomers for different polymeric compositions (epoxy resins, polyurethanes and so on [1]). The use of special epoxidizing agents such as peracids, organic hydroperoxides or hydrogen peroxide [2] complicates substantially the technology of epoxidized FAME manufacture. Consequently, in this report applying atmospheric oxygen as an epoxidizing agent was proposed. The complex of molybdenum with propylene glycol was used as the catalyst. It has been assumed that peroxide compounds, which form *in situ* through the radical oxidation, can epoxidize double bonds of unsaturated fatty acid esters in the presence of catalyst [3].

It has found out that changing of process parameters in the reaction mixture (temperature, air consumption, catalyst concentration) doesn't influence on the way of the process and on the ratio of the products got. Wherein, the composition of a feedstock is affecting considerably on the process, i.e. the type and the content of fatty acid residues. The highest epoxide selectivity was detected in the monounsaturated systems, where the concentration of methyl oleate (MO) is the largest (palm olein biobiesel: 90 wt% of MO). Simultaneously, in the polyunsaturated systems (for example, sunflower, linseed biodiesels with the great content of methyl linoleate and methyl linolenate) the side reactions occur predominantly. In addition, the rate of side reactions strongly depends on the concentration of high reactive compounds and intermediates such as peroxides and radicals. It should be noted, that there were no hydroxyl-compounds in the reaction mixture. Thus, the tradition mechanism of olefin substances epoxidation catalyzed by transition metal complexes has not been confirmed.

Acknowledgement. This work was funded by RFFI and Ministry of Education and Science (Project № 4.2512.2014/K). The analyzes were carried out on the equipment of The Center for Collective Use of D.Mendeleev University of Chemical Technology of Russia.

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Effect of Water on Hydrocarbons Formation from CO and H_2 over Co/H-Zeolite Catalysts

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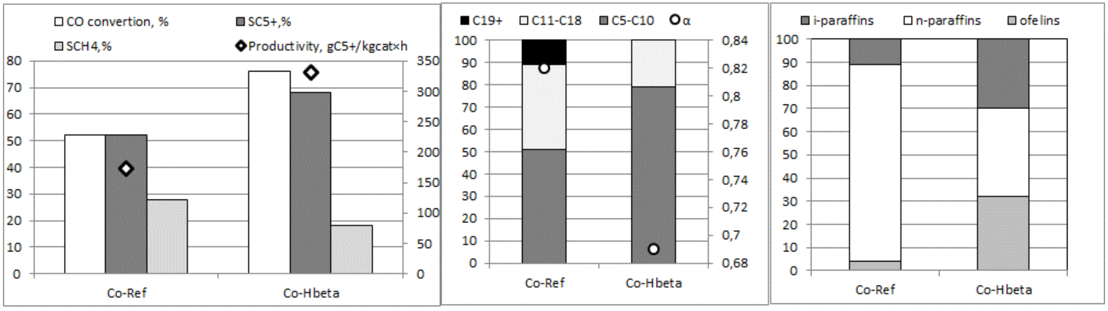
Fischer–Tropsch synthesis (FTS) is well known as the main stage of XTL technology — high-quality synthetic oil production from coal, biomass or natural gas. Co catalysts provide formation of linear hydrocarbons as the main product, which makes these catalysts most common in use. It is known that obtaining hydrocarbons with chain-length below C_{19}, requires the use of zeolite as a support [1-2]. Since Co has low activity in WGSR, water tends to accumulate in the system. Literature suggests various concepts for water effect in FTS catalyzed by supported Co such as negative [3], negligible [4] or even positive [5]. However, the mechanism of water impact over Co/H-zeolite catalyst seems to be different from cited above. There are indications in literature, which give evidence that zeolites can be involved in secondary reactions interacting with water and producing additional amount of Bronsted acid sites [6].

The aim of our work was to show that FT water may play a positive role in activity of Co-Hbeta catalyst and help to obtain desirable products with higher selectivity and productivity of FTS.

The investigated catalysts were produced by the extrusion of pastes followed by impregnation of cobalt nitrate solution. Co content was 20 wt. %, Al metal — 25–27 wt. %, binder — balance. Co-Hbeta contained 30 wt. % of Hbeta. A reference catalyst Co-Ref was zeolite-free. All the catalysts were active in FTS in fixed bed. The content of olefins and isoparaffins increased, which is due to secondary reactions of FTS products proceeding on Bronsted acid sites of Hbeta in accordance with carbocationic mechanism. Meanwhile, C_{19+} (wax) hydrocarbons content dropped due to the same mechanism. Al metal in Co-HBeta catalyst stayed almost intact during FTS due to secondary reactions, while Co-Ref was destroyed by aluminum oxidation.



a) b) c)

Figure 1: Influence of zeolite support on a) CO conversion, selectivity of C_{5+} and C_{CH4} and productivity b) fractional and c) group composition

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PP-76

Reductive Activation of the Ru-promoted Co-Al Catalyst: Kinetics and Mechanism

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We report the experimental study of the effect of ruthenium on the kinetics and mechanism of cobalt-alumina catalyst reduction by means of thermal analysis (TG-DTA) and in-situ synchrotron radiation (SR)-XRD, as well as of the catalytic performance of these Co-Ru/alumina catalysts in the Fischer-Tropsch synthesis.

Cobalt-alumina catalyst (CoAl) was prepared by deposition by precipitation of Co (11.4 wt. %) during urea decomposition method using δ-Al_2O_3. Ruthenium promotion was performed by impregnation with aqueous solutions of $RuNO(NH_3)_2(NO_3)_3$ complex with concentration corresponded to Ru loading of x = 0.2, 0.5 and 1 wt. %. The precursor of the catalysts were calcined in flowing argon at 350 °C.

TG-DTA and XRD data concord that ruthenium promotes both reduction steps $(Co,Al)_3O_4 \rightarrow (Co,Al)O_{1+x}$ and $(Co,Al)O_{1+x} \rightarrow Co^0$ and lowers the reduction temperatures by more than 100 °C. The metallic cobalt phase is distinguished by XRD: at 500 °C for Co-Al, at 350 °C for Co-Ru(0.2)Al, and at 300 °C for Co-Ru(1.0)Al. The model-free kinetic analysis (Ozawa-Flynn-Wall isoconversional method) showed that the activation energy values for the reduction processes accordingly decrease. Analysis of the coherent scattering size of the main cobalt-containing phases (spinel like $(Co,Al)_3O_4$, NaCl-like $(Co,Al)O_{1+x}$ and metallic Co) together with non-linear regression kinetic modelling of the thermal (TG/DTG) curves allowed to elucidate some common features of the reduction mechanism for promoted and non-promoted Co-Al catalysts: (1) formation of multiple nuclei of CoO phase within one crystallite of Co-Al spinel-like oxide and further transformation following Johnson-Mehl-Avrami-Erofeev-Kholmogorov (JMAEK) kinetics, (2) kinetic control of CoO reduction process by the step of the metallic nucleus formation, which is followed by its slow growth, limited by 3D Jander diffusion of oxygen through the Co-Al oxide shell. According to these findings, the ruthenium promoter affects the rate of new phase nuclei formation.

The promoted catalysts can be activated at moderate temperatures, they retain high activity and have beneficial selectivity in the Fischer-Tropsch synthesis.

Acknowledgement. The work was performed in the framework of the joint Research and Educational Center for Energoefficient Catalysis (Novosibirsk State University, Boreskov Institute of Catalysis) and was supported by Russian Government Decree № V.45.3.6.

The Investigation of the Mechanism of Heck Reaction with Aromatic Carboxylic Anhydrides Using Advanced Methods of Competing Reactions

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Arylation of alkenes with aromatic carboxylic anhydrides using palladium catalysts being the modification of well-known Heck reaction is the very attractive for fine organic synthesis [1]. But at the moment there are virtually no systematic mechanistic investigations of the catalytic system operation in the reaction. The study of the fine details of the catalytic cycle of the reaction using "ligand-free" catalytic systems has been carried out using the set of approaches based on competing reaction method having a number of advantages due to artificial multi-route character [2]. The analysis of dependence of differential selectivity in competing reaction of two competing substrates (aromatic carboxylic anhydrides or alkenes) on different factors (ratio of concentrations of competing substrates, nature and concentration of coupling partner) allows us to establish that steps of the catalytic cycle where anhydrides and alkenes participate are irreversible. The results of the analysis of integral kinetic curves of competing substrates consumption together with the results of additional studying including the analyses of Hammett plots of competitive and non-competitive experiments and joint analyses of the rates of products formation under competitive and non-competitive conditions point to the step of the catalytic cycle with the participation of aromatic anhydrides and alkenes are fast. Based on the data obtained the conception of operation mechanism of catalytic systems in the arylation of alkenes with aromatic carboxylic anhydrides has been developed.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-13-00062.

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PP-78

Peroxide Oxidation of Hydrocarbons Mediated by Heteropolycompounds and Affected by Ionic Liquids

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Hydrogen peroxide is a perfect reagent for oxidation of hydrocarbons due to delicate effects on the environment and low-temperature selective conversion of the substrates to desirable oxygenates. In addition to these attractive characteristics, it would also desirable to provide high efficiency of H_2O_2 consumption for oxidation of substrate and minimize its unproductive decomposition under reaction conditions. Some ionic liquids (IL) have been found to be effective additives for oxidations with H_2O_2 and with a peroxide in situ generated from H_2 and O_2 gases. In both cases, the ionic liquids did not change the mechanism of catalytic reactions, but affected stability and concentration of reactive intermediates, thereby improving the efficiency of oxidation reactions.

Phosphotungstates are known as catalysts for epoxidation of olefins with hydrogen peroxide. By analogy with the olefins, 1,3-butadiene reacted with solution of aqueous hydrogen peroxide and salts of phosphotungstate anion with TBA^+ and $EMIm^+$ cations. The selectivity of 1,3-butadiene to epoxy-1-butene conversion approached 97%, and activity of the catalytic system varied among $(Bu_4N)_3\{PO_4[WO(O2)_2]_4\} \approx (Bu_4N)_5Na_{0.6}H_{1.4}[PW_{11}O_{39}] < (EMIm)_5NaH[PW_{11}O_{39}]$. Presence of the $EMIm^+$ cation provided close to 100% efficiency of hydrogen peroxide consumption. The high efficiency is explained by increased stability of the most reactive peroxo complexes, as determined by ^{31}P-NMR [1].

A modern trend in selective oxidation is replacement of H_2O_2 by peroxides in situ generated from hydrogen and oxygen. Pt/C-$H_3PMo_{12}O_{40}$ bifunctional catalyst allows oxidizing of various hydrocarbons by the gas mixture of O_2 and H_2 at a room temperature. As with hydrogen peroxide, there is also an urgent problem of effective use of the reagents, in this case, hydrogen. Small additives of Bu_4NBr, BuMImBr and $Bu_4N(HSO_4)$ increased the efficiency of hydrogen consumption in oxidation of cyclohexane. The gas consumption for water was decreased and production of cyclohexanol and cyclohexanone was increased. As a result, the selectivity of hydrogen consumption for oxidation of cyclohexane increased from 1% to 20% in the presence of Bu_4NBr and $Bu_4N(HSO_4)$. The mechanisms of the effective promotion are discussed.

This work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations, Project V.44.1.15.

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Detailed Characteristic of the Pt-HPA-IL Catalytic System Applied to Oxidation by O_2/H_2 Gases

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Two-component system consisting of Pt/C catalyst and solution of $H_3PMo_{12}O_{40}$ heteropolyacid (HPA) in acetonitrile can be used for the oxidation of hydrocarbons with a mixture of O_2 and H_2 gases at a low temperature. In our study, we found that the presence of some ionic liquids (IL) has a promoting effect on the oxidation of cyclohexane, improving the yield of alcohol and efficiency of the gas consumption. In the presence of Br^- containing BuMIBr and Bu_4NBr salts and acid salt Bu_4NHSO_4, cyclohexane was converted selectively to cyclohexanol, the selectivity of H_2 consumption being increased from 1% to 20% under the action of the IL. Mechanism of the oxidation reaction and a nature of IL-promoted effect become more understandable in light of the information on the state of the components of the catalytic system.

C,H,N-analysis and X-ray fluorescence analysis of Mo and P were used to determine composition of the reaction solutions initially containing HPA (0.0046M) and IL (0.026 M) in CH_3CN (2.0 mL) + C_6H_{12} (0.2 mL). Specificity of the method was analyzing the samples prepared by impregnation of silica with the solution. It was shown that IL and HPA were mainly kept in the solution after the contact with the Pt/C catalyst in air and during the catalytic reaction, and <10% only was adsorbed on the catalyst. UV-VIZ spectra of solutions showed no interaction between IL and HPA. UV-VIZ spectroscopy and ^{31}P NMR allowed us to observe the change in the Mo(V)/Mo(VI) oxidation state in HPA. The HPA was observed to be reduced in the course of the reaction in the presence of Pt/C catalyst, and its reduced form was oxidized in air without a damage of the molecular structure. The reversible red-ox transformation allowed HPA to participate in the transfer of peroxide species from the surface platinum to cyclohexane.

IL performed different functions depending on their composition. Bromide containing IL BuMImBr and Bu_4NBr modified Pt surface sites by means of adsorption of Br^- ions, thus reducing contribution of water in conversion of the H_2 and O_2 gases. Acidic salt Bu_4NHSO_4 stabilized the Pt generated active peroxide intermediates from conversion to water and increased possibility of their interaction with cyclohexane.

The Pt/C catalyst was stable in several times repeated testing in presence of Bu_4NHSO_4, but in presence of Br^- containing IL platinum was partly dissolved during reaction, and the catalyst could be regenerated by post-reaction treatment of the reaction mixture with H_2.

This work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations, Project V.44.1.15.

PP-80

In-Situ SAXS Study of Sol-Gel Process to Prepare Ag/P_2O_5/SiO_2 Catalysts

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Sol-gel synthesis of Ag/P_2O_5/SiO_2 catalysts with phosphorus promoter is convenient one-pot way of the catalyst preparation for selective ethylene glycol oxidation [1]. Despite the abundant literature dealing with agglomeration of SiO_2 nanoparticles in water-alcohol solutions, effect of additives (nitrous and phosphoric acids, silver nitrate, etc.) is not thoroughly studied. For example, phosphorous acid could be adsorbing on the silica particle surface and therefore changing of mechanism of particle aggregation as well as porous structure [2]. Thus, the aim of the present work is to give experimental evidences of additive effect on the catalyst porous structure.

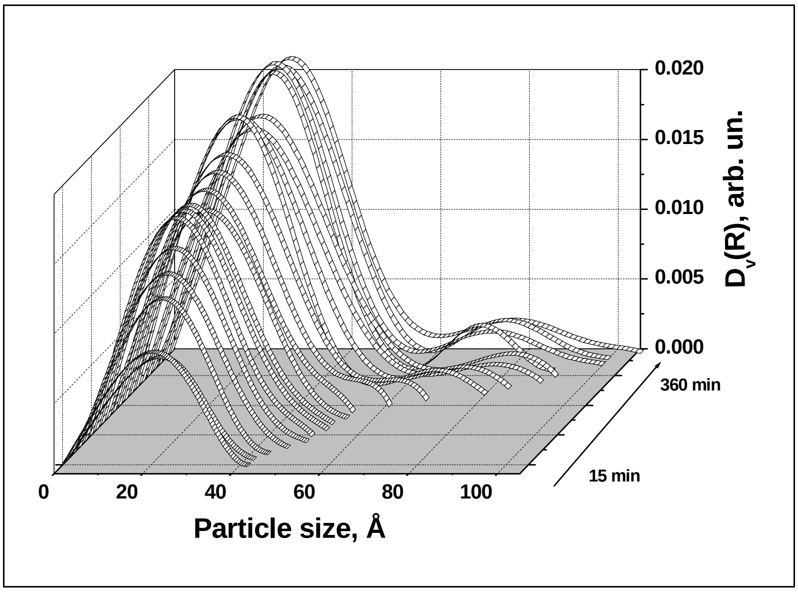

Fig. 1 Volume particle size distributions in mixture of tetraethylorthosilicate, $AgNO_3$, H_3PO_4, HNO_3, C_2H_5OH and H_2O depending on aging time.

It has been found that the structure of silica gels in all cases are formed from primary sphere-like particles with sizes of 2-4 nm and larger secondary particles (up to 12 nm). Composition of reaction mixture during sol-gel stages allows varying the distribution of primary/secondary particles. Ratio between phosphorous and nitrous acids effects on the ratio between primary and secondary silica particles in material structure. Different mechanisms of silica particles aggregation such as Ostwald ripening and/or particle coagulation process will be discussed.

Acknowledgement. The work is supported by the RAS and FASO Russia (project № V.44.1.15.)

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Self-oscillating Dynamics in the Partial Oxidation of Methane over a Ni Foil in Relations with Reversible Oxidation and Carbonization of the Catalyst Bulk

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Studying the mechanism of the partial oxidation of methane (POM) reaction over a Ni foil in a flow reactor we observed the self-oscillatory dynamics of CH_4, O_2, CO, H_2 and CO_2 partial pressures which were accompanied by oscillations of the catalyst temperature. Moreover, we found that in the oscillatory regime the morphology of the foil surface was changed significantly [1]. These changes were presumably caused by the reversible oxidation and carbonization of the catalyst bulk.

To study the self-oscillatory dynamics we use also the methods of mathematical modelling. Formerly in [2], we developed the model which predicts the self-oscillations of small periods in POM. The model was based on the mechanism, which considered the dissociative adsorption of methane and oxygen on the catalyst surface, reaction of the surface intermediate, desorption of the reaction products and formation of the surface oxide.

In this work we add to the reaction mechanism the steps describing the oxidation and carbonization of the catalyst bulk. The resulted model describes the relaxation self-oscillations of partial pressures of the species in gas phase as well as the catalyst temperature. Most of the period carbonization of the catalyst proceeds and CH_4 and O_2 partial pressures are maximal, while sharp decreasing of the pressures accompanied by catalyst oxidation.

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PP-82

Design of Mixed CeO_2-ZrO_2/SiO_2 Supports and Ag Catalysts on the Basis Thereof for Low-Temperature CO Oxidation

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Ceria is a well-known support for various catalysts. However, its application is limited due to low specific surface area, high cost, complexity of granulation, etc. In the literature mixed ceria and zirconia are shown to increase thermal stability of ceria. However, this method does not solve the problem of the low specific surface area and granulating complexity of this system. One of the possible solutions is to support ceria and zirconia on the surface of primary inert support, e.g., alumina or silica. This method allows obtaining granular support combining high specific surface area, thermal and mechanical stability caused by silica or alumina primary support, while ceria and zirconia are used as secondary supports providing surface functional properties required to stabilize active component. Different distribution of ceria and zirconia on the surface of silica can be obtained by variation of deposition conditions. This defines the properties of resulting mixed supports and catalysts on the basis thereof.

The series of CeO_2/SiO_2 and $Ce_{0.5}Zr_{0.5}O/SiO_2$ supports were prepared by impregnation techniques with and without citric acid. A series of Ag-containing catalysts was prepared on the basis of mixed supports. The low-temperature nitrogen adsorption, mathematical modeling using the RDS model, TPR, and XRD methods were used to characterize both supports and catalysts. The catalytic properties of catalysts were tested in low-temperature CO oxidation.

The use of citric acid as a stabilizing additive was shown to lead to formation of ceria or ceria-zirconia nanoparticles with sizes of ~4 nm on the surface of silica (Fig . 1b). Uniform layerwise distribution of CeO_2 and ZrO_2 on the surface of silica was observed, when citric acid was not used.

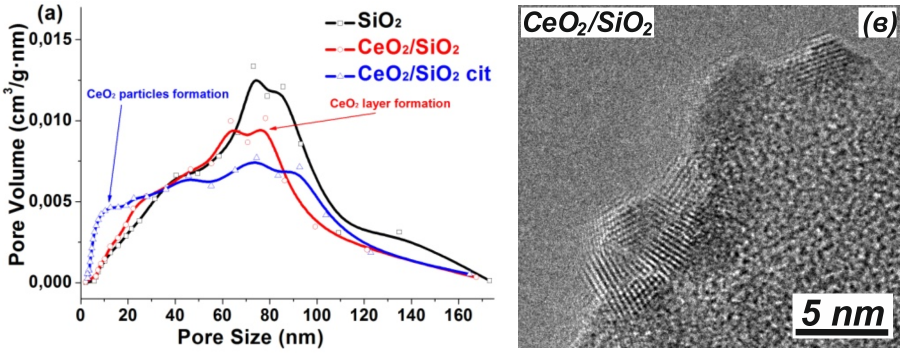

Fig.1. Pore size distribution (a) and TEM image (b) for CeO_2/SiO_2

Ag catalysts were synthesized on the basis of the supports obtained. The features of interaction between Ag and ceria/zirconia as well as the role of these interactions in CO oxidation were studied. The distribution of ceria and zirconia on the silica surface was obtained, and influence of this distribution on activity of supported silver was discussed in the present work. Control of distribution of secondary support (ceria or zirconia) on the surface of primary support was shown to be a possible way to designing new catalytic materials.

This research was supported by “The Tomsk State University Academic D.I. Mendeleev Fund Program” grant in 2015-2016.

Lignosulfonate Destruction with Ozone-Catalyst Systems

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Modern science and technology are directed to a development of environment friendly technologies. So, it is the actual problem of wastewaters purification. Advanced Oxidation Processes (AOP) is between the most perspective technologies today. Ozone-catalyst systems as one of AOP pathways opens up perspectives for solution problems related to lignin-cellulose materials delignification. These systems can be used for resistant pollutants wastewaters purification, too.

An effect of transition ions (Fe^{3+}, Co^{2+}, Mn^{2+}) on lignosulfonate as well as lignin structural models (quaiacol, 2,6 dimethylphenol, maleic, oxalic acid) ozonation was investigated.

Kinetic analysis, as well as IR, NMR, UV-spectroscopy data revealed the main pathways of lignosulfonate conversion in water solution ozonation. As shown, the presence of transition ions in water solution doesn't influence aromatic ring destruction. Hence, it resulted in enhance of the byproducts oxidative destruction rate. As oxidation of byproducts (saturated acids, ketoacids, aldehydes) takes place, the ozone demand significantly increases.

The mechanism of lignosulfonate oxidation by ozone in the presence of catalyst was proposed. It is supposed that intermediate complexes of LS and byproducts with both oxidized and reduced forms of metal catalyst are formed. As for Mn^{2+}, it is supposed that Mn^{2+} is oxidized into Mn^{3+} by ozone. Then Mn^{3+} and LS oxidation products form chelate complexes, which act as low molecular mediators and initiate a lot of radical processes.

It was found a similarity of lignosulfonate oxidative destruction products obtained both in (O_3/Mn^{+2}) and (O_3/H_2O_2), in which radicals are generated by hydrogen peroxide degradation with ozone. As compared to (O_3/H_2O_2), in ozone-catalyst system (O_3/Mn^{+2}) byproduct oxidation is performed by $OH^{\cdot}$ radical as well as by direct participation of Mn^{3+} ions characterized by the high value of oxidative-reduction potential.

It was shown effectiveness of a mutual usage of ozone and transition metal ions for lignin destruction as well as for oxidation of resistant carbon acids, ketoacids and aldehydes.

PP-84

Oxidative Destruction of DDT Photocatalyzed by Dioxo-Mo(VI) Complex Anchored on TiO_2

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High catalytic activity of dioxo-Mo(VI)-complexes, anchored on a TiO_2, under UV-irradiation, recently, was shown in oxidation of a number classes of organic compounds with dioxygen [1]. Oxidative destruction of halogenated derives of aryl hydrocarbons, such as persistent pesticide DDT and its homologs, present a great interest for chemical industry, organic syntheses, and, especially, for green chemistry and environmental sustainability [2]. In this work the feasibility of the selective oxidation of DDT (1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane) with dioxygen, in “mild” conditions, catalyzed by dioxo-Mo(VI) dichloro[4,4′-dicarboxylato-2,2′-bipyridine], anchored on TiO_2 was investigated under UV-irradiation. The aim of this work was to achieve the selective formation of oxygenated products, other than the total hotochemical destruction by TiO_2.

The reaction was carried out under UV-irradiation (λ= 253.7 nm) at room temperature, in acetonitrile suspension of DDT, as a two stage process. The first stage was reaction of DDT (C_0=1.6x□10^{-2} mol/l) with the mentioned anchored complex (1,6x 10^{-4} mol/g), in the absence of oxygen (in argon atmosphere) and under UV-irradiation:

$(ClC_6H_4)_2C(H)CCl_3$+O=MoVI(O)(Cl_2)[L]/TiO_2 $\rightarrow$$(ClC_6H_4)_2C(OH)CCl_3$+ MoIV(O)$(Cl_2)$[L]/$TiO_2$, where L is 4,4′-dicarboxylato-2,2′-bipyridine.

In the second stage, the complex Mo(IV) was reoxidized by molecular oxygen, in the dark:

MoIV(O)(Cl_2)[L]/TiO_2 + O_2 $\rightarrow$ O=MoVI(O)(Cl_2)[L]/TiO_2

The obtained experimental results clearly show the catalytic role of the anchored complex in this reaction. For instance, the turnover number (Δ[DDT]/[anchored complex]) reaches about 3.7 (during 2-4 experimental cycles), corresponding to 36% consumption of DDT, which is about 11.5 times more, than that for the “pure” TiO_2. Reaction mixtures consist of a large spectra of chlorinated and non-chlorinated organic compounds C_2-C_{14}, as well as the products of the complete destruction of DDT, such as CO_2, H_2O and HCl. Among them, the main product of reaction is dicofol (2,2,2-trichloro-1,1-bis-(4-chlorophenyl) ethanol, 21%). Apparently, it plays a role of intermediate for other products of the further oxidative destruction of DDT, the composition of which, in general, is similar to the products on “pure” TiO_2. However, the reaction mixture contains also a noticeable amount of DDE (9%, dichlorodiphenyl- dichloroethylene) and a small amounts of the reductive decomposition products, as DDD (1,1-dichloro-2,2-bis(p-chlorophenyl) ethane), DDM (bis(p-chlorophenyl) methane), diphenylmethane, and others, for a total 14%.

On the basis of the kinetic data, it has been drawn the conclusion that the primary act of reaction is oxo-atom transfer from the anchored complex to DDT by the formation of dicofol. Apparently, the second stage of reaction, reoxidation of Mo(IV) to Mo(VI) with molecular oxygen in the dark, occurs via the formation of peroxo moieties in Mo-complex of the type O=Mo^{VI} (-O-O-), which is evidenced by the fact of nearly twofold increase of the turnover number of reaction in the second and further experimental cycles of the process in comparison with the first cycle.

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Magnetically Recoverable Catalysts for Cellulose Hydrogenolysis into Glycols

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The catalyst recycling which is essential for successful industrial applications is usually not performed, because recycling of conventional supported catalysts requires an aggressive oxidative treatment which leads to deactivation via sintering [1, 2]. We used magnetically recoverable Ru catalysts supported on a Fe_3O_4-SiO_2 support that can be separated from the reaction mixture with a magnet. It was shown that the magnetically recoverable catalyst characterized by high selectivity to lower polyols (ethylene and propylene glycol). The catalyst was synthesized by a group led by Dr. L. Bronstein. For addition of Ru species, $Ru(acac)_3$ was dissolved in of THF and mixed with Fe_3O_4-SiO_2. The suspension was stirred overnight in air to allow THF evaporation. The sample was then dried in vacuum at room temperature for a minimum of 2 hours until the sample was entirely dry. The sample was heated in a quartz tube in a tube furnace under argon to 300°C for 3 hours. The catalyst was reduced in hydrogen at ambient pressure during 2 hours at 300 °C.

Cellulose conversion to polyols was carried out in subcritical water under the following conditions: temperature 205 - 260 °C, hydrogen partial pressure 4 - 106 MPa, process time 10 - 60 min. The experiments were performed in a steel reactor with volume 50 cm^3 (Parr Instrument, USA.). It was shown, that optimal reaction temperature of cellulose hydrolytic hydrogenation process was 255 °C. Optimal hydrogen pressure was found to be 6 MPa. At reaction pressures lower than 5 MPa the colored reaction solutions are formed, containing glucose destruction products. Starting form 6 MPa of overall reaction pressure the selectivity to diols decrease. Optimal cellulose hydrolytic hydrogenation time was found to be 50 minutes. The optimal conditions for cellulose hydrolytic hydrogenation over 5 % Ru-Fe_3O_4-SiO_2 catalysts sample was founded: temperature: 245 °C; hydrogen partial pressure: 6 MPa; process time: 50 minutes. The achieved results are: cellulose conversion - 100 %; propylene glycol selectivity ~ 23 %, ethylene glycol selectivity ~ 12 %.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 15-08-00455.

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PP-86

Modification of Catalysts Properties for Methane Dehydroaromatization by the Creation of the Secondary Mesoporous in the Zeolite ZSM-5 Structure

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The synthesis of hierarchical zeolites with the secondary mesoporous structure and investigation of MFI (ZSM-5) zeolites were carried out. This type of zeolite having the secondary mesoporous structure was formed by the introduction of carboxymethylcellulose (Na-CMC), starch and carbon nanoparticles (CN) with practical size of 13 nm as a solid template at the stage of crystallization gel preparation. It was showed that the presence of mesopores in the catalysts reduces the coke formation.

The using of Na-CMC (ZRN-3) or CN (ZRN-4) as the templates for creation of mesoporous structure doesn't reduce the zeolite degree of crystallinity. According to the data of XRD analysis the crystallinity of ZRN-1 (without the secondary template) is 93%, the crystallinity of ZRN-3 is 95% and for ZRN-4 it is approximate to 100%. The results of SEM shows high density of particles but the crystals size is small. The generation of mesoporous structure is confirmed by the data of N_2 adsorption and desorption and IR-spectroscopy. The presence of mesopores at the synthesized samples is favorable to methane dehydroaromatization from the point of reagents mass carry to the catalyst active sites and methane dehydroaromatization products carry into the reaction volume which also is favorable to reducing of coke formation. According the data of TPO and TGA analysis high-temperature peak relative to dense coke depositions is disappeared with the formation of mesoporous structure into the ZRN-3 and ZRN-4. Among all investigated supports during the catalytic tests the sample of Mo/ZRN-4 demonstrates the best combination of activity, methane conversion (8%) and aromatic hydrocarbons selectivity (85%) and yield (700°C).

Among all means of mesoporous structure formation the method of starch introduction as a solid template demonstrates its own unsuitability because it leads to reduction of crystallinity from 93 to 80% and it increases the SiO_2/Al_2O_3 molar ratio from 35 to 250. The selectivity of aromatic hydrocarbons formation for catalyst prepared with ZRN-2 isn't exceed 35%, and the methane conversion become less than 1% already in the early hours of catalytic experiment. Thus, the optimal method is the using of carbon nanopowder to create the mesoporous structure by the introduction of the secondary template at the stage of zeolite synthesis. This method allows to the increasing of zeolite crystallinity and provides good characteristics of catalysts for the methane dehydroaromatization. The optimal combination of zeolite acidity, high crystallinity, micro and mesoporous volume allows to the increasing of methane conversion, yield and selectivity of aromatic hydrocarbons formation.

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Dimers Intermediates in Chlorophenols Oxidation over Ti Supported Electrocatalysts

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Removal of chlorinated phenols CP (a major class of environmental pollutants) is achieved by different treatment processes including adsorption, bio-, photo- or enzyme degradation and electrochemical oxidation over catalysts as anodes. It is not easy to evaluate the detail mechanism for CP oxidation even for gaseous phase of catalyzed reaction.

In this work the role of associated CP molecules in the first step of electro catalytic transformations, including CP adsorption, is investigated. Several Ti-electrodes coated iridium oxide or/and platinum were prepared, characterized (SAM, ESCA, UV and FTIR spectroscopy) and tested in cyclic voltammetry measurements and galvanostatic oxidation of 3-chlorphenol, 4-chlorphenol, 2,4-dichlorphenol and 2,4,6-trichlorphenol in acidic and alkaline solutions. Nonlinear dependences current density I_{OX} via initial concentration (see fig.1 in case of 3-chlorphenol) were typical for all systems, but in coordinates $I_{OX} - C^{1/2}$ good lines confirm the formal effective kinetic order n = ½. So associated molecules X–X exist in liquid phase due to hydrogen bonds, tend to adsorb on anode surface and are the main reactants in electrocatalytic steps. The value of rate constant of oxidation $K_{1/2}$ [$A \cdot L^{1/2} \cdot mole^{-1/2}$] depends on substance and anode material (fig.2).

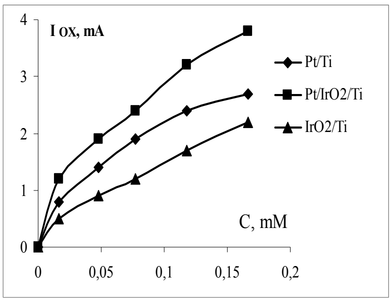

Fig.1.

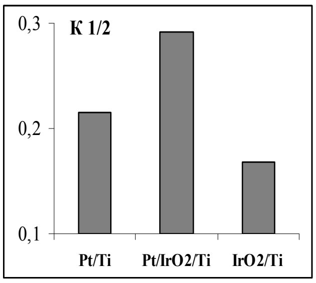

Fig.2

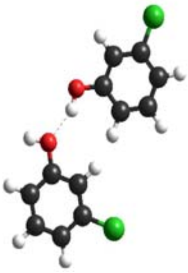

Fig.3

Using quantum-chemical calculations (HyperChem 8.0.8) we estimate intermolecular interactions (dimmers formation) and the role of Cl atoms. Energies of hydrogen bonds in X–X and in X-H_2O associates are the same. Value E_{X-X} for 3- and 4-CP differs from phenol. In case 2,4-DCP atom Cl participates in bonding, so distance R_{X-X} is increased (see table).

Molecule X	phenol	3-CP	4-CP	2,4-DCP	2,4,6-TCP
Dipole moment, D	1.165	2.814	2.045	2.678	1.089
E_{X-H_2O}, kcal/mole	–2.01	–1.71	–1.81	-	-
R_{X-H_2O}, Å	1.83	1.83	1.83	3.36	3.22
E_{X-X}, kcal/mole	–2.1	–3.9	–4.0	–1.9	-
R_{X-X}, Å	1.83	1.83	1.84	2.59	3.25

PP-88

Adsorption and Catalytic Activity of Nickel Nanoparticles Used as Catalyst for Hydrogenation of Unsaturated and Aromatic Hydrocarbons

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Adsorption properties of nickel nanoparticles mixed with silochrome C-120 in an amount of 15% by weight were investigated by method of inverse gas chromatography. Adsorbates were various saturated and unsaturated, aliphatic and cyclic hydrocarbons, consisting of 6 carbon atoms: benzene, cyclohexane, hexane, 1-hexene, 1-hexyne, 1,5-hexadiene, cyclohexene, 1,3-cyclohexadiene, 1,4-cyclohexadiene. These substances are reactants and products in the hydrogenation of hydrocarbons. Heat of adsorption and entropic components of adsorption were calculated. Shares of specific interactions of unsaturated hydrocarbons and the test adsorbent were determined. We can assume that the values of the specific interactions of sorbates with sorbent containing nickel nanoparticles are associated with the energy of formation of the activated complex on catalyst containing these nanoparticles.

Then, the catalytic properties of the catalyst containing 15% of the nikel nanoparticles were investigated in hydrogenation reactions 1-hexyne and benzene. The experiment showed that the reaction of hydrogenation of 1-hexyne proceeds rapidly even at 60 ^{0}C. Chromatographic analysis of the reaction mixture showed that 1 minute after the start of the reaction the 1-hexyne is absent in the reaction mixture. The main product of the reaction is hexane, hexene-1 and is also present in the reaction mixture. The result can be explained by using the data on the adsorption of reactants and products. 1-Hexyne has a larger proportion of the specific interactions with the sorbent containing nickel nanoparticles (40.7%), 1-hexene has a significantly smaller share of specific interactions (18.0%), hexene-1 therefore can be easily desorbed from the catalyst surface, 1-hexene must again adsorbed on the catalyst to continue the reaction. This reduces the speed of the process, but under certain conditions the selective conversion hexyne-1 to hexene-1 can be achieved.

The kinetics of the hydrogenation of benzene on this catalyst is different from the kinetics of the hydrogenation of 1-hexyne. The reaction takes place virtually without formation of intermediate products. This is partly due to the fact that the intermediates of hydrogenation of benzene have sufficiently high proportion of the specific interactions with the catalyst.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant № 15-43-02115.

Microkinetic Model Explaining CO Oxidation Activity and CORPOX Selectivity of CuO-CeO$_2$ Catalyst

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CuO-CeO$_2$ catalysts are prospective catalysts both for water-gas shift reaction and for preferential CO oxidation (COPROX). In recent years, there were a number of works dedicated to the identification of active sites and species involved in CO oxidation on CuO-CeO$_2$ catalysts [1,2]. However, the full mechanism of CO oxidation and the reasons for CO/H$_2$ selectivity remain unclear.

On the basis of literature data from DFT, experimental studies of CuO-CeO$_2$ catalysts and previously proposed CO oxidation models we construct a microkinetic model, which involves more than 100 reaction steps. We distinguish various active sites: CuO$_x$ fine species, bulk CuO species, ceria surface. The model accounts for oxygen exchange with ceria subsurface. After that, we fit the model parameters to the experimental data for CO low-temperature oxidation on copper-ceria and ceria catalysts, CO preferential oxidation on copper-ceria catalysts. We should note that it is not the common "fitting-the-curve" study. Search ranges for the values of the kinetic parameters are taken from the literature, the special database being constructed for that purpose. At the initial search phase we investigate points from quasi-random Sobol sequence, which helps to investigate the parameter space more efficiently [3]. Then, the evolutionary optimization algorithm starts working. The objective function is formulated so as to include thermodynamic constraints (thermodynamic consistency estimate) and the experimental information on oxidation state of copper during reaction.

At last, the analysis of the obtained model is performed to investigate main pathways for CO and H$_2$ oxidation. We reduce the model to make it usable in computational fluid dynamics. The whole task is solved in our problem-oriented software mech_optimiz$^{©}$.

The resulting model is known to be capable to predict CO and H$_2$ conversion for CuO-CeO$_2$ with Cu loading below 10 wt% in CO/H$_2$/O$_2$ mixtures. Also, it captures the inhibiting effect of CO$_2$/H$_2$O. We hope that the model would be useful both for further mechanistic investigations on CuO-CeO$_2$ catalysts and for the practical needs.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 14-07-00960.

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PP-90

Generation of $ZnO.CuO.K_2O/SiO_2$ Catalyst Activity during Methanol Dehydrogenation to Formaldehyde

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Catalytic activity of the model supported catalyst in reaction of methanol dehydrogenation to obtain formaldehyde was determined in the temperature range 400-500 °C at keeping the catalyst in a reaction mixture during several hours. The change in catalyst activity towards a target product until reaching stationary value of productivity is achieved by varying the quantity and the ratio of the components applied on it. It is at this stage that partial reduction of metal oxides and the formation of surface hydrocarbons up to a coke layer appearance take place.

Dehydrogenation of methanol occurs via a step-by-step splitting out of hydrogen atoms to form methoxy- and formil groups that produce formaldehyde during desorption and surface polyoxymethylene fragments during polymerization. The latter are not stable compounds and gradually undergo compaction to form carbonaceous compounds, giving off carbon dioxide and hydrogen. One observes certain fluctuations in the concentration of the reaction products during the experiment carried out at a constant temperature. These facts can be attributed to the formation and growth of a new phase. On that account, fluctuations in the velocity symptomatic of the solid phase growth is meaningful for its formation on the catalyst surface.

Along with hydrogen and formaldehyde, a small amount of dimethyl ether is formed on these catalysts. The primary direction of the reaction is due to both catalyst formulation and preparation and the composition of the feed gas. Making carbon monoxide a component of the initial mixture increases significantly activity of copper-containing systems relative to formaldehyde. Hydrogen being the product of the main dehydrogenation reaction of methanol, the gain in its concentration in the feed gas mixture lowers the rate of the target route. Hence, the mutual influence of gas components provides the acceptable level of catalyst activity under conditions of reducing reaction environment.

Potassium being an active element in reactions of transformation of carbonaceous compounds, the approach of a stationary regime occurs much quicker. There are different ways to make potassium a component of the catalyst: first, preliminary impregnation of a carrier with silicate and carbonate compounds followed by its heat treatment; secondly, by means of a simultaneous insertion of potassium carbonate and ammonical carbonate solution of copper and zinc. Potassium compounds with copper and zinc oxides forming no solid solutions during heat treatment, their phases will be segregated. At preliminary application of potassium which is uniformly distributed on the surface of the carrier, its efficiency in the catalytic reaction being higher. Clearly, testing of potassium-containing samples demonstrates that $CuO.ZnO/K_2O/SiO_2$ type catalysts with potassium introduced by means of preliminary impregnation of porous silicagel, highlight better catalytic properties such as selectivity, activity and stability when the composition of the original feed mixture is varied.

Mechanisms of the Phase Transitions of Gibbsite and χ-Al_2O_3 into Boehmite under Hydrothermal Treatment in an Aqueous Suspension

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An important place in catalytic processes of the petrochemical synthesis, performed in a fluidized bed, is occupied by microspherical catalysts based on aluminum oxide supports with a γ-Al_2O_3 structure. The precursor phase of γ-Al_2O_3 is boehmite, which can be produced by recrystallization of gibbsite or χ-Al_2O_3. The phase transitions mechanisms of gibbsite into boehmite and χ-Al_2O_3 into boehmite are different. In the former case, the gibbsite-to-boehmite phase transition takes places the dehydration of gibbsite. In the later case, phase transition of the χ-Al_2O_3 into boehmite is accompanied by the hydration of χ-Al_2O_3.

The effect of the hydrothermal treatment conditions of gibbsite and χ-Al_2O_3 floccules at T = 150–210°C, P = 1.0–1.9 MPa and pH = 4.0 – 10.0 on the phase composition of products obtained was studied. It was established, that the phase transition of gibbsite into boehmite occurs by the dissolution–precipitation mechanism upon delamination of gibbsite crystals along the (001) plane forming a multitude of layers with thicknesses of 20–100 nm and cracks in between them, with widths of 10–50 nm. Upon the dissolution of gibbsite $[Al(OH)_4]^-$ anions release into solution and react with protons of hydroxyl groups on the (001) planes of gibbsite, with the subsequent nucleation of boehmite and growth of its crystals. The crystallization of coarse boehmite particles favors formation of nonporous floccules. Boehmite particles don't form strong crystallization bonds with each other, which lead to decrease of their abrasion resistance.

Boehmite and bayerite are the products of the hydrothermal treatment of χ-Al_2O_3 in water suspension. Hydroxides are formed together by the parallel routes by dissolution-precipitation mechanism around the surface of particles without release of alumina ions into the mother liquor. Under the hydrothermal treatment needle-like crystals of bayerite with length of 10 nm are formed. Favorable conditions for the bayerite formation are treatment at the 150°C and pH = 4.0, under which the concentration of bayerite during 180 min is constant and reaches the (6 – 8 wt %). Bayerite is undergone to phase transition into boehmite at the 180 – 200°C and pH = 6.0 – 10.0. Concentration, form and coherent scattering region sizes of boehmite forming particles depend on pH value and time of hydrothermal treatment. At the pH = 8.0 – 10.0 the three-dimensional boehmite particles are formed as parallelepipeds with edge size ≥ 200 nm and coherent scattering region sizes of 49 to 85 nm along the (020) plane and 39 to 64 nm along the (120) plane. At the pH = 4.0 – 6.0 two-dimensional boehmite particles are formed as rhombic plates with the edge size of 80 to 500 nm, the width of 20 to 100 nm and coherent scattering region sizes of 27 to 32 nm along the (020) and (120) planes.

PP-92

Heteropoly Compounds of Tungsten and Molybdenum Modified Containing Rare-Earth Elements as Active Catalysts of Oxydation Unsaturated Alicyclic C6-C12 Hydrocarbons in the Presence of Hydrogen Dioxide

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The increasing demand of various sectors of the economy for the oxygen-containing organic materials determine the need to build their production capacity. This sets the problem of the chemical industry to expand the already existing processes for the production of oxygen-containing organic materials, as well as to bring forward the introduction of new methods of their production using environmentally friendly oxidant, such as oxygen from the air and hydrogen peroxide, with application of new efficient catalytic systems. Oxidation processes involving hydrogen peroxide occur under mild conditions and with high selectivity for target products.

Compounds Mo^{+6}, W^{+6} both salt and complex compounds, form the heteropoly compounds (HC) of various structure, which successfully are used in oxidizing reaction of saturated and unsaturated hydrocarbons. HC can be used both in a condition of soluble heteropoly acids (HA) and in the form of hydrogenizated systems.

We synthesized catalyst systems by reaction of compounds $(NH_4)_6Mo_7O_{24}$ with rare-earth elements in the presence an aqueous solution of ethanedioic acid at the temperature of 90-95^{0}C, with subsequent evaporation of the solution up to forming HC. containing rare-earth elements. Water environment helps to form the condensed multinuclear anions in the composition of which hydroxy group is wholly absent, and M-O-M or M=O fragments constitute the basis. anionic fragment of heteropoly compounds $[Mo_7O_{24}]^{6-}$ have regular geometric shapes and consist of octahedral $[MO_6]^{6-}$ and tetrahedron $[MO_4]^{2-}$. Iso-poly-anion has the spaces between octahedral where can be implemented successfully other heteroatoms, in particular rare earth metals such as Nd, Ce and La. In HC of such type, heteroatoms are located in tetrahedral or octahedral cavities of anion which are formed by oxygen atoms in nearby octahedra.

Oxidation of alicyclic unsaturated hydrocarbon by 30% aqueous solution of hydrogen peroxide was carried out in a thermostated glass microreactor with the volume of 100 cm^3 and equipped with a dropping funnel, a condenser, a thermometer and a magnetic stirrer for intensive mixing. Pre-determined amount of cyclohexane or dodecene and the catalyst was placed into the reactor and at a temperature 40-50^{0}C hydrogen peroxide was added drop by drop. During the reaction, the temperature was increased up to 60-80^{0}C. The concentration and the flow of the hydrogen peroxide was monitored by the method of the iodometric titration. Conversion of cycloolefins reached 25% of weight. The main products of the reaction are relevant oxides (86-92%). In the capacity of a by-product the relevant vicinal diol is formed.

Experimental data show that the heteropoly compounds modified by rare earth elements as catalysts of oxidizing reaction of cycloolefins show a high selectivity in comparison with the unmodified samples.

The Radical Nature of Cobaltmolibdenum Cataysts

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Question of synthesis and study of paramagnetic properties of previously studied geteropoly compound different structural type are very relevant .From numerous studies it is known that the main role in oxidation reactions olefins, obtaining acetals, epoxides it is the active complex Mo^{82} ,promote active cobalt .However in what form is included in the complex cobalt and its role in the activation and of catalytic process it is certainly not found.

The purpose of this work is to study the ESR spectra newly synthesized cobaltmolibdenum catalysts, to denermine the paramagnetic centers and radicals determine their nature and concentration. In Fig.1. provides the ESR spectras of cobaltmolibdenym catalysts with different ratios of cobalt: (1:1) by scheme I (fig.1) and (1:3) by scheme II (fig.2):

$(NH_4)_6Mo_7O_{24}+CoBr_2=(NH_4)_4CoMo_7O_{24}+2NH_4Br$(I),
$(NH_4)_6Mo_7O_{24}+3CoBr_3=Co_3Mo_7O_{24}+6NH_4Br$ (II)

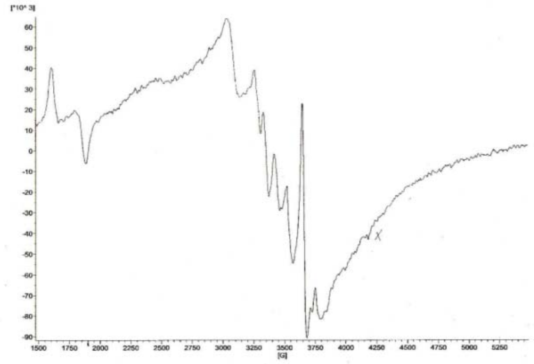

Fig.1

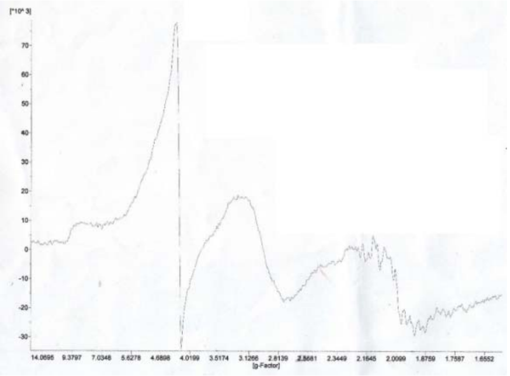

Fig.2

As shown in fig.1 the ESR spectra have a total length of 265 mTs. The spectra consist of two signals : of triplets a width line equal to 20 mTs from the Co^{+2} ions with g = 4,25 and broud line of equal 80 mTs with g=2,0039 typical for molybdenum ions .The spectrum of cobaltmolibdenum complex is a superposition of several radicals of which signal with a width of 5 mTs according to some authors belongs Mo^{5+},which realized short bond M_o =0. The rest of ESR lines presumably formed electron hole centers , generated mainly in in polycrystalline cobaltmolibdenum catalysts .In fig.2 also shown that the concentration of Mo is significantly reduced and the spectrum clearly appears superhyperfine structure the radical Co^{+2}. Increasing the concentration of Co^{+2} in relation to Mo spectra ESR will contain only radical from Co^{+2}. Increasing Co content relative to Mo from 1:1 to 3:1 results in increasing the conversion of the substrate to 10-15% in oxidation reactions of saturated and unsaturated hydrocarbons.

PP-94

Thioarylation of Vinyl Bromides Catalyzed by Pd-Polypyrrole Nanocomposite

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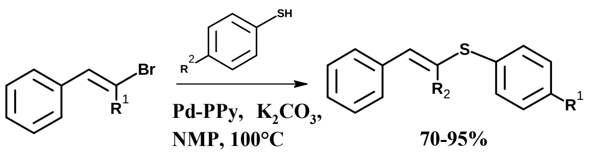
Elucidation of the mechanism of a multistep catalytic process is a complicated but very important issue since it is a straight way to a rational design of an efficient process. Catalytic Csp^2–S bond formation is synthetically important process but only few publications on the elucidation of its mechanism can be found in literature. Here we report our recent results on the reaction of vinyl bromides with S-nucleophiles catalyzed by new palladium polypyrrole nanocomposite. The composite can be obtained via direct redox reaction between palladium (II) salt and pyrrole monomer in organic or aqueous medium. Oxidative polymerization of heterocyclic monomer by metal ions results in formation of non-toxic conducting polymer matrix which stabilizes Pd(0) nanoparticles and prevents their aggregation (Fig.1). This allows avoiding an addition of surface stabilizers (as it is often the case in preparation of stable nanosize systems) since thus formed conducting polymer matrix itself stabilizes nanoparticles. Formation of the metal surface free of adsorbates is promising for catalytic application.

New Pd-polypyrrol nanocomposite is efficient in thioarylation of a wide range of vinyl bromides; the yields of arylvinylsulfides are high enough (70-95%). Screening of base showed that the maximal efficiency was obtained using K_2CO_3. An important feature of the process is stereoselectivity: the configuration of the starting halide is reserved. The kinetics of the thioarylation of β-bromosterene was studied in a temperature range of 353-403K; the activation energy of the reaction was found to be 71 kJ/mol.



R_1 = H, Ph, COOMe, R_2 = H, Me, NH_2

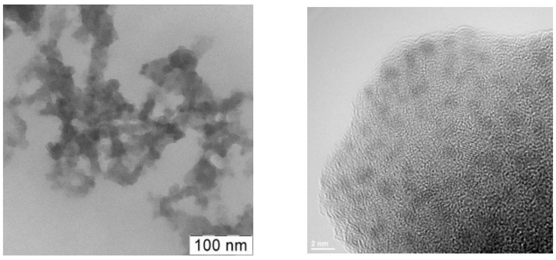


Figure 1. SEM and TEM images of Pd- polypyrrol nanocomposite

This work was supported by the Russian Foundation for Basic Research (Project № 15-03-06351-a) and Russian President Foundation (Project № MK-4875.2016.3)

Means of Influencing an Efficiency of Alkynol Hydrogenation over Polymer-based Pd Catalysts

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Selective hydrogenation of unsaturated carbon-carbon bond using Pd nanoparticles (NPs) is of great importance as widely applicable in synthesis of fine chemicals, vitamins and pharmaceuticals. However, to achieve high selectivity along with high activity is still a challenge, which requires a careful choice of catalyst and reaction conditions.

In spite of numerous data on the hydrogenation of alkynols [1-4], it is still a challenge to achieve high selectivity in hydrogenation of terminal alkynes. On the other hand, the analysis of all possible factors influencing the alkene selectivity (the ability to form a certain hydride phase, the preferential alkyne adsoprtion, definition of small ensembles in order to reduce oligomerization [5]), the size of Pd NPs seems to be the key factor of a triple bond hydrogenation. At the same time, another challenge is to provide high stability of catalytically active Pd NPs, as carbonization of palladium surface as well as sintering and leaching of NPs often cause the loss of catalytic activity and selectivity at multiple reuses.

Kinetic studies allowed us to better understand the influence of the reaction parameters on the catalytic reaction of selective hydrogenation of alkynol C5 while using polymer-based Pd-containing catalysts. Developed catalysts were found to contain Pd NPs with mean diameter of 3-5 nm and provide high selectivity (up to 98.5% at 100% of the substrate conversion). It was shown that the right choice of the substrate-to-catalyst ratio is of a crucial importance. Another important parameter was the reaction temperature, which influences the reaction rate constant and also changes the adsorption-desorption equilibrium of the substrate and hydrogenation product, thus altering the process selectivity. The predominant influence of the thermodynamic factor (the strength of the alkynol C_5 adsorption) was also confirmed by studying the hydrogen consumption rate, which was carried out in detail for the first time for this reaction in a batch mode, as well as by the results of kinetic modeling.

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

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PP-96

Development of XPS Method for Study of Supported Metal Catalysts

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In this work, a new approach to the study of model supported metal catalysts by the XPS method is discussed. The originality of the work is to use AgL$_\alpha$ monochromatic radiation as a radiation source. This is fundamentally important for the platinum catalysts on aluminum-containing carriers since the use of conventional X-ray radiation based on Al or Mg anodes does not allow correctly interpreting the data on the electronic state of Pt due to overlapping the Pt4f and Al2p spectral lines. When using AgLα (hν = 2984.3 eV) as the radiation source, the Pt3d$_{5/2}$ and Al1s lines which differ significantly in energy can be analyzed [1]. FWHM of the Pt3d$_{5/2}$ line in the studied compounds and catalysts is higher than that of the MgKα-excited Pt4f$_{7/2}$ line by approximately 1.5 eV. Nevertheless, the use of AgLα irradiation for measurement of the Pt3d$_{5/2}$ spectra might be very helpful for the Pt/Al$_2$O$_3$ catalysts and many other particular systems where the Pt4f doublet line is strongly screened by the Al2p line, so the researchers have to analyze the broad Pt4d$_{5/2}$ line (FWHM of 4.5 – 5.0 eV) instead. It is shown that this method allows to analyze the electronic state of platinum in Pt/Al$_2$O$_3$, Pt/MgAlO$_x$, Pt/Mg(Zn)AlO$_x$, Pt/MgAl(Ga)O$_x$ and other aluminum-containing oxide catalysts.

However, for studying the systems that actively interact with atmospheric gases (oxygen and water vapor), XPS facilities are very limited. Working with such materials requires special chambers with controlled atmosphere, the glove box, and transport of the samples to the spectrometer is an important problem because the ordinary commercial devices involve loading the samples in contact with atmospheric gases. The important feature of this work is the ability to load samples directly from the reactor to the spectrometer in an inert dry medium, which excludes contact with atmospheric gases. The autonomous mobile glove box system was designed and constructed by the authors for XPS SPECS spectrometer. Samples were loaded in the spectrometer via fast entry lock system. This system enables to investigate the supported catalysts sensitive to both oxygen and water vapor. The original results for a number of model Ziegler type Ti-based catalysts for ethylene polymerization were obtained.

The combination of the above approaches can significantly extend the capabilities of the XPS method for study supported metal catalysts, bringing the conditions for obtaining the spectral data, in fact, to operando studies of model and real catalysts.

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PP-97

The Mechanisms of Ortho-Para Protium Conversion Reaction on Gold Nanoparticles

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Every year, an increasing number of articles of studying the adsorption and catalytic properties of gold nanoparticles in various reactions appear [1, 2], whereby inert metal becomes available for use as a catalyst, including reactions with molecular hydrogen, such as deuterium-protium exchange reaction and ortho-para protium conversion reaction. The reaction of deuterium-protium exchange runs only on chemical [3, 4] mechanisms, while ortho-para protium conversion reaction able to run both in the chemical and magnetic mechanisms [5].

In this work, ortho-para conversion reaction catalyzed by gold nanoparticles measuring 0.7 to 40.1 nm, synthesized by different methods and supported on γ-Al_2O_3 were studied.

Ortho-para protium conversion reaction under static conditions without gas circulating at pressure 0.5 Torr and temperature of 77 K was investigated.

The results of our studies indicate that the rate of ortho-para conversion reaction not dependent on particle size in the size range from 0.7 to 40.1 nm, in contrast to the deuterium-protium exchange reaction, having a positive size effect.

The difference between the specific catalytic activity values for both reactions at 77 K varies from a factor of 2 (for particle size d=0.7 nm) to a factor of 1000 (for particle size d=40.1 nm).

The rate of ortho-para protium conversion reaction increases by 60% when subjected to an external magnetic field of magnitude 700-800 Gauss.

Thus, we can assume that the reaction of ortho-para conversion proceeds on the magnetic mechanism.

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PP-98

Design of PdZn/(Ti,Ce)O_2 Coating Doped with Cerium and Comparative Kinetic Study in the Selective Hydrogenation of 2-Methyl-3-butyn-2-Ol in Microcapillary Reactor

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To intensify processes in fine chemical synthesis, microfluidic technologies were recently developed. The selective hydrogenation of 2-methyl-3-butyn-2-ol(MBY) in methanol on $Pd_{25}Zn_{75}/TiO_2$ and Pd/TiO_2 thin films has been previously investigated in the capillary microreactors with diameter 250 μm [1]. To perform hydrogenations in a microreactor, Ce-doped titania films were recently prepared via evaporation induced self-assembly [2]. In this paper we propose Ce-doped titania coating as catalyst immobilization matrix on the walls of a microcapillary reactor. We report on a comparative study on the catalytic activity and selectivity of Pd and $Pd_{80}Zn_{20}$ particles embedded onto Ce-doped and pure titania in the hydrogenation of MBY in a stirred reactor at 5 bar and 333 K and in the microcapillary reactor. The effect of the MBY concentration on catalytic activity and selectivity was studied in the range from 0.04 to 0.3 M, the hydrogen partial pressure in the range from 0.28 to 0.1, and the reaction temperature between 308 and 333 K.

This study demonstrated that the activity and selectivity of the thin coatings deposited onto the inner surface of the microcapillary reactor in selective hydrogenation of MBY is strongly influenced by the catalyst composition. The highest activity was observed when Ce-doped TiO_2 matrix was used, with the activity sequence being: $Pd/(Ti,Ce)O_2 > Pd_{80}Zn_{20}/(Ti,Ce)O_2 > Pd/TiO_2$. The effect of Ce doping and Zn addition to Pd nanoparticles, as well as initial MBY concentration and hydrogen partial pressure, the reaction temperature on activity and selectivity to MBE was explained. The highest yield of MBE (94%) was obtained on the $Pd_{80}Zn_{20}/(Ti,Ce)O_2$ coating at 313 K and hydrogen partial pressure of 0.5. The proposed kinetic model suitably describes the kinetics of MBE hydrogenation. A higher activity of Ce-doped catalysts was explained by donation of electron density from Ce^{3+} to Pd and weakening of the binding with alkyne.

Acknowledgement. This work was supported by the Russian Academy of Sciences and Federal Agency of Scientific Organizations (Project V45.1.10).

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Mechanism of Hydrogenation of Butadiene-1,3 on Single-Atom Gold Catalyst: The DFT Study

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Despite of bulk gold is chemically inert, gold nanoclusters possesses high activity and selectivity in many catalytic reactions. Surprisingly, a single atom can exhibit a catalytic activity, for instant in hydrogenation of butadiene-1,3[1]. On gold atom supported on carbon nanotube (CNT), the process was experimentally investigated using PHIP (parahydrogen-induced polarization). It was found that hydrogen atoms which hydrogenate double C=C bonds may belong to different H_2 molecules. The real mechanism of the butadiene-1,3 hydrogenation including the active site and the rate-determining step has not been understood until yet. Here we present the theoretical insight on the mechanism of multistep hydrogenation of butadiene-1,3 to butene-1, *cis*- and *trans*-butene-2 on Au and Au/CNT models.

The study was performed with the DFT/PBE96 level using the PRIRODA code[2]. Valence shells of all atoms were described with extended basis sets: Au [51111/51111/5111], C [311/311/11], and H [311/1]. Core electrons of Au and C atoms were described by the SBK pseudopotential. We used this level of theory in our previous papers to model isomerization of allylbenzene[3] and butene[4] on the gold atom. The structures of initial compounds, intermediates, products and transition states were optimized, and the total energy including the zero-point vibrational energies were calculated.

In this paper we considered the «pairwise» H_2 addition to double bond of hydrocarbon. The steps of butadiene-1,3 hydrogenation to the *cis*- and *trans*-butene-2 on Au catalyst were investigated. The process is described by the metal-hydride mechanism and occurs through the HAuH and AuH_2 complexes. It begins with the activation of the double C=C bond of hydrocarbon on Au atom. After the reaction and dissociation of H_2 on π-AuC_4H_6 complex, the two-hydride HAuH-C_4H_6 complex is formed. We found two alternative pathways of HAuH-C_4H_6 transformation to butene. The subsequent hydrogenation of C_4H_8 to C_4H_{10} is also found to be probable. It was found that for *cis*- and *trans*-pathways ΔE and E_a of the corresponding steps have the similar values.

Based on the obtained results, the assistant of two H_2 molecules in the butadiene-1,3 hydrogenation observed on Au/CNT is simulated. We suppose that gold atoms supported on CNT play different role in the hydrogenation; one of gold atoms only adsorb and activate hydrocarbon, while another atoms are active sites of H_2 dissociation. It is the field for further theoretical investigations.

Considered mechanism of butadiene-1,3 hydrogenation on Au atom explains the formation of butene-1 and butane in the case of «pairwise» H_2 addition to double bond of hydrocarbon. However, using the simple model, gold-hydride-allylic complex is predicted to be a key intermediate.

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PP-100

The Selectivity and Stability of Skeletal Nickel in Reactions of Nitro Reduction in the Presence of Catalyst Poisons

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It is found the activity of nickel catalysts rather strongly depends on the nature of the medium and on the presence of catalyst poisons in the system [1]. According to the previously conducted experiments and the literature [2] sulphur compounds physically blocks the active sites of the surface with a certain energy and takes them out of the reaction zone. Thus, it can reasonably be argued that a purposeful introduction into the reaction the catalyst poisons can influence not only on the activity, but also on the selectivity of the transition metals.

The objective of the work is studying of activity, selectivity and stability of skeletal nickel catalyst in separate and in joint reactions of reduction of the nitro group and of the double bond "carbon-carbon" at the presence of sulphur compounds.

We used a skeletal nickel catalyst obtained by treating a nickel-aluminium alloy (mean particle radius is 4.8 μm) of sodium hydroxide (specific surface is 170±2 m^2/g, a porosity is 0.50±0.1). All experiments were carried out at atmospheric pressure and at a temperature 303K in an aqueous solution of 2-propanol. 4-nitrotoluene and maleic acid dimethyl ester (MADE) were selected as compounds for hydrogenation. Reduction processes of them are fairly well known. Methods of the kinetic experiment is described in the [1]. Analysis of quantitative and qualitative composition of the reaction samples was performed by liquid chromatography («Shimadzu LC-6A»). Stability of partially deactivated nickel work was tested by carrying out the reaction under extreme conditions (high pressures and temperatures, as well as the increased load on the catalyst of the compounds for hydrogenation).

Experimental data obtained in the work confirms the fact that the partial targeted deactivation of skeletal nickel by sulphide ion allows to receive a catalyst with predetermined parameters of activity and selectivity in the reduction reactions. For example, ultra-small amounts of Na_2S increases the catalytic activity of skeletal nickel in the hydrogenation reaction of 4-nitrotoluene almost 1.5 times. Furthermore, it was found that the treatment of skeletal nickel by sodium sulphate does not lead to increased stability of the catalyst during sequentially hydrogenation of MADE, while the reduction of 4-nitrotoluene the stability of the catalyst was greatly increased.

Acknowledgement. This work was carried out at the Laboratory of Adsorption Processes and Heterogeneous Catalysis of Research Institute of Thermodynamics and Kinetics of Chemical Processes as part of a state assignment, project no. 1800.

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Isomerization of n-Butane on Pd-SZ Catalyst. Effect of Reaction Conditions

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Nowadays, n-butane isomerization on Pt-modified sulfated zirconia catalysts (Pt-SZ) is intensively studied. Due to the unique acid–base properties sulfated zirconia (SZ) may have significant potential for use in industrial processes, provided that high activity of the catalysts shall be ensured [1]. It was reported in [1, 2] that high activity and stability of Pd-modified catalyst Pd-SZ can significantly improve the process of n-butane isomerization.

The prospects for industrial implementation of the process require further in-depth kinetic studies; this was the main goal of the present work.

Isomerization of n-butane over Pd–SZ catalyst (Pd load 0.35 wt.%) was studied in a flow-type fixed-bed reactor within 5÷25% n-butane conversion range. Catalyst preparation procedure, its physical–chemical characteristics and details of the lab-scale setup have been specified in [1]. The influence of parameters on the reaction rates and products selectivity was investigated by varying n-butane WHSV 1.3-11.1 h^{-1}, temperature 125-160°C, molar ratio H_2/C_4 0.1-1.0, and pressure 6–25 bar. For kinetic studies, the catalyst granules were crushed and sieved as 0.25÷0.5 mm fractures. To verify possible subsequent transformations of iso-butane on Pd-SZ catalyst at n-butane isomerization conditions, additional experimental studies of pure iso-butane conversion were performed. No significant catalyst deactivation was observed during the long-time operation on-stream at standard experimental conditions: at a total pressure 24 bar, molar ratio H_2/C_4 0.2 and temperature 150°C.

Along with kinetic investigations, the contribution of mono- and bimolecular mechanisms in isobutane formation, as well as the impact of parameters on the changes in isomerization mechanism were analyzed. On the background of experimental kinetic studies on Pd-SZ catalyst, a simplified kinetic model of n-butane isomerization was elaborated and a set of kinetic parameters was evaluated by by means of the standard computer procedure.

Acknowledgement. This work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (project V.46.2.6).

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PP-102

In-Situ XPS Study of a New Phenomenon of Kinetic Hysteresis over Pt, Rh Catalysts in Selective Methane Oxidation

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Recently, we discovered a new phenomenon of kinetic hysteresis in selective oxidation of methane over platinum catalysts [1,2]. We found that the activity and selectivity of the platinum catalysts in a steady state depends greatly on a way of achieving the steady state. Using this hysteresis one can directly control the selectivity and activity of the platinum catalyst even with low initial activity, improve the conversion from 10 to 90%.

To establish the reasons of this phenomenon, we studied changes in oxidation state of the active component in real platinum and rhodium catalysts by *in-situ* X-ray photoelectron spectroscopy (XPS).

In-situ XPS experiments were carried out on a photoelectron spectrometer VGESCALAB "High Pressure" [3] equipped with a special high-pressure cell and a quadrupole mass spectrometer with two-stage differential pumping and high-precision mass flow-controllers. Experiments were conducted at constant methane concentration (partial pressure of about 0.008 mbar) with varying the O_2:CH_4 ratio in the range from 0.2:1 to 2:1.

Previous studies of the hysteresis were conducted in reactors at the atmospheric pressure. However, our *in-situ* XPS experiments showed the presence of similar kinetic hysteresis at low pressures. Study included testing possible catalytic activity of the alumina support and *in-situ* cell. It was shown that the pure support and *in-situ* cell were not active in the reaction. The experimental data showed that the activation was associated with predominant formation of the metallic form, whereas oxidation of metal species was responsible for a less active state. The reaction mechanisms for explanation of these data are discussed.

Acknowledgement. V.N. Parmon appreciates financial support of the Russian Science Foundation (grant 14-13-01155). I.Yu. Pakharukov and I.P. Prosvirin appreciate financial support Russian Academy of Sciences and Federal Agency of Scientific Organizations (projects V.45.3.2. and V. 44.1.15, respectively).

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PP-103

The Influence of Preparation of Co-Fe/Spinel FTS Catalysts on Physico-chemical Properties: Mossbauer Spectroscopy and XPS

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Many researchers have attracted the attention to magnetic materials because of their unique and excellent physical and chemical properties, such as high surface area, great degree of reduction, superparamagnetism etc. It's worth to note, that the Fe–Co bimetallic catalysts with or without promoters favors the formation of C_2–C_4 alkenes in Fischer–Tropsch Synthesis because of formation of Fe–Co alloy. It's known that the addition of small amounts of Co to iron-based catalyst results in an enhanced activity and selectivity compared with the individual metal oxides.

At present study the physico-chemical properties of the Fe-Co/spinel systems were investigated by several methods: magnetometric method *in situ*, Mossbauer spectroscopy and XPS. Three 3%Co-7%Fe/support catalysts were prepared by co- and sequential impregnation of 0.5%$MgO \cdot A_2lO_3$ support by aqueous solution of Co and Fe nitrate salts [1].

It was shown by magnetometric method *in situ* [2] that the CoFe/support catalyst had the highest reduction degree, if iron was impregnated on the support at first. It was suggested that cobalt is surface promoter of iron-supported catalysts. The XPS results quantitatively confirms this conclusion. The results of Mossbauer spectroscopy showed that the size of oxide particles of the catalysts prepared by sequential impregnation was much larger (the spectrum form – sextet) than one of the catalyst prepared by co-impregnation (the spectrum form – doublet). In the latter case the size of catalyst particles is close superparamagnetic particles ($d < 7$ nm).

Carbidization of catalyst during Fischer-Tropsch synthesis was also investigated by magnetometric method *in situ*. The minimum value of activation energy of catalysts carbidisation observed for specimen in which iron was impregnated at first and this catalyst has the best catalytic activity compared with other catalysts. Thus, the effect of surface modification by promoter (Co) on the properties of iron-based catalyst in CO hydrogenation was demonstrated. The change in physical and chemical properties of catalysts can be explained by the structural and electronic effects of promoter.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research (Grant №16-03-00215a).

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PP-104

Mechanisms of Metallocene Catalysis in Reactions of Alkene Functionalization by Organoaluminum Compounds

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Catalytic systems based on Ti subgroup metallocene complexes and organoaluminum compounds are well known and widely used in modern chemistry, primarily in Ziegler-Natta type polymerization, di- and oligomerization, as well as hydro-, carbo- and cyclometalation of unsaturated compounds [1, 2].

The report presents recent advances on the experimental and theoretical research of the mechanisms of alkene hydro-, carbo- and cycloalumination, catalyzed with zirconocene complexes. Various intermediates of bimetallic structure were found to be the active sites of the reactions. DNMR studies on the exchange processes showed the effect of the intra- and intermolecular dynamics in the bimetallic complexes on the activity of the metallocene catalytic systems. In the framework of these studies a high efficiency of chiral Zr complexes as the stereochemical tests of the reaction mechanisms was demonstrated. The structures of the catalytically active centers were proposed and probability of the reaction pathways was estimated using quantum chemistry methods.

Comparison of the catalytic action of conformationally labile Zr complexes and complexes with a fixed geometry in the reactions of alkenes with AlR_3 (R = Me, Et) revealed a significant influence of a ligand mobility on the activity of the studied catalytic systems and the degree of asymmetric induction.

Thus, the current models of Ziegler-Natta type catalytic processes requires the consideration of the contribution of bimetallic structures as catalytically active centers formed by the interaction between the metal complexes and organoaluminum compounds, as well as accounting the features of σ- and π-ligand dynamic processes occurring in the intermediates. Studies on the Ziegler-Natta catalysis from these positions will help to solve the existing problems in the development of new catalytic systems and methods for the synthesis of practically important products and materials.

Acknowledgement. This work was supported by the Russian Foundation of Basic Research, grants 15-03-03227a, 16-33-00162mol_a, 16-33-60203mol_a_dk).

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The Kinetics of Glycidol Obtaining by Allyl Alcohol Epoxidation by Hydrogen Peroxide on Titanium-containing Zeolite Catalyst TS-1

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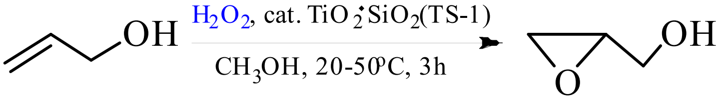
The glycidol and other epoxides (ethylene oxide, propylene oxide, epichlorohydrin, etc.) are important intermediate products of basic and fine organic synthesis. One of the methods for glycidol producing is liquid-phase epoxidation of allyl alcohol by hydrogen peroxide on titanium-containing zeolite catalyst TS-1. Deterrent to the use of this catalyst in industrial scale has been the lack of granular form. Recent work [1] aimed at obtaining a granular form of the catalyst, exhibiting high activity and selectivity in the epoxidation processes, remove this restriction. Therefore, of particular practical importance are kinetics studies of this process.



Based on the literature data [2] proposed several structural kinetic models. The results of the univariate experiments series determined the optimal model parameters that best describe experimental data. Hypotheses discrimination made on statistical criteria. To confirm the working hypotheses were conducted additional experiments.

Acknowledgement. This study was supported by the Ministry of Education and Science of the Russian Federation (grant agreement no. 14.577.21.0093, unique project identifier RFMEFI57714X0093).

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PP-106

Kinetics of Allyl Chloride Epoxidation with Hydrogen Peroxide Catalyzed by Extruded Titanium Silicalite

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Among the α-oxides, epichlorohydrin (ECH) is the world's third most abundant industrial product, exceeded only by ethylene oxide and propylene oxide. The world ECH output is estimated at >1.8 million tons per year. Owing to its molecule having an epoxide group and a mobile chlorine atom, epichlorohydrin reacts readily with various classes of compounds, making it possible to synthesize a number of epichlorohydrin-based products demanded by many industries (epoxy resins, varnishes, glues, synthetic fibers, rubbers, etc.). While ECH is used to obtain a really wide variety of products, over 80% of the epichlorohydrin output is consumed in epoxy resin production.

The most interesting method of producing epichlorohydrin is the liquid-phase epoxidation of allyl chloride with hydrogen peroxide, an environmentally friendly oxidizer, in the organic solvent methanol in the presence of titanium silicalite

The formation of the target product is accompanied by a number of side reactions yielding 1-chloro-3-methoxypropan-2-ol, 1-chloropropane-2,3-diol, and small amounts of other compounds. In addition, one of the reaction products is oxygen.

We study the kinetics of the liquid-phase epoxidation of allyl chloride with an hydrogen peroxide solution in an organic solvent in the presence of extruded titanium silicalite as the heterogeneous catalyst and to construct a kinetic model of this process.

In order to determine the parameters of the model suggested and to check its adequacy, we carried out several series of experiments differing in initial conditions. In these experiments, we varied the catalyst bed height, volumetric feed flow rate ($(2–14.8) \times 10^{-5}$ L/s), temperature (30–60°C), initial hydrogen peroxide concentration (0.11–2.28 mol/L), initial allyl chloride concentration (1.37–4.86 mol/L), and methanol concentration (14.03–24.16 mol/L).

Statistical processing of the kinetic model using Fisher's test demonstrated that, at a significance level of 0.05, the model adequately describes the experimental data and provides means to predict the composition of the reaction mixture in a wide range of variable factors at different hydrogen peroxide conversions.

Acknowledgement. This study was supported by the Ministry of Education and Science of the Russian Federation (grant agreement no. 14.577.21.0093, unique project identifier RFMEFI57714X0093).

Catalytic Properties of Sulfur-containing Compounds on the Gold Nanoparticles Surface

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Nowadays metal-based nanoparticles electrodes are widely used for the electrochemical determination of biologically active substances. It is allowing them to be competitive in the methods along with electrophoretic and spectrophotometric ones. The electrodes modified with nanoparticles of noble metals exhibit specific adsorption and electrocatalytic properties different from the compact and disperse metals. In this paper the catalytic signals of thiol compounds on the graphite electrodes (GE) modified with gold nanoparticles.

Gold nanoparticles were prepared by chemical reduction in the absence of high-molecular stabilizers. Reducing agents are sodium borohydride and the sodium citrate at different molar reactant ratio of $HAuCl_4$: $Na_3C_6H_5O_7$: $NaBH_4$ by the procedure described in [1]. Characterization of gold sols was performed using transmission electron microscopy techniques (JSM-5500), spectrophotometry (Carry 80), pH-metry (pH-150 M), voltammetry (TA-2). Electrochemical measurements were performed in a three-electrode cell. The working electrode was a GE modified with gold nanoparticles, an Ag/AgCl reference electrode and a Ag/AgCl auxiliary electrode.

The GE was modified with gold nanoparticles by the following method. The GE is put into an electrochemical cell containing 10 ml of gold sol. The deposition of gold nanoparticles was carried out on the working electrode surface under the potential E = -1.0 V for 60 – 300 s. After the modification of the surface electrode is was removed from the solution, rinsed with double distilled water and placed in an electrochemical cell filled 0.1 M NaOH supporting electrolyte. Cyclic voltammograms of glutathione (GSH), cysteine (Cys) were registered under the following conditions: scan rate 0.100 $V \cdot s^{-1}$, potential range E = -1.0 V to 1.0 V.

There was wave at potential E = 0.2 V on the anodic branch of the cyclic curve on the surface GE modified with disperse gold. On the cathode branch of the cyclic curve at the GE modified with gold nanoparticles the wave was observed at potential E = 0.15 V. On the anodic branch of the cyclic curve at the GE modified with gold nanoparticle in the presence $1 \cdot 10^{-8}$ $moll \cdot l^{-1}$ the wave was observed at potential E= 0.2 V. On the cathodic branch of the cyclic curve at the GE modified with the wave is observed at potential E= 0,15 V.

Gold nanoparticles act as a mediator. On the anode branch of the cyclic curve at GE modified with the wave was observed at E = 0.0 V. On the cathode branch of the cyclic curve on the surface GE modified with gold nanoparticles inverse maximum was observed at E = 0.05 V. In the presence $2 \cdot 10^{-12}$ $mol \cdot l^{-1}$ Cys at GE a modified with gold nanoparticles on the anode branch of cyclic curve a peak was observed at E = -0.05 V. There was an inverse peak at a potential E = 0 V on the cathode branch of cyclic curve [2].

Thus, the potential of the anode wave of Cys on the surface GE modified with gold nanoparticles shifts to a more negative potential values. The potential of the cathode maximum of Cys was shifted to a more positive potential values. These facts indicate to the facilitation of the electrochemical oxidation and reduction processes, accordingly a decrease in the activation energy by increasing the the gold nanoparticles surface area.

In the presence $1 \cdot 10^{-8}$ mol·l^{-1} a wave observed at E = 0.3 V on the anode branch of the cyclic curve on the surface GE modified with disperse gold. The wave was observed at E = -0.15 V on the cathodic branch of the cyclic curve at GE modified with disperse gold. In the presence $2 \cdot 10^{-12}$ mol l^{-1} peak was observed at E = 0.1 V on the anode branch of cyclic curve at the GE, modified with gold nanoparticles There was an inverse peak at a potential E = 0.05 V on the cathodic branch of cyclic curve at the GE modified with gold nanoparticles [3]. There are similar effects in the presence of GSH at the GE modified with gold nanoparticles. I

The mechanism of electrocatalysis in the presence of thiols with a contribution adsorption and regeneration of the initial form of the catalyst:

$$6RSH + Au_2O_3 \leftrightarrows 3RSSR + 2Au + 3H_2O.$$

Thus, we have shown that thiol compounds exhibit catalytic signals of gold nanoparticles. The mechanisms of electroreduction and electrooxidation thiols were preposed. The use of gold nanoparticles allows increasing the sensitivity of detection of Cys and GSH on the order of 4 compared with compact gold.

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Effect of Potassium Modification on Electronic and Absorption Properties of Active centers of CoMoS Catalyst: A DFT Study

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Alcohols are widely used as solvents and starting reagents in many branches of industry. Synthesis gas, which is obtained from sulfur-containing natural raw materials, is a source for the production of alcohols; therefore, it can contain from a few to tens of parts per million of sulfur-containing impurities. The use of transition metal sulfides as catalysts for the synthesis of alcohols can solve the problem of catalyst resistance to sulfur [1]. In our previous studies the catalysts based on molybdenum sulfide of different compositions (promoted with Co and K) were synthesized and investigated [2]. Transmission electron microscopy data made it possible to quantitatively evaluate the effect of a potassium additive on the morphology of the active phase; the hypothesis that potassium was intercalated between the layers of molybdenum sulfide was proposed.

Density functional theory (DFT) calculations were successfully used to study structure and properties of mixed transition metal sulfide catalysts and their active sites [3].The effects of potassium (K) doping on the reactivity of CO hydrogenation over MoS_2(100) catalysts were investigated using periodic DFT calculations [4].

Using DFT approach we studied the effect of Co-Mo bimetallic sites modification by potassium. It was found that potassium donates electrons to *d*-orbitals of the metals of the bimetallic site and reduces oxidation states of the metal atoms. This decreases Lewis acidity and inhibits adsorption of CO and H_2 molecules (Fig. 1) but favors dissociative adsorption of H_2.

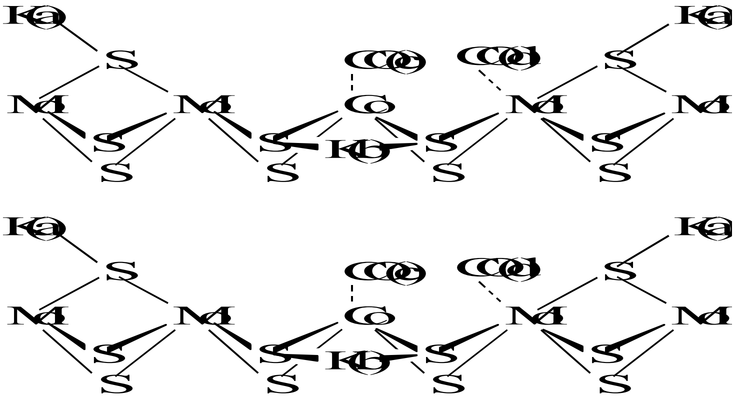

Figure 1. Structure of a bimetallic site on Mo-edge modified by potassium in two positions(a,b) and CO adsorption in two possible positions (c,d)

The reduced Lewis acidity of potassium-modified sites inhibits C-O bond cleavage, while reduced oxidation states of the metal atoms stabilize hydride atoms and other intermediates. This gives us ground to suppose that other electron donors could promote alcohol formation on CoMoS catalysts as well.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-13-12345.

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PP-109

Effect of Co/Mo Ratio on the Mo- and S-Edge Reactivity

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Hydrotreating is a key important process in oil refinery. In (Co/Ni)MoS/Al_2O_3 catalysts usually employed in this process the promoter atoms (Co or Ni) are located on the edges of the Co(Ni)MoS crystallites of the active phase with mobile SH groups [1]. Maximal TOF in DBT HDS is achieved at Co/Mo ratio on the on S-edge equal to 0.3-0.4 [2]. The dependence between catalytic activity and total SH group number was established [3]. As it was formulated in [4] and later supported by DFT calculations [5], the SH groups can react with hydrogen molecules forming active sites.

The higher catalytic activity observed on the samples with partially promoted edges comparing to that observed on the samples with fully promoted edges needs to be explained. In this work we report the results of DFT calculations of energetic profiles of the reactions of the SH groups with molecular hydrogen on M- and S-edges (Table 1).

Table 1. Activation energyof interaction of the SH groupswith H_2 on M- and S-edges at optimal sulfidation degree (eV).

Co : Mo ratio	M-edge (at sulphidation)	S-edge
Unpromoted	1.50 (S – 50 %)	0.88 (S – 62.5 %)
1 : 3	0.92 (S – 37.5 %)	-
1 : 1	0.35 (S – 25 %)	1.06 (S – 50 %)
4 : 0	-	1.47 (S – 50 %)

As it follows from Table 1 promotion of the M-edge by Co positively affects the SH + H_2 interaction whereas promotion of the S-edge demonstrates negative effect.

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Catalytic Activity of Anion-Exchange Resins in Disproportionation of Trichlorosilane

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Nowadays the most promising method for producing silane and dichlorosilane (DHS) is the catalytic disproportionation of trichlorosilane (TCS). For this process it is possible to use several types of catalyst, such as aluminum trichloride, heterocyclic or acyclic nitriles arena. However, they are a source of impurities in the reaction product. Thus, the use of organic homogeneous catalysts containing a nitrogen atom as a donor of an electron pair, there are difficulties associated with separation of reaction products from the reaction mixture. Therefore, interest in the non-volatile nitrogen-containing ion exchange resins, which, because of low volatility are not subject to reaction products and a matrix which is chemically inert with respect to chlorosilanes, have become the most popular in the process and used in all modern industries for derivatization chlorosilanes.

The work has been to study the kinetics of the reaction of the catalytic disproportionation of trichlorosilane on anion exchange vinylpyridine (VP-1P, VP-3P) and styrene (TOKEM 800, 840) resins. It is shown that the limiting stage of the process is the desorption of silicon tetrachloride with active sites of the catalyst. Samples of anion exchange resins have shown catalytic activity comparable to known literature by types of catalysts. It has been shown that the resin retains the catalytic activity in the temperature range from 80 to 120 °C for the vinylpyridine resins and from 60 to 100 °C for styrene resins.

It is found that the major products are silicon tetrachloride and dichlorosilane and their contents become stationary at the time of contact with the anion exchange resin for about 2 seconds.

The temperature dependence of the equilibrium constant for the disproportionation reaction of trichlorosilane and also found activation energy: 31 ± 3 kJ/mol (VP-1P), 35± 2 kJ/mol (VP-3P), 25±2 kJ/mol (TOKEM 800) and 27±3 kJ/mol (TOKEM 840). It has been shown that increasing the reaction temperature to 120°C catalytic disproportionation beneficial effect on the desired reaction kinetics when using vinylpyridine resins.

Acknowledgement. The reported study was funded by RFBR, according to the research project No. 16-38-60192 mol_a_dk.

PP-111

Structure-sensitive Reactions over Ceria-based Nanocatalysts: The Catalytic Oxidation of Soot and Carbon Monoxide

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A set of CeO_2 nanocatalysts with different structural properties (nanocubes, nanorods, two high-surface area CeO_2) was prepared to investigate the shape-dependency activity of two oxidation reactions: the soot combustion under different soot-catalyst contacts (namely in "loose" and "tight" conditions) and CO oxidation [1,2]. An analogous study has been carried out with nanostructured Ce-Zr-O catalysts (Zr-contents in the 10-30 at.% range) [3,4]. The physico-chemical properties of the prepared materials were investigated by complementary techniques (e.g. XRD, N_2-physisorption at -196 °C, H_2-TPR, FESEM, TEM, micro-Raman, FT-IR, XPS). The best performances in terms of soot combustion have been achieved for the CeO_2-nanocubes (S_{BET} = 4 m^2g^{-1}), due to the abundance of highly reactive (100) and (110) exposed surfaces. However, better results in terms of the onset of soot oxidation ($T_{10\%}$) have been obtained for high-surface-area materials (S_{BET} = 75 m^2g^{-1}), thus reflecting the key role of the surface area at low reaction temperature. Activity tests have confirmed the structure-sensitivity for the soot oxidation above 410 °C or 370 °C (in "loose" or "tight" conditions, respectively). On the other hand, the reaction has appeared surface-insensitive at lower temperatures. Thus, soot oxidation over ceria can be considered a reaction that displays both surface-sensitive and surface-insensitive behavior, depending on the operating conditions. The same catalytic trend has been obtained with Ce-Zr-O systems [1,2].

The highest CO oxidation activity has been achieved for ceria nanocubes, thus confirming the structure-sensitivity for the CO oxidation reaction over CeO_2-based systems. On the other hand, high-surface area materials (either CeO_2 or Ce-Zr-O_x) were unable to outdo the activity of nanocubes and nanorods due to the abundant presence of (111) crystalline planes. Regarding the Ce-Zr oxide catalysts, the highest activity for the CO oxidation has been reached for nanopolyhedra with sizes of ca. 30 nm. The latter, indeed, exhibited the best compromise between the structural defects and redox-active centres (Ce^{3+}/Ce^{4+} pairs). In conclusion, both reactions, kinetically described via a Mars-van Krevelen mechanism, may exhibit a structure-sensitive behavior over Ceria-based catalysts.

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Grants in the Field of Catalysis at Scientific Institutions of St. Petersburg

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The science of catalysis is a solid foundation for the creation of catalytic technologies that serve as the innovative and structure-forming basis of key industries. The development of the fundamental component of catalysis science is currently a pressing strategic task. Here, a prominent role is played by public research funds, which are involved in selecting the best and most significant projects and their funding on a competitive basis.

Currently, there are no analytical assessments of the impact of competitive funding to the development of research in the field of catalysis at the Petersburg institutions of science.

The aim of the study was to determine the contribution of public research funds to the development of catalysis science at scientific institutions of St. Petersburg.

We have performed a qualitative and quantitative analysis of available electronic and printed documents at two public research funds: RFBR (2009-2015) and RNF (2014-2015). Firstly, we analyzed the thematic focus of projects supported by RFBR and RNF grants during this period at St. Petersburg scientific institutions; the distribution of grants in the field of catalysis by types of activity (competition), areas of knowledge and affiliation of organizations; and information support of research. Secondly, an attempt was made to estimate the percentage of applications and received grants operated by academic institutions of St. Petersburg among the total number of applications and grants in the field of catalysis in the country both by activity and area of expertise. Thirdly, we evaluated the level of funding for the development of catalysis in St. Petersburg and the share assigned to the field of chemistry and materials science for the year 2014.

Thus, by analysis of research in the field of catalysis we have shown that competitive funding from public research funds starts to play a significant role in the development of work on priority areas of research in St. Petersburg.

PP-113

Simultaneous Reduction of Hexachloroplatinic Acid and Graphene Oxide for Fuel Cell Electrocatalyst Preparation

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Highly dispersed catalysts on a conductive support, commonly platinum and platinum-based catalysts, are used as electrode materials in low-temperature fuel cells. Carbon blacks are commonly used as fuel cell catalysts supports, but their properties are not completely satisfactory. Thus, in the last years alternative materials have been proposed as fuel cell catalyst supports [1].

Graphene is a subject of great interest due to its unique structure and excellent properties such as superior electronic conductivity, extremely high specific surface area, large surface to volume ratio and high stability. The excellent properties of graphene enable it to be a suitable catalyst support.

The aim of this study is to synthesize high-active platinum electrocatalysts supported by reduced graphene oxide using simultaneous reduction of platinum and graphene precursors [2]. Graphene oxide obtained by modified Hummer’s method was used as graphene precursor and hexachloroplatinic acid was used as a platinum precursor and ethylene glycol was used as reducing agent. The key advantage of this method is a good dispersability of graphene oxide at organic solvents instead of reduced graphene oxide which is prone to form irreversible agglomerates because of the van der Waals interaction and even restack to form graphite in the reduction from GO suspension solution or drying process [3]. This advantage is allowed to obtain electrocatalysts with high electrochemically active surface area. Influence of synthesis parameters on the electrocatalyst activity has been studied.

Acknowledgement. The reported study was financially supported by the Russian Foundation for Basic Research within the framework of research project No. 16-08-01070 A.

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PP-114

Catalytic Properties of Bi- Co, Bi- Co- K-Oxide Systems in Diesel Soot Oxidation with Oxygen

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1. By Method XRD, SEM, XPS received bismuth-based metal oxides: Bi-Co, Bi-Co-К were characterized. Catalytic activity of these systems in diesel soot oxidation with oxygen was studied in microcatalytic reaction cell in pulsed mode at 300-520°C in a tight and loose contact with soot.

2. In a tight contact both systems demonstrate high catalytic activity in diesel soot oxidation at 400°C. Initial temperature of progressing soot oxidation corresponds to 320 - 340°C in both cases, while pure soot starts noticeably to oxidize only at 460-480°C. In this case the activity of the system Bi- Co- K is higher. In loose contact with soot the catalytic activity of the system Bi-Co-C is slightly decreasing but still remains high, while the system Bi-Co without potassium practically loses activity.

3. XPS was used to determine the chemical state of synthesized catalysts and soot/catalyst mixtures' surfaces before and after oxidation. As a result, in the process of soot oxidation in presence of Bi- Co and Bi- Co -K was detected C1s state of the electron with binding energy 286.6eV and 288.8eV indicating the formation of soot on the chemical bond of C-O surface. According to [1], these lines can be linked to the presence on the soot surface of the carbonyl (286.6 eV) and the carboxyl (288.8 eV) functional groups. The K2p 3/2 binding energy is about 293.0eV, which is typical for K 1+. The Co2p 3/2 binding energy is about 780.1eV; this is similar for all samples and corresponds to Co_3O_4. The Bi4f 7/2 binding energy is about 158.8eV and this is typical for Bi 3+.

4. The concentration of oxygen bound with the soot surface varies depending on the treatment conditions. XPS data demonstrate that the lowest oxygen concentration is un-oxidized soot surface specific (the value of C/O = 60). During the oxidation of initial soot at 500°C the oxygen concentration on the soot surface increases (C/O = 40). In presence of Bi- Co and Bi- Co –K the soot surface is strongly saturated with oxygen. For sample Bi- Co -K the oxygen concentration is maximal (C/O = 3) and 5 times more than for the sample Bi-Co (C/O= 14).

In such a manner the presence of catalysts (this more relates to potassium containing system) effectively increases the soot surface quantum capable to adsorb O_2 with formation of surface oxygen-bearing functional groups. Comparing XPS data with the results of the catalytic activity of systems in the soot oxidation makes note: the system Bi- Co -C demonstrating the highest catalytic activity in the soot oxidation also shows the maximum activity in the soot surface' oxygen saturation (ratio C/O = 3); the carbon oxygen system Bi- Co is less able to saturate the soot surface with oxygen (C/O = 14) and is less catalytically active. In [2] the high catalytic activity of the transition-metal oxides in the soot oxidation with oxygen is explain by formation and decomposition of the surface oxygen-bearing functional groups (≡C-OH, ≡C-OOH, = C = O, and others) to CO and CO2 and the role of oxides is a strong saturation of the soot surface by these groups. Besides this behavior is explained by a redox mechanism due to the oxide' own oxidizing action.

Our results demonstrate that in presence of Bi-Co, Bi-Co-K system the soot oxidation is carried out via, probably, the formation and decomposition of surface groups, since the XPS data show that the K, Co, Bi oxidation degree in soot oxidation conditions is not changing.

Potassium ion, according to [3], is prone to strong saturation of carbon with surface groups, in particular with OH – groups, at this formed is a phenolate complex $\equiv C_{(soot)}$ - OK causing thus deformation of the C-C -bonds on the soot surface that further facilitates these bonds rupture under the influence of oxygen. It is also important that potassium ion introduces into the interlayer space of graphite structure with the formation of intercalates, and their subsequent transformation into graphite oxide. It appears that the combination of these factors results in high activity of a Bi-Co-K systems.

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PP-115

Activity of Bi –Mg, Bi – Cu – Mg, Bi – Cu Catalytic Systems in Soot Oxidation with Oxygen

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Catalysts have been received by annealing in the atmosphere of air of mixed nitrates Bi, Mg and Cu at 700-720°C. The crystal phase of freshly prepared catalysts were identified by methods: XRD, SEM, XPS. XRD data showed that the catalyst based on Bi-Mg consists of phases $Bi_{12}MgO_{19}$ and MgO; based on of Bi-Cu-Mg, consists of phases $Bi_{12}MgO_{19}$ and Cu_4MgO_5 while the catalyst based on of Bi-Cu is presented only by one phase $CuBi_2O_4$. With the help of SEM it is revealed that received catalytic systems crystallize in the form of aggregates. The surface of aggregates for all catalysts is smooth (candy like). The sizes of formed aggregates is in the range 0-1000nm while most mass of aggregates is in the range 200-600nm.

Before and after soot oxidation in presence of Bi-Mg, Bi-Su-Mg, Bi-Cu in XPSs detected are Bi 4f 7/2 (158.7eV), Mg 2p (49.6, 49.7, 49.8eV) and Cu 2p 3/2 (933.3eV) lines which bond energies are identical to freshly prepared samples without soot. This corresponds to Bi3+, Mg2 + and Cu2+ oxidation levels. This gives evidence that in the process of soot catalytic oxidation the change of oxidation level of the elements forming catalytic system is not observed. From XPS it, as well, follows that oxidation of soot in presence of Bi-Mg additive strongly saturates soot surface with oxygen - C/O ratio equals to 8.3. In case of soot oxidation without additive the concentration of oxygen on a surface falls-off: (C/O = 40).

Experiments on detection of catalysts activity in soot oxidation with oxygen were run with the help of molecular oxygen containing microamount of water in flow-through microcatalytic reaction cell at 300-580°C in pulse mode with immediate evaluation by chromatograph of CO2 and CO. Samples of mixtures soot-catalyst were prepared with mass ratio 2:1.

The catalysts activity based on Bi in oxidation of diesel soot with oxygen was identified. The temperature of soot oxidation start corresponds to 340°C for all catalysts. The catalytic activity jump observed at 400ºC. The series of catalysts' activity in soot oxidation with oxygen is as follows: Bi-Mg > Bi-Cu-Mg > Bi-Cu. Correlation between catalytic activity of the system and its ability to saturate the surface of soot with oxygen is noted.

The Bi-Mg system found to be more stable in soot oxidation with oxygen in comparison with all other studied catalysts.

It is supposed that catalytic action of the studied systems at soot oxidation with oxygen can be connected with their enhanced ability to initiate and facilitate saturation of a surface with oxygen as well as formation and disintegration to CO and CO2 of various surface oxygen-containing functional groups.

Effect of Electrochemical Treatment of Activated Carbon Fibers on the Supported Platinum Electronic State and Catalytic Properties

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The two main features of carbon sorbents in the form of activated carbon fibers (ACF) are large specific surface area, up to 1500 m^2/g, and high resistance to strong acids and alkalis. An additional electrochemical treatment (ECT) of the ACF increases their hydrophilicity and improves adsorption characteristics. Those modified carbon materials may be of interest as supports for effective catalysts preparation.

The present work is devoted to investigation of ACF electrochemical treatment effect on the electronic state and structure of the supported platinum and its catalytic properties.

Woven activated carbon fabric Busofit, manufactured by carbonization of rayon fibers, and its forms modified by ECT were used as supports for Pt-containing catalyst preparation. During ECT fabric feed rate of the Busofit into the reaction bath was 20 m/h, amperage of the electric current - 10, 15 and 20 A. Pt/C catalysts were prepared by means of the ion exchange method from H_2PtCl_6. Prepared catalysts were calcined in He at 200 °C for 2 h and reduced in H_2 at 450°C for 2 h. The Pt content in the catalysts was 1 wt. %. All prepared Pt/C samples were studied by XPS, HRTEM, XANES, EXAFS methods. HRTEM images were obtained on a JEM-2010 electron microscope (JEOL, Japan) at a 0.14 nm lattice-fringe resolution and a 200 kV accelerating voltage. The XANES and EXAFS spectra (Pt-L_3 edge) were measured on an EXAFS spectrometer under transmission mode at the SSTRC (Novosibirsk). XPS studies were carried out on a SPECS spectrometer equipped with a source of X-ray radiation (AlKα).

Catalytic activities for Pt/C systems were determined in the CO oxidation reaction: dry reaction mixture (0,3 vol.% CO in air), 5,5 mg of Pd in catalyst loading, 400 ml/min, 3300 h^{-1}.

Significantly enhanced activity of Pt/C catalyst after EC treatment of Busofit with a current of 15 and 10 A was revealed. The temperature of 50% CO conversion was shifted from 145 °C to 115 °C by ECT Busofit treated with 10 A current was used as the support.

Analysis of the binding energy values ($E_{bPt4f7/2}$= 71.3 ± 0.1 eV) and forms Pt4f line in XPS spectra of Pt samples leads us to a conclusion that almost all the platinum in the synthesized catalysts is in the metallic state, that was confirmed by XANES data. According to HRTEM, Pt nanoparticles in the catalysts prepared on the basis of Busofit ECT (10A, 15A) were considerably smaller in comparison with those on the initial Busofit. This fact is in a good agreement with the EXAFS results, which show reduced coordination numbers for the Pt-Pt distances by ~20-30%. The local structures of the prepared Pt samples were studied in detail. All possible structural models were discussed.

Acknowledgement. This work was supported by the Belarusian Republican Foundation for Fundamental Research, project № X14P-090, RFBR (140301066, 160301139).

PP-117

Transfer Hydrogenation Reaction Catalyzed by Homogeneous and Polymer Supported Ruthenium Complexes

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During the last decade Ionic liquids (ILs) which can be described as a salt in the liquid state have been recognized and the number of researches on this field of compounds has spreaded [1, 2]. However, much of the recent expansion of ILs-based chemistry is expected to be great contributions related to their utility as environmentally friendly solvents with multiple applications in product synthesis, catalysis, and separation.[3] For this purpose ILs have been used in polymer science, mainly as polymerization media in several types of polymerization processes.[4]

A set of new soluble homogeneous and polymer-anchored ruthenium(II) catalysts containing imidazolium based ionic liquids have been synthesized, characterized with SEM and XRD spectra and their catalytic activity was investigated in the transfer hydrogenation reactions.

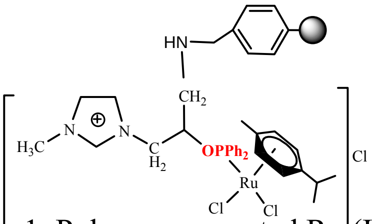

Figure 1. Polymer supported Ru(II) complexes

Table 1 - Transfer hydrogenation of acetophenone with 2-propanol catalyzed by polymer supported $[Ru((Ph_2PO)\text{-}C_7H_{14}N_2Cl)(\eta^6\text{-}p\text{-cymene})Cl_2]Cl$, 1 and $[Ru((Cy_2PO)\text{-}C_7H_{14}N_2Cl)(\eta^6\text{-}p\text{-cymene})Cl_2]Cl$,2

Catalyst	S/C/KOH	Time	Yield(%)	TOF(h-1)
1[a]	100:1:5	30min	85	274
1 [b]	100:1:5	48h	<5	....
2 [a]	100:1:5	10min	89	596
2 [b]	100:1:5	48h	<5	....

Reaction conditions: [a] Refluxing in 2-propanol; acetophenone/Ru/KOH; [b] At room temperature; acetophenone/Ru/KOH.

NOTE: This study was supported by Ministry of Education and Science of the Republic of Kazakhstan (1318/GF4, 1752/ GF4) and Dicle University (FEN.15.021 and FEN.15.022). The analysis conducted by the Dicle University Science and Technology Research Center (DUBTAM) is also gratefully acknowledged.

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PP-118

Use of Transition Metal Complexes of an Ionic Liquid Based Phosphinite as Catalyst in Transfer Hydrogenation of Aromatic Ketones

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Asymmetric catalysis is considered to be an ideal method for synthesis of optically active compounds [1]. Although some phosphinite ligands and their derivatives have been employed successfully as ligands in the transfer hydrogenation of ketones [2,3,4], a screening of catalytic activities of ionic liquid based phosphinites in this reaction is not common in literature.

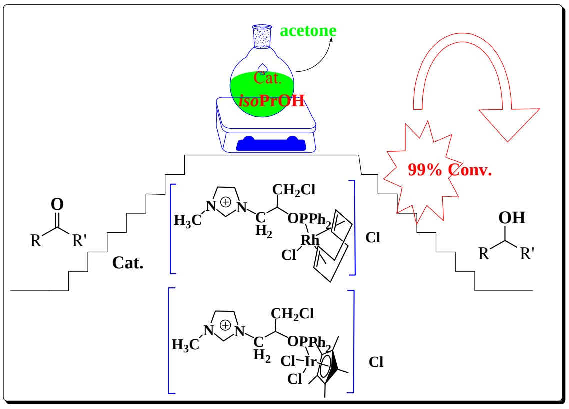

Figure 1. Ionic liquid based monodendate Rh(I)- 1, Ir(III) -2 complexes

In the present study, ionic liquid based monodendate Rh(I), Ir(III) complexes, (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinitechloride) (chloroη^4-1,5-cyclooctadiene rhodium(I))], **1** and (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinitechloride) (dichloroη^5-pentamethylcyclopentadienyl iridium(III))], **2** are efficient homogeneous catalytic systems that can be readily implemented and lead to secondary alcohols from good to excellent conversions. Especially, we found that complex **1** was a more efficient catalyst in the transfer hydrogenation reaction.

NOTE: This study was supported by Ministry of Education and Science of the Republic of Kazakhstan (1318/GF4, 1752/ GF4) and Dicle University (FEN.15.021 and FEN.15.022). The analysis conducted by the Dicle University Science and Technology Research Center (DUBTAM) is also gratefully acknowledged.

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PP-119

Kinetic Peculiarities of Alkylphenol Oxidation Using Heteropoly Acids

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Alkylphenols such as 2,3- and 2,6-dimethylphenols (Me_2Ps) can be converted to *p*-benzoquinones (Me_2BQs) in preparative yield using molecular oxygen as oxidant and aqueous solutions of Keggin molybdovanadophosphoric heteropoly acids of the general formula $H_aP_zMo_yV_xO_b$ (HPA-x, x = 1–12) as catalysts. The interest in these catalysts arises from their exceptional characteristics such as strong Brønsted acidity, high proton mobility, fast multielectron transfer, high solubility in various solvents and excellent resistance against hydrolytic or oxidative degradations. The reduced catalyst solutions can be easily reoxidized in a separate step by O_2 at the temperature of 160ºC and oxygen pressure of 3-4 atm.

The influence of various parameters such as concentration of substrate, nature of solvent, temperature and reaction time on the catalytic process was examined in details considering the yield and selectivity. Performing oxidation in a two-phase system consisting of an aqueous solution of HPA-x in concentrations of 0.1–0.4 M and organic solvent, the best yields of the target quinones (85–88%) were achieved using trichloroethylene at 60ºC in inert atmosphere at complete substrate conversion.

The composition of the catalyst solutions before and after target reaction was investigated by ^{31}P and ^{51}V NMR. It was shown that HPA-x solutions are reduced easily and reversibly to form mixed-valence species, retaining the structure of the initial oxidized HP-anions. The total number of accepted electrons at reduction of such anions can be quite high. As the anion structures retain upon this process, the additional negative charge is compensated for by protonation of the HP-anions. Therefore, the observed pH value after reaction is higher. Ones of the important factors affecting the oxidation rate and product selectivity are initial oxidation potential of the catalyst and vanadium(V) content in it. When these values were higher, the yield of monomeric *p*-quinone was better. The main oxidation by-products were the C=C coupling dimers.

On the basis of kinetic and spectroscopic studies, an electron-transfer mechanism involving dissociation of HPA-x in acidic medium to generate the active species VO_2^+ and rapid stepwise oxidation of Me_2P to Me_2BQ by VO_2^+ with intermediate formation of several highly reactive particles was suggested. Insertion of forming at the first stage VO^{2+} species back into the coordination sphere of HP-anions with subsequent oxidation of V^{IV} to V^V therein by dioxygen proceeded in the separate stage. Aqueous solutions of heteropoly acids were prepared by the method of Odyakov et al. [1].

Acknowledgement. The work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (project V.44.2.8).

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Structure and Catalytic Behavior of Ni-containing Catalysts Produced by Laser Electrodispersion Technique

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The catalytic activity of Ni nanoparticles deposited on carbon or oxide supports by laser electrodispersion (LED) at extremely low loading is orders of magnitude higher than that of conventional supported catalysts in a wide range of reactions, and depends on nanoparticle surface density [1–3]. In this work the structure and reducibility of Ni and/or Pd nanoparticles supported by LED on Al_2O_3 were studied using XPS in combination with hydrogen reduction. Ni and $Ni_{0.65}Pd_{0.35}$ alloy were used as targets for the metal particle production. TEM images demonstrated the uniform distribution of particles on the surface of support with the mean particle size of about 2 nm. According to EDX the mean Ni:Pd ratio in the supported material was equal to that in the alloy used, whereas XPS data demonstrated Ni enrichment on the surface (Ni:Pd=7.6). At the loading below 0.01 wt.% Ni2p XPS spectra of both samples contain only Ni^{2+} related structure with E_B= 856.1 eV. At higher loadings the Ni^0 component at E_B=853.2 eV starts to appear. Ni^{2+} peak can be deconvoluted into NiO and $Ni(OH)_2$ line shapes. In the spectra of LED catalysts the NiO component predominates in contrast with the spectra of similar size Ni particles supported on Al_2O_3 from colloidal dispersion. According to XPS NiO is reduced first during in situ experiment, providing easier reduction of LED samples at lower temperatures and their better catalytic efficiency. The features of structure and reducibility of Ni and NiPd nanoparticles prepared by LED provide their unusual behavior in chlorobenzene hydrodechlorination and CO oxidation.

Acknowledgement. This work was supported by Leading Scientific Schools (grant NSh–8845.2016.3) and Lomonosov Moscow State University Program of Development.

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PP-121

Study of Key Stages of Gas Phase Oxidative Desulfurization of Diesel Fuel on CuZnAlO Catalyst

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At present, much attention is given to research for methods of deep purification of diesel fuel. For this, application of unconventional methods of fuel treatment is proposed after its hydrodesulfurization (HDS) under mild conditions to 350-500 ppm S content. One of such promising methods is a process of gas phase oxidative desulfurization of diesel fuel (ODS) by air oxygen over oxide catalysts. An advantage of this process is its efficiency in the removal of refractory sulfur compounds, such as dibenzothiophene derivatives more resistant to HDS treatment in comparison with thiophene [1]. In the present work, key stages of the ODS reaction (adsorption, oxidation, removal) over CuZnAlO catalyst are examined in presence of diesel fuel with S content 1 wt.%. The CuZnAlO catalyst preparation is described in [2].

According to GC analysis, sulfur containing compounds are oxidized on the catalyst with the evolution of SO_2 and CO_2 into the gas phase. While sulfur removal from the fuel amounted to 60% at 400°C, the SO_2 evolution corresponded only to 35% conversion of sulfur compounds in the fuel.

Physico-chemical properties of the CuZnAlO catalyst before and after the ODS reaction were studied by XRD, DTA-TG-MS, XPS, TPR-H_2, SEM, HR-TEM, IRS, Raman spectroscopy, CHS analysis, etc. The XRD showed transformation of CuO into Cu_2O and Cu, the phases of ZnO and CuZnAlO did not change during the ODS. The DTA-TG-MS data showed the sulfur accumulation in the form of metal sulfides, polysulfides and sulfates and also accumulation of products of hydrocarbon polycondensation. The SEM study of the spent catalyst revealed the enrichment of the surface with sulfur and copper, while SEM of the fresh catalyst exhibited uniform distribution of metals over the surface and in the bulk.

Thus, the results of kinetic and physico-chemical studies point to the staged mechanism of oxidation of sulfur compounds over the CuZnAlO catalyst. According to TPR with H_2S and TPO with oxygen, sulfur containing compounds are adsorbed on the surface in the form of sulfides/polysulfides and after attaining monolayer coverage are oxidized and removed to the gas phase in the form of SO_2. The formation of metal sulfates is undesirable because most of them are decomposed only at high temperatures

Acknowledgement. This work was financially supported by SAUDI ARAMCO under contract No.6600022642.

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Oxidation of Ethanol over Pt(111): *In Situ* XPS and PM IRAS Study

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The oxidation of ethanol over a Pt(111) single crystal were examined between 300 and 650 K using *in situ* XPS, PM IRAS, and temperature-programmed reaction spectroscopy. The *in situ* XPS and TPRS experiments were performed at the synchrotron facility BESSY II, Berlin, using the ISISS beamline equipped with an on-line quadrupole mass spectrometer Prizma QMS-200 [1]. The experiments were carried out in a flow regime at 0.5 mbar. The *in situ* PM IRAS measurements were performed at atmospheric pressure on an apparatus equipped with a Bruker Vertex-80v spectrometer at the Boreskov Institute of Catalysis. The construction of the apparatus is similar to an apparatus described elsewhere [2].

It was found that even in the oxygen presence, platinum is in the metallic state in the whole temperature range. At low temperatures the surface of platinum is partially blocked by carbon that inhibits the reaction rate. After heating to approximately 450 K the oxidation of ethanol starts and CO, CO_2, H_2, and H_2O are detected as products in the gas phase. Increase in the oxygen content leads to increase in the ethanol conversion and to shift the reaction to the total oxidation of ethanol.

Acknowledgement. This work was partially supported by the Russian Foundation for Basic Research (Research project No 16-33-00578 mol_a). The authors thank A.Yu. Kluyshin, M. Hävecker, and A. Knop-Gericke for their assistance in carrying out the XPS measurements.

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The Mechanism of 5-Vinyl-2-norbornene Selective Oxidation with Nitrous Oxide into 1-Pyrazoline Derivative

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Investigations of the last decades indicate the availability of nitrous oxide (N_2O) application as an effective oxygen donor for the selective oxidation of olefins into ketones and aldehydes [1]. Thus, in 2009 BASF company put into operation two large-scale processes for the cyclopentanone and cyclododecanone production using N_2O as oxidant with total productivity of 30 000 tonnes per year. According to quantum-chemical calculations, the target reactions proceed via the mechanism of 1,3-dipolar cycloaddition of N_2O to C=C bond forming 4,5-dihydro-[1,2,3]-oxodiazole intermediate. Its subsequent decomposition to ketone or aldehyde is accompanied by elimination of N_2. Evolution of the nitrous oxide from the exotic reactant to the common oxidant forces the subsequent search of the novel reactions involving N_2O as well as investigation of their mechanism.

In the present work, the selective oxidation of 5-vinyl-2-norbornene (VNB) with N_2O was studied. This reaction is very unusual. First of all, the VNB molecule has two different types of double C=C bonds (internal and terminal) with different reactivity. Our study indicated that mostly the internal double bond reacts with N_2O. Secondly, the VNB is a mixture of exo- and endo- isomers which also can be critical for reactivity and products composition. The exo-isomer conversion exceeds that one of endo-isomer (84.7% versus 75.9%, correspondingly). According to product analysis, the oxidation of internal double bonds in the VNB isomers yields few isomers of aldehydes and ketones. But the most interesting fact is the formation of stable product with molecular weight of 164 a.m.u. Using NMR spectroscopy, this product was identified as 3a,4,5,6,7a-hexahydro-3H-4,7-methanindazole-5-carbaldehyde (1-pyrazoline derivative).

Thus, for the first time, after the olefin oxidation with nitrous oxide, the product of nitrogen insertion from N_2O into hydrocarbon was isolated and identified. It is well known that norbornene derivatives with pyrazoline ring could be interesting as biologically active compounds [2]. However, the known synthetic methods are complex and use extremely hazardous reagents. The formation of norbornene derivative with 1-pyrazoline ring during the VNB oxidation with nitrous oxide is a very important experimental result confirming the N_2O cycloaddition mechanism mentioned above.

Acknowledgement. This work is supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (project V.44.2.3).

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Relativistic Electrons of sp^2 Nanocarbons

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The nineteenth century was marked by the discovery of a highly peculiar molecule named by M. Faraday in 1825 as benzene which has become one of the pillars of the modern organic chemistry. The twentieth century was enriched in 1926 by the Hückel explanation of the benzene molecule peculiarity which has formed the grounds of the π-electron theory of aromaticity that was the ground of the modern quantum chemistry in general. The twenty first century has faced a conflict between compositions of condensed benzenoid units and the aromaticity theory. This conflict makes to abandon the benzene-aromaticity view on the compounds formed by the condensed benzenoid rings and stimulates finding conceptually new approaches for their description. The current paper is an attempt to answer this demand. The author suggests spin-orbit coupling to be laid in the foundation of the conflict resolution [1]. The concept has arisen on the basis of a set of extended quantum chemical computational experiments performed by the author as well as by other scholars, results of which have found a convincing empirical support. In the way of the concept formation, one had to answer the question how nonrelativistic formalism of tools used in the course of the above computational experiments is able to exhibit pure relativistic issues. The solution of this and other problems met in the way is described in the current paper. The following issues will be outlined in the paper:

- General characteristics of open-shell molecules as the main objects of the concept;
- Empirical confirmation of the UHF peculiarities of open-shell molecules;
- Spin-orbit nature of the sp^2 nanocarbons peculiarities;
- Spin orbit coupling in quantum chemical calculations;
- Adequacy of UHF results to the SOC expectations;
- Evaluation of the SOC parameter of sp^2 nanocarbons on the basis of UHF computations.

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Structural Peculiarities and Catalytic Properties of Perovskite $(Gd,Sr)_{n+1}Fe_nO_{3n+1}$

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Perovskite-type oxides with structure ABO_3 have attracted significant interest in many areas of solid-state chemistry, including catalysis. High metal dispersion from perovskite emerges as a practical alternative and can be applied in the CO hydrogenation.

Perovskite materials of composition $GdFeO_3$, $SrFeO_{3+x}$, $GdSrFeO_4$, $Gd_2SrFe_2O_7$ were prepared by sol-gel citrate method. The complex physico-chemical methods of investigation showed that synthesized catalysts are well-crystalline homogenous perovskite-type ferrites with different number of perovskite layers $GdSrFeO_4$ (n=1), $Gd_2SrFe_2O_7$ (n=2), $GdFeO_3$ (n=∞) and solid solutions $Gd_{2-x}Sr_{1+x}Fe_2O_7$. SEM showed that the average crystallite size of the order 0.05 µm. Mossbauer spectroscopy shows that Iron atom is in a heterovalent state (Fe^{+3} coexists with Fe^{+4}) in three different symmetry fields. A lowering of the symmetry of the surrounding of Fe^{+3} atoms is attributable to the presence of oxygen vacancies. Found that the adsorption of H_2 and CO occurs at different centers. Suggested that the Fe^{+3} ions are responsible for the formation of atomic hydrogen and carbonate complexes occur at ions Gd^{+3} and Sr^{+2}.

Catalytic performances are obtained in the hydrogenation of carbon monoxide: main product is C1-C4 hydrocarbons, selectivity to olefins (C_2H_4 and C_3H_6) at 673 K was 30-45%, the catalytic activity increased in the series $SrFeO_{(3-x)}$, $GdSrFeO_4$, $Gd_{2-x}Sr_{1+x}Fe_2O_7$, $GdFeO_3$, that is, there was a correlation between the number of perovskite layers (n = 1,2, ... , ∞) in the structure of the complex oxide and the reactants convertion, the specific catalytic activity (Wi - mol / h*g) and selectivity to olefin.

Complex research of the catalysts after the catalytic processes by X-ray diffraction, scanning electron microscopy with elemental microprobe analysis and Mössbauer spectroscopy revealed the following: no noticeable changes in particle morphology samples of $Gd_2SrFe_2O_7$ during catalytic reactions; for $GdFeO_3$ samples, some of $Gd_{2-x}Sr_{1+x}Fe_2O_7$ occurs agglomeration due to their sintering; phase structure of ferrite remains unchanged: partial degradation of catalysts under the action of the reaction medium does not occur; there is a change of state of iron atoms (Fe^{4+} recovery to Fe^{+3}) under the action of the reaction medium; the presence of carbon was found on the surface of the spent catalysts. However, since the catalyst activity is unchanged in repeated experiments and preserved for a long time, it is assumed that the carbon is active. High catalytic properties of ferrites Gd and Sr synthesized by sol-gel technology can be associated with their nanocrystalline state, a porous structure, as well as with heterovalent iron state.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-03-00940.

Mixed-valence Co^{+}/Co^{2+}Structures in Carbon Monoxide Oxidation on Co-modified ZSM-5

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Design of single–site heterogeneous catalysts based on zeolites and understanding their mechanism of action is of growing interest and practical importance. One of the typical features of zeolites is their ability to exchange cations which are retained in their channels at specific sites. The aim of this work is to find conditions for the formation and stabilization on the surface of Co-containing zeolites of the mixed-valence Co^{+}/Co^{2+} structures by thermal reduction with carbon monoxide, to establish the characteristics of their structure and catalytic activities in CO oxidation under mild conditions.

Cobalt modified zeolites Co-ZSM-5 ($SiO_2/Al_2O_3 = 55$) were prepared by the methods of solid–state ion exchange, incipient wetness impregnation and a combination of aqueous ion exchange and impregnation. The Co coordination geometry and electronic state was investigated by TEM, XPS and EXAFS/ XANES. New adsorption and catalytic sites resulting from the modifier introduction into the zeolite and its post reduction in CO atmosphere were detected by diffuse reflectance UV–vis spectroscopy (DRS) and infrared Fourier transform (DRIFT) spectroscopy, including the carbon monoxide adsorption technique. Catalytic activities of the materials were evaluated in CO oxidation. The reaction was performed in a tubular quartz reactor in a pulsed regime under atmospheric pressure.

According to XPS, X–ray spectroscopy and TEM in addition to isolated Co^{2+} ions cobalt oxide particles as Co_3O_4 or CoO and oxide-like structures $[Co\text{-}O\text{-}Co]^{2+}$, are also may present on the surface of modified zeolites, especially at degree of exchange >100%. The ratio of the different types of cobalt species depends on the method of preparation. DRIFT spectra of adsorbed CO show the bands of carbonyl complexes with Co^{2+} cations (2205 cm^{-1}), oxide-like structures $[Co\text{-}O\text{-}Co]^{2+}$ (2190 cm^{-1}) and even oxide structures including oligomeric oxides or small nanoparticles (2180 cm^{-1}) appearing in the overexchanged samples. The low oxidation states of cobalt (Co^{+}) may perform on the surface of Co-containing zeolites in the course of the CO adsorption at RT, which is manifested *in situ* in the DRFT spectra by the carbonyl complexes detected below 2140 cm^{-1}. The proportion of $[Co\text{-}O\text{-}Co]^{2+}$ oxide like structures on the Co-ZSM-5 surfaces was evaluated with using the DRIFT spectra of adsorbed CO based on the various ability of the cobalt forms to reduce by CO considering that the cobalt reduction in this case was mainly associated with the reduction of $[Co\text{-}O\text{-}Co]^{2+}$ ions . The obtained samples Co-ZSM-5 exhibit catalytic activity in CO oxidation with molecular oxygen at temperatures of 100-400°C. The CO conversion reaches 100% already at 200°C. More over the activity of this catalyst even increases during the reactions.The best catalyst prepared by zeolite impregnation by cobalt acetate includes the highest amount of active $[Co\text{-}O\text{-}Co]^{2+}$ species that can be easily reduced in Co^{2+}/Co^{+} couples.

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New Chemical Models for Non-Heme Oxygenases

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Oxidation of hydrocarbons to oxygen-containing compounds are industrial processes of considerable importance. In nature C-H bond oxidations are effected by O_2 activating metalloenzymes (oxygenases) involving diiron sMMO capable of methane oxidation. In order to model the active site of sMMO the new heptadentate ligand L=$(PyCH_2)_2NCH_2$-$C_6H_3(CH_3)$-$CH_2N(CH_2Py)(CH_2CH_2COOLi)$ and diiron complex $[Fe_2OL_2]^{2+}$ have been synthesized and characterized. This complex promotes efficient oxidation of alkanes and alkenes using H_2O_2 as terminal oxidant. The product distribution and reactivity tests (KIE, RC, 2°/3°) suggest the metal-based oxidation. Low-temperature UV/vis spectroscopy and ESI-MS indicate the formation of a transient peroxide/diferryl species, $[Fe_2O(O_2)L_2]^{2+}$~ $[(Fe{=}O)_2(O)L_2]^{2+}$, which might be an intermediate in the oxidation process. [1]

Two new pentadentate ligands based on N4Py framework, $(PyCH_2)_2NCH(Py)_2$, have been synthesised, where one (L^1) or two (L^2) pyridylmethyl arms replaced by corresponding (N-methyl)benzimidazolyl–containing arms. The complexes $[Fe^{II}(CH_3CN)L^{12}]^{2+}$ were synthesised and characterized, and new ferryl complexes $[Fe^{IV}(O)L^{12}]^{2+}$ were prepared by the reaction with PhIO. The ferryl complexes were characterized by UV-vis and Mössbauer spectroscopy, and ESI-MS. The reactivities of the new ferryl complexes in hydrogen atom transfer (HAT) and oxygen atom transfer (OAT) reactions show that both ferryl complexes exhibit enhanced reactivities when compared to analogous N4Py complex. The second-order HAT rate constants correlate with the hydrocarbon C-H bond dissociation energies. Computional modelling of of the HAT reactions indicates that the reaction proceeds via a high spin transition state. [2]

Acknowledgement. This work was supported by COST Action CM 1003 and European Union.

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Oxidative Carbonilation of Methanol over Copper-Aluminum Delafossite

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One of the prospective routes of natural gas conversion is dimethyl carbonate (DMC) synthesis from methanol. DMC is used as a valuable chemical, e.g. for diphenylcarbonate (a monomer for polycarbonate) synthesis and as the methylating agent. It is also perfect solvent: non-toxic and VOC exempt. Finding efficient routes for its synthesis will make it cheaper and allow wide use of DMC for various applications. DMC synthesis from methanol and CO_2 is an exothermal process (I), which is thermodynamically restricted even at 298 K.

$$2CH_3OH + CO_2 = (CH_3O)_2CO + H_2O \qquad (I)$$

$\Delta_I H^o_{298} = -17.9$ kJ/mol, $\Delta_I G^o_{298} = 28.5$ kJ/mol. The process of oxidative carbonylation (II) is much more favourable with $\Delta_{II} H^o_{298} = -300.9$ kJ/mol and $\Delta_{II} G^o_{298} = -227.1$ kJ/mol:

$$2CH_3OH + CO + ½\ O = (CH_3O)_2CO + H_2O \qquad (II)$$

Many studies report that Cu^+-containing catalysts are selective for DMC synthesis from methanol. In this study we consider the interaction of methanol, CO and oxygen with monovalent copper and aluminum oxide, $CuAlO_2$, with delafossite structure. We used *in-situ* FTIR for elucidation of the surface species generated by the consecutive treatments of $CuAlO_2$ by CO, oxygen and methanol, or in the opposite order: by methanol, oxygen and CO (pressure was 1 Torr for each of the reactants).

If CO adsorption is followed by oxygen treatment and then methanol is fed over the surface of Cu-Al delafossite, then bidentate and unidentate methoxy-groups are the main surface species at low temperatures. Increasing the temperature leads to oxydation of methoxy to formate and carbonate groups. The catalyst surface becomes reduced and methanol is oxidized via formates to carbon dioxide. If methanol is fed first, then it is replaced by oxygen and CO adsorption comes the last, then the oxydation of methoxy species leads to carbonates and monomethylcarbonate groups. The latter are considered as the intermediates on the route from methanol to DMC [1]. However further treatment of the surface with CO removes methoxy- and methylcarbonate groups and CO_2 and water are produced.

Thus, the FTIR data show that the route of oxidative carbonylation of methanol is simultaneous to CO oxidation at Cu-Al delafossite surface. Therefore, thermodynamics of process (I) determines the yield of DMC. These findings are in the agreement with catalytic experiments, which show that DMC formation requires elevated pressure.

Acknowledgement. This work was supported by Ministry of Education and Science of the Russian Federation (project no. 2211-2014/139).

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The Development of Synthesis Procedures of the Nanocrystalline Catalysts $V_2O_5/(CeO_2\text{-}TiO_2)$ and $V_2O_5,WO_3/(CeO_2\text{-}TiO_2)$ for NO Reduction by NH_3 Using Anatase with Enhanced Thermal Stability

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Purification of harmful gases from nitrogen oxide is carried out by selective catalytic reduction (SCR) NO by ammonia in the presence of oxygen to N_2 using V_2O_5/TiO_2 catalysts. These catalysts are characterized by high activity in the temperature range of 220-350 °C where nitrogen oxide conversion reaches 90-97%, and the main reaction product is N_2. The SCR process over a wide range of the oxygen concentration occurs most efficiently at V_2O_5/TiO_2 oxide catalysts modified with tungsten. [1,2]. Main drawback of these catalysts is their low thermal stability: activity dramatically and irreversibly decreases at temperatures above 350 °C. It due to the sintering of fine vanadium forms on the surface of anatase and formation of the phase of V_2O_5, and the phase transition of anatase to rutile.

The aim of this work is to develop a method for controlling the thermal stability of the binary and modified with tungsten oxide additives vanadium-titanium catalysts in SCR NO by ammonia.

Synthesis of the CeO_2-TiO_2 support was performed by incipient wetness impregnation of titanium dioxide xerogel (anatase) with an aqueous solution of cerium nitrate followed by drying and heating. Obtained supports have higher specific surface and more developed porous structure compared to pure TiO_2 over a wide range of calcination, that indicates on their higher thermal stability compared to pure TiO_2. This is due to the formation of a nanocrystalline structure consisting of incoherently intergrown fine anatase crystallites with formation of interblock boundaries in which Ce^{3+} ions are stabilized.

Supported binary and modified with tungsten oxide vanadium-titanium catalysts were prepared by impregnating the CeO_2-TiO_2 supports with vanadyl oxalate or the mixture of vanadyl oxalate and metatungstate solutions followed by drying and heating in air at 650 °C. The catalytic properties of the catalysts were measured in SCR NO by ammonia in the presence of oxygen and water vapour impurities in the temperature range of 150-600 °C.

Obtained catalysts have much higher thermal stability under the reaction conditions compared with the known analogues until 550 °C and provide practically complete cleaning gas mixture from nitrogen oxide.

Acknowledgement. This work was supported by the RFBR grant 16-33-00798 mol_a.

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XRD PDF *Operando* – A Promising Tool for Catalyst Diagnostics

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An effective heterogeneous catalyst should have specific surface as large as possible and therefore small particle size. So, the surface sensitive methods such as X-ray photoelectron spectroscopy (XPS) seem to be most suitable for diagnostics of catalyst and catalytic processes. XPS is well developed and widely used tool for characterization of catalyst, including experiments *in situ* at high temperature in vacuum or under small pressure of the reaction media. X-ray diffraction (XRD) is rather volume sensitive method mostly applicable for large particle size systems but it allows *in situ* experiment execution at normal and high pressure of reagents. On the other hand, XRD experiment in combination with pair-distribution-function (PDF) analysis is a powerful tool for structure diagnostic of catalyst as well as its transformation under reaction conditions. For small particle the fracture of surface atoms is high and any process on the surface of catalyst particle causes detectable structure transformation in the body of the particle.

To execute XRD PDF analysis one needs experimental powder diffraction pattern covering momentum transfer range ($q=4\pi\sin\Theta/\lambda$) as wide as possible. Since angular range Θ is always limited, the way to expand q is to make wavelength of radiation, λ, smaller, i.e. to use radiation of high energy. Synchrotron radiation with its wide smooth spectrum, outstanding brilliance and high natural collimation seems to be ideal for XRD PDF experiments [1-3].

The report describes the results of first experiments on XRD PDF which were carried out at Siberian Synchrotron and Teraherz Radiation Centre on VEPP-4 storage ring operating at electron energy of 4 GeV. The spectrum of emitted radiation stretches for hard X-ray region up to 100 keV and makes possible to obtain XRD data within the range of q's up to 1000 nm^{-1}. Future plans on the development of XRD PDF technique especially to *in situ* and *operando* modes for catalytic systems at SSRTC are discussed.

Acknowledgement. We acknowledge financial support from the Skolkovo Foundation (Grant Agreement for Russian educational organizations No. 5 of 30.12.2015).

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Structural Special Features of the Gold Nanolayer on the Glass Surface Modified by Surface Ion Exchange and Chemical Etching

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The research data are related to X-ray structure analysis of the gold nanolayers (50, 100, 200 nm thick) on glass surface modified by the surface ion exchange, chemical etching or by combined treatment. Na+/Li+ ion exchange with Surface Ion Exchange Paste (SIEP) [1-3] of the soda lime silica glass (4 mm thick) has included next stages: glass surface degreasing and washing; the SIEP laying on the glass surface; thermal treatment at ~ 300º C for 15 – 20 min.; washing with running water. The chemical etching of glass has been carried out with the composition containing hydrofluoric acid [4]. The glass surface morphology has been observed by the SEM JSM-6460 (Jeol, Japan); the gold nanolayers were deposed on glass by the special device JVC-1600 (Jeol, Japan). X-ray data have been measured with diffractometer D8 Advance (CuKa) and one-dimensional detector Lynx–Eye with nickel filter. The range of 2q was 10 – 120° with step 0,02° and acquisition interval 35,4 c. The program Topas 4.2 (Bruker AXS, Germany) and structural data of inorganic base ICSD, FIZ Karlsruhe, Germany have been used in calculations. X-ray data analysis allows make conclusion that the surface modification of the soda lime silica glass by the surface ion exchange and chemical etching has a substantial influence upon the size of gold crystal grains (Figure 1). Gold crystal grains have elongated shape in direction <111>. The increase of the gold nanolayer thickness leads to decreasing of the crystal grains size. The least size has been related to gold nanolayer 200 nm thick on glass surface modified by combined two methods: in direction <111> average calculated grains size is ~ 14.7 nm; grains size averaged in directions <200>, <220> and <311> is ~ 6.8 нм. Authors express thanks to N.V. Bulina for technical support.

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Two Directions of Chain Propagation in Methyl Methacrylate and Styrene Polymerization in the Presence of Metallocenes

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The process of radical-coordination polymerization of methyl methacrylate and styrene, initiated by benzoyl peroxide or azobisisobutyronitrile in the presence of metallocenes Cp_2Fe, Cp_2ZrCl_2, Cp_2TiCl_2 ,$(C_5Me_5)_2Fe$, $(C_5Me_5)_2ZrCl_2$ и $(AcC_5H_4)(C_5H_5)Fe$ was investigated. A quantum - chemical modeling of possible interactions in the system monomer - metallocene - radical initiator - free radical It was shown, that radically initiated polymerization of methyl methacrylate and styrene in the presence of metallocenes is characterized by chain growth with participation of two kinds of active centers – free radical and coordination. Contribution correlation of each kind active centers in general view of kinetic dependences of polymerization reaction is dependent of metallocene nature and polymerization conditions (temperature, component ratio). Products of that polymerization are able to excite polymerization of monomers in the presence if initiator. Catalytic activity of ’’metallocene’’ polymers is determined by prehistory of their production.

PP-133

Hydrodeoxygenation of Pentanoic Acid Catalyzed by Pt(Re)/TiO_2

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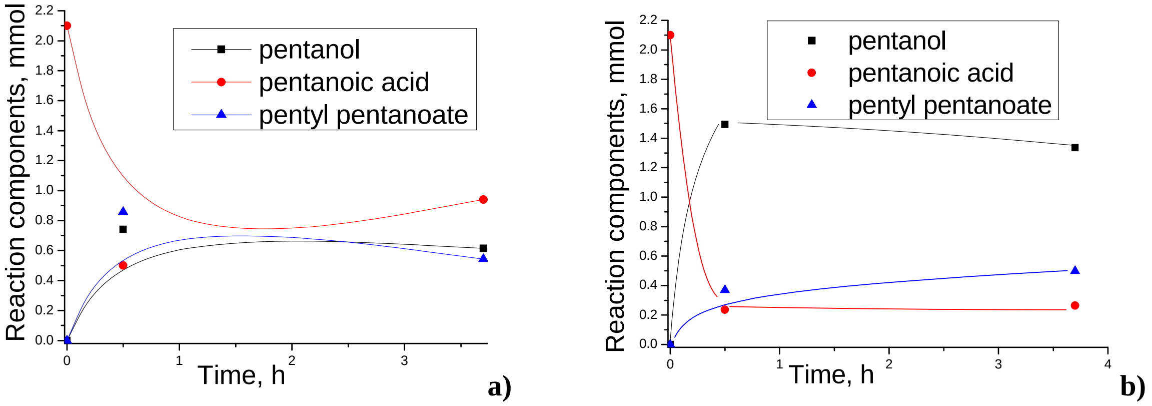
Alcohols are important bio–based chemicals used as non–ionic surfactants and emulsifiers, emollients and thickeners in alimentary and cosmetic industry [1]. They are mainly produced selectively through catalytic hydrogenation of carboxylic acids and their derivatives over environmentally hazardous Cu-Cr catalysts at 200–300°C and hydrogen pressures 20–30 MPa. Hydrodeoxygenation (HDO) of acids to alcohols can be performed at lower temperatures (110–150°C) and hydrogen pressures (2 MPa) with 90–93% selectivity over Pt/TiO_2 [2,3]. In this paper we report selective pentanoic acid (PA) HDO into pentanol under mild conditions (150-180°C, 1.5-2.5 MPa H_2) using TiO_2 based Re catalysts modified with VIII group metals and elucidate kinetic and mechanistic aspects of this reactions.

Liquid phase PA hydrogenation in decane or hexadecane was studied over Re/TiO_2 *per se* or modified with Pt, Pd, Ru, Rh. The reaction products were analyzed by “Chromos 1000” GC (FID) with Stabilwax-DA column (50 m/0.32 mm/0.5µm) (USA) at 373-473K with ramp 10K/min. Catalysts were characterized by H_2 TPR, XRD, XPS and HRTEM.



a) b)

Fig. 1. PA HDO 4.4 mmol PA/g catalyst, $C_{16}H_{34}$, 150°C, 2.5 MPa on Re/TiO_2 (a) and PtRe/TiO_2 (b)

PA conversion increased in the row PdRe/TiO_2 < RuRe/TiO_2 < RhRe/TiO_2 < ReOx/TiO_2 < PtRe/TiO_2 [4]. The highest selectivity to pentanol was observed over Re on thermally treated TiO_2 while Re over unmodified titania was completely inactive. Kinetic regularities and mechanistic aspects of PA HDO will be discussed. It was shown that PA is converted into pentanol followed by esterification with unreacted pentanoic acid into its pentyl ester, resulting in an equilibrium mixture of pentanoic acid - pentanol – pentyl pentanoate without 1-pentanal formation (Fig. 1). Insertion of Pt to Re/TiO_2 noticeably enhanced pentanol yield.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 15-03-09329.

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PP-134

Nitrous Oxide Decomposition over Supported Nickel and Cobalt Catalyst as a Method for the Evaluation of the Metallic Phase Surface Area

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Measuring the specific surface area by means of non-specific adsorption is a routine procedure of catalysts characterization. These data, however, can't be used for estimating the dispersion of the active component of the metallic supported catalysts. Thermal desorption of hydrogen may allow such estimation or specific metallic surface may be determined by measuring the amount of nitrous oxide converted to nitrogen while interacting to the catalyst at ambient or slightly elevated temperatures.

$$N_2O + \square_s \rightarrow O_s + N_2 \qquad (1)$$

The method was earlier proved to give reliable data on specific metallic copper surface area, despite diffusion of oxygen to metallic bulk may lead to some overestimation of copper ares (see e.g. [1]). For supported nickel or cobalt catalysts, the rate of oxygen diffusion from the metallic surface to the bulk (i.e. the rate of bulk oxidation) is significant and may hinder metallic surface evaluation.

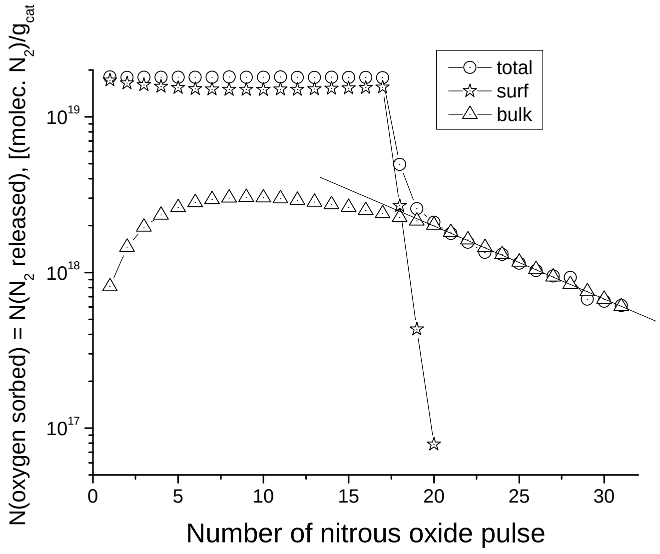

Figure.
Experimental data on the amount of sorbed oxygen during the decomposition of nitrous oxide pulses (50°C, carrier gas He) over Co/δ-Al_2O_3 versus number of N_2O pulse.

In our presentation we report that nitrous oxide adsorption can be reliably used for measuring the specific surface area of the metallic cobalt or metallic nickel active component. The surface oxygen adsorption and oxygen diffusion processes can be discriminated and the impact of bulk oxidation can be subtracted from the total amount of the sorbed oxygen. That information can be further used for estimating the amount of metallic atoms at the surface of the active component and for calculating TOF of the catalytic reaction.

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PP-135

Catalytic Advantages of Solid Solutions, Based on Transient Metal Oxides

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Comprehensive physicochemical study of transient metal oxides with excessive SEM, XRD, and specially developed and improved methods of processing the results of the study led us to a discrepancy between traditional views on catalytic system and both structure and composition of the samples obtained. Subsequently, applying directed synthesis and controlled phase formation it has been shown, that solid solutions are responsible for superadditivity and many other advantages, that do improve structure, composition and operating conditions of novel oxide materials and provides some benefits against traditional monocatalysts or mechanical mixes of those. According to notions on oxide catalyst formation, precursor calcination within vacuum or inert atmosphere leads to simultaneous formation of simple, double and complex oxides within an unstable equilibrium, that spontaneously shifts and leads to decomposition so only simple oxides present. We improved calcination process and stabilized the equilibrium by adding the flux, containing various organic ammonia salts, that resulted in reduction atmosphere within the calcination zone and process. Structural substitution of iron oxide with other transient metal oxides (Mn, Co, etc.) during the calcination process is well-described with anti-Ginstling model and reveal two phases: dendrite-like solid solution of magnetite Fe_3O_4 in magghemite γ-Fe_2O_3 and spinel sites that contain ferrite ($Me^{+2}Fe_2O_4$).

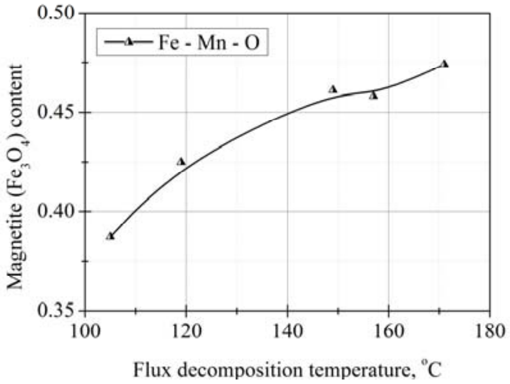

Fig.1

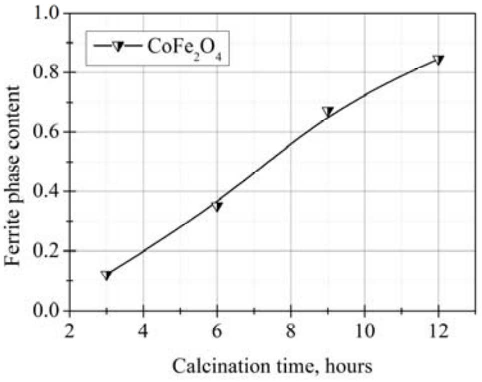

Fig.2

As calcination time increase, magnetite content shorten because of conversion to ferrite. Both phases are involved in catalysis, share oxygen transport, but activity is primarily determined by magnetite content, so we keep it by complicating the flux and rising it's decomposition temperature, as shown on fig.1. The same measures allow us to shorten calcination time to prevent ferrite excess, as shown on fig.2, because it shows negative influence on 50% conversion temperature. Ferrite content stands for thermal stability of the catalyst, so it has to present in amounts less or equal to magnetite.

Alkyne and Alkene Hydrogenations on Immobilized Iridium Complexes Investigated by PHIP Technique

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Parahydrogen-induced polarization (PHIP) can significantly boost the sensitivity of NMR methods (for ^1H up to 10^4 times), and is a powerful investigation tool for hydrogenations of unsaturated compounds. Increasing the sensitivity is very important since the conventional NMR or MRI methods are very difficult or impossible to use when an NMR-active substance is in a low concentration, which often takes place for intermediates of hydrogenation reactions. Also having the characteristic signals, PHIP allows one to identify hydrogen atoms originated from parahydrogen molecule uniquely, acting as a spin labeling technique.

Here we present an investigation of heterogeneous hydrogenation of unsaturated substances catalyzed by immobilized iridium complex $Ir(COD)/SiO_2^P$ using PHIP. The catalysts of this kind are interesting due the fact that they can combine advantages of homogeneous (high enhancement of NMR signals) and heterogeneous (facilitated catalyst separation) catalysis. The immobilized complex $Ir(COD)/SiO_2^P$ was prepared by covalent binding of $[Ir(COD)Cl]_2$ with phosphine groups (PPh_2-) of surface-modified silica gel. It was found that the gas phase hydrogenation of propyne led to a significant enhancement (200-250 fold) of NMR signals of vinyl protons in propene molecule. At the same time, only a weak signal enhancement was observed in the hydrogenation of propene. Characteristic PHIP signals were also observed in the liquid-phase hydrogenation of phenylacetylene, 3-butyn-2-ol and acrylamide, while in the case of styrene hydrogenation, 3-buten-2-ol and acrolein only thermally polarized signals of reaction products were detected. Styrene deuteration has shown the formation of HD. Thus, we assume that on $Ir(COD)/SiO_2^P$ the intramolecular exchange of hydride ligands of dihydrogen complex with hydrogen atoms of coordinated substrate or phenyl groups of immobilized complex occurs [2]. These processes lead to the non-pairwise H_2 addition, excluding possibility of PHIP production. It is probable that in the hydrogenation of substrates with double bond, the rate of hydrogen exchange is higher in comparison to the rate of the hydrogenation reaction and PHIP is not observed. At the same time, observation of PHIP in alkynes and acrylamide hydrogenation indicates that the influence of these processes is not significant in the case of such substrates.

Acknowledgement. This work was supported by RFBR, grant 16-33-60198 mol_a_dk

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PP-137

Innovative TMR-GC/MS System for Rapid Characterization of Catalysts: Ethanol and Citrus Unshui Peel Conversion

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Due to the increased demand for the renewable energy, many researchers are focusing the thermal and catalytic conversion of biomass [1] and bio-ethanol [2]. Micro scale lab reactors are applied to the catalyst research as the first step for developing catalytic conversion process, offering many advantages such as cheaper equipment, less feeding material, screening capabilities, lower utility requirements and higher accuracy. Recently, a new tandem micro-reactor system, consisted with two independent micro reactors and directly interfaced with a conventional GC/MS system, was introduced for the fast and simple test of catalyst [3].The tandem micro reactor system consisted of two furnaces in series and is online coupled with a conventional GC/MS. Gas, liquid or solid samples can be introduced into a 1st furnace using a micro-syringe, micro feeder, or sample cup for gas preheating, liquid vaporization, or solid pyrolysis. The vapors from the 1st furnace meet the catalyst located in the catalytic bed of 2nd reactor and converted to other chemicals over a catalyst. The final products are moved to the GC via a deactivated metal needle, separated in the column and finally detected by MS. As first application conversion of Ethanol to Butadiene (→styrene butadiene rubber →tires) is shown. The efficiency and selectivity of the catalytic conversion of Ethanol to Butadiene affects the profitability and productivity of the entire process. It is therefore critical that each new catalyst be screened so that those with the potential to increase either the efficiency or the conversion selectivity are quickly identified and advance to the next level in the evaluation process. Catalytic conversion can be also influenced by adding high pressure capabilities. The second application is considering inedible C. unshiu peel, representing an example of waste material, as bioenergy source because the peel contains pectin, hemicellulose, cellulose and lignin as the main cell wall components. Therefore, a desirable treatment method is needed to use C. unshiu waste peel for producing value added fuel or chemical source from it. The tested applications for the catalytic conversion of ethanol and citrus unshiu peel well indicated the feasibility of tandem micro reactor-GC/MS system as a simple and fast screening tool for the catalytic reaction.

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Multifunctional Combined Catalyst for Diesel Engine Exhaust Aftertreatment System

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It was repeatedly shown that physical mixture of oxidation catalyst (*e.g.* Mn/$Ce_xZr_{1-x}O_2$) and zeolite (*e.g.* H-BEA, Fe-ZSM-5) showed significant increase of NH_3-SCR activity due to the synergetic effect between the two components [1,2]. Our studies indicated that such combined catalysts (CombiCats) were also effective for soot oxidation and NH_3-slip removal [1,3]. This study was focused on two main aspects: (1) simultaneous removal of NO_x, CO, hydrocarbons and NH_3-slip over CombiCat; (2) possible interferences between NH_3-SCR and oxidation processes.

[Mn-Ce/$Ce_{0.75}Zr_{0.25}O_2$ + FeBeta] CombiCat was prepared by mechanical mixing of Mn-Ce/$Ce_{0.75}Zr_{0.25}O_2$ with FeBeta at a weight ratio 3/1. In soot oxidation experiments [Mn-Ce/$Ce_{0.75}Zr_{0.25}O_2$ + FeBeta] was mixed with PrintexU (synthetic model soot) at a weight ratio 10/1. Catalytic activities of CombiCat, CombiCat+soot and individual components were measured using a feed gas simulated real diesel engine exhaust: 500 ppm NO, 600 ppm NH_3, 10% O_2, 5% CO_2, 200 pmm CO, 500 ppm C_4H_{10}, 6% H_2O balanced with N_2.

It was shown that, in addition to high efficiency in NH_3-SCR, [Mn-Ce/$Ce_{0.75}Zr_{0.25}O_2$ + FeBeta] CombiCat demonstrated promising activity in simultaneous CO, hydrocarbons, soot oxidation and NH_3-slip removal. Comparative studies of NH_3-SCR performance of CombiCat and individual components indicated that NH_3-SCR proceeds on FeBeta via a “bifunctional” SCR mechanism (reactions 1 and 2) proposed in [1], and NH_3-slip removal process is an integral part of this mechanism (reaction 2).

$2NO + O_2 \rightarrow 2NO_2$ – NO oxidation on Mn-Ce/$Ce_{0.75}Zr_{0.25}O_2$ (1)

$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$ – Fast SCR on FeBeta (2)

In contrast, oxidation of hydrocarbons, soot and CO proceeds over Mn-Ce/$Ce_{0.75}Zr_{0.25}O_2$ component independently of NH_3-SCR.

The data obtained indicated that [Mn-Ce/$Ce_{0.75}Zr_{0.25}O_2$ + FeBeta] CombiCats, combining in one catalytic break oxidation and SCR functionalities, can be considered as a perspective multifunction system for diesel exhaust abatement.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant 15-03-07802 A.

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PP-139

"Polyfunctional" Mn-Ce/Beta Catalysts for Simultaneous NH_3-DeNO$_x$ and CO/HC Oxidation

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Due to the limited volume of the aftertreating system, an integrated catalytic system with several functions combined in a single catalyst brick can provide an attractive solution. Previously we have developed an effective catalyst Mn-Ce/Beta [1,2], combining high activity in selective catalytic reduction of NO_x by ammonia and NH_3 oxidation.

This study has been focused on the following issues: 1) to investigate of the catalyst with in simultaneous oxidation of CO and hydrocarbons proceeding in parallel with NH_3-DeNO$_x$; 2) to unravel possible interferences between these processes.

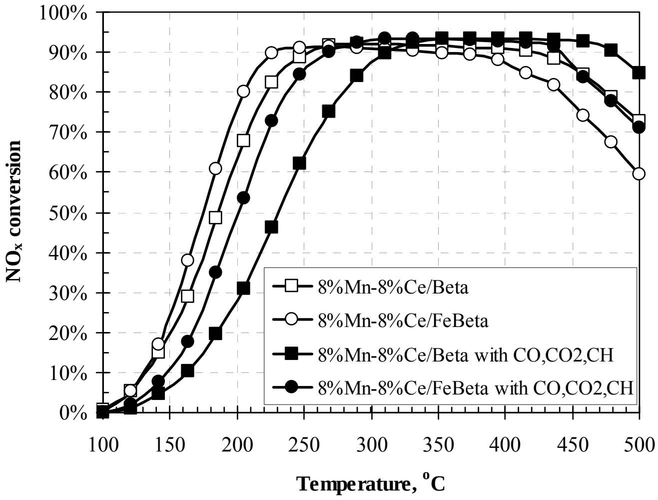

Fig.1. Effect of CO and hydrocarbons on DeNO$_x$ activitiy of Mn-Ce/Beta catalyst.

DeNO$_x$ activities of Mn-Ce/Beta in a single DeNO$_x$ process and in DeNO$_x$ coupled with CO/HC oxidation are compared in Fig. 1. Introduction of CO and HC in the reaction mixture decreases activity of Mn-Ce/Beta due to the competition between SCR and CO/HC oxidation intermediates for the active sites.

On the other hand, oxidation of CO and hydrocarbons occurs essentially independently on DeNO$_x$ process. These results suggest the several processes (DeNOx, oxidation of NO, CO, hydrocarbons) can be combined over polyfunctional Mn-Ce/Beta catalyst.

Acknowledgement. The support of Russian Foundation for Basic Research (Grant: 15-03-07802 A) is gratefully acknowledged. D. Krivoruchenko is grateful to Haldor Topsøe A/S for financial support in the framework of Ph.D. student support programme.

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Selective Liquid-Phase Hydrogenation of Internal and Terminal Alkynes over Novel Pd-In Bimetallic Catalysts

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Performances of the novel Pd-In catalysts supported on Al_2O_3 and $MgAl_2O_4$ have been studied in selective liquid-phase hydrogenation of terminal and internal alkynes (phenyl- (**PA**) and diphenylacetylene (**DPA**), and 1-phenyl-1-propyne (**PP**)). The catalysts were synthesized via novel Pd-In(OAc)$_5$ heterobimetallic acetate complex with unique structure as a precursor. Since Pd and In are linked by acetate bridges until reduction, this enables formation of highly homogeneous bimetallic nanoparticles in a final catalyst. Monometallic Pd/Al_2O_3 and the commercial Lindlar catalyst 5%Pd-Pb/$CaCO_3$ (Alrdich #62145) were used as the references.

The structure of synthesized catalysts was characterized by TPR, FTIR-CO and TEM techniques. Characterization data reveal formation of Pd-In bimetallic particles (~ 6 - 8 nm size) after reduction at 550°C.

Pd-In catalysts exhibit excellent selectivity in *cis*-alkene upon hydrogenation of internal alkynes, though their activities are lower then the activity of monometallic Pd. It should be noted that Pd-In/Al_2O_3 demonstrates activity and selectivity identical to Lindlar catalyst (~ 95% at ~ 90% DPA conversion), but at a substantially lower noble metal content and in the absence of toxic Pb compounds. On the other hand, no selectivity improvement was observed in hydrogenation of terminal **PA**. Pd-In compositions demonstrate selectivity similar to the selectivity of Pd catalyst, and lower than that of Lindlar catalyst.

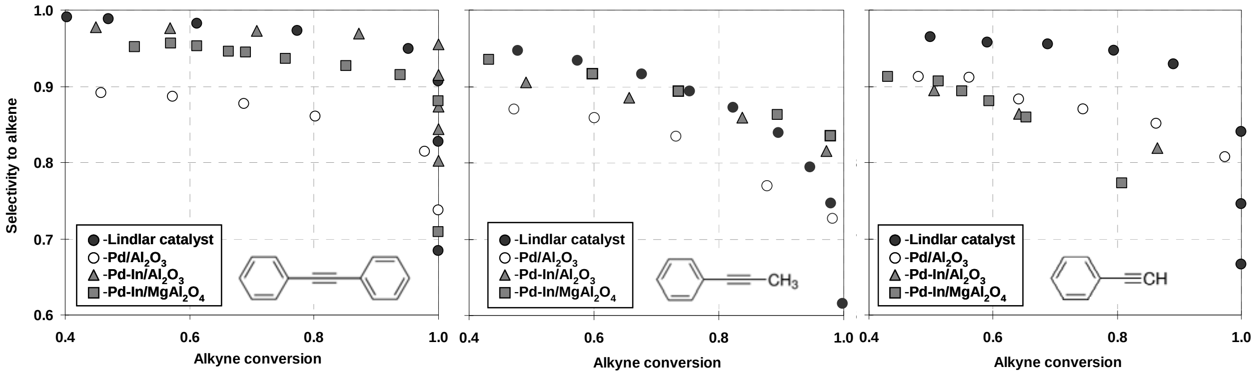

Figure 1. Dependencies of the selectivity in alkene on alkyne conversion for Pd-In catalysts in hydrogenation of internal and terminal alkynes.

Acknowledgement . The authors are sincerely grateful to the Department of Structural Studies of the ZIOC RAS for studies by electron microscopy.

This work was supported by the Russian Foundation for Basic Research (Grants #15-03-07652 and #16-29-10788).

PP-141

The Reaction Thermodynamics and Mechanisms of H_2S Decomposition into Hydrogen and Elemental Sulfur

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Three possible pathways of H_2S decomposition into hydrogen and elemental sulfur are considered. In the thermal process, H_2S dissociation is attended with the formation of both diatomic hydrogen and sulfur into the singlet state according to the spin conservation rule [1].

$$H_2S \xrightarrow{\Delta T > 1000\ oC} H_2 + ½\ {}^1S_2^{(gas)} \qquad (1)$$

On the surface of sulfide catalysts, H_2S splitting proceeds at low temperature through the stage of disulfane, H_2S_2 formation as a key surface intermediate, followed by its decomposition due to release of hydrogen into the gas phase and recombination of the adsorbed singlet sulfur into cyclooctasulfur [2,3].

$$2\ H_2S \xrightarrow{\text{sulfide catalyst, 25 oC}} \{H_2S_2\}_{ads} + H_2 \rightarrow H_2 + ¼\ S_8^{(solid)} \qquad (2)$$

On the metal catalysts, H_2S decomposition occurs at low temperature through the stage of H_2S dissociation into the adsorbed atomic surface species resulted in the formation of both diatomic reaction products in the ground electronic state – the singlet hydrogen and the triplet diatomic sulfur [1,4].

$$H_2S \xrightarrow{\text{metal catalyst, 25 oC}} H_2 + ½\ {}^3S_2^{(gas)} \qquad (3)$$

To shift equilibrium of the reaction (3) towards the formation of the desired reaction product – hydrogen, the process of H_2S decomposition is proposed to carry out at ambient temperature in the three-phase reactor when the solid catalysts are placed into a layer of solvent capable of dissolving H_2S and sulfur produced [5,6]. Removal of hydrogen from the reaction medium caused in achieving H_2S conversion close to 100 %. This gives grounds to consider hydrogen sulfide as a potential inexhaustible source of hydrogen, a valuable chemical reagent and environmentally friendly energy product.

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C4-C5 Alcohols Condensation Reactions over VIII Group Metals

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Availability of bio-based alcohol feedstock provides a huge interest to the development of novel synthetic routs for the synthesis of commercially valuable chemicals [1]. C4-C5 alcohols produced selectively from bio-derived acids [2] can be used in coupling reaction representing an attractive way to produce C8-C10 branched-chain Guerbet alcohols valuable in biofuel production terms. These alcohols have extremely low melting points and excellent fluidity [1]. The industrial production of Guerbet alcohols employs homogeneous catalysts with disadvantages such as in product purification, recovery and cost of the catalyst and waste treatment. As an alternative way, the implementation of mixed homogeneous and heterogeneous systems can be applied. This study focuses on the heterogenization of the catalytic systems when mixed catalytic systems are applied composed of heterogeneous dehydrogenation-hydrogenation catalysts complemented by the presence of alkali/alkaline earth hydroxide or oxide.

Heterogeneous catalysts applied were Ir/ZrO_2, Ir/CeO_2, Pt/C as well as dual IrRe/SiO_2 while basic co-catalysts were chosen such as NaOH, MgO, CeO_2, $Al(OH)_3$. Liquid phase condensation of C4-C5 alcohols (15 mL) were carried out in autoclave (150 mL) at 180°C and 10 bar of H_2 pressure. The reaction products were analyzed by GC (FID) with ZB-Wax (30 m/0.25 mm/0.25μm) column at 50-260°C with temperature ramp 8°C/min. Catalysts were characterized by H_2 TPR and HRTEM.

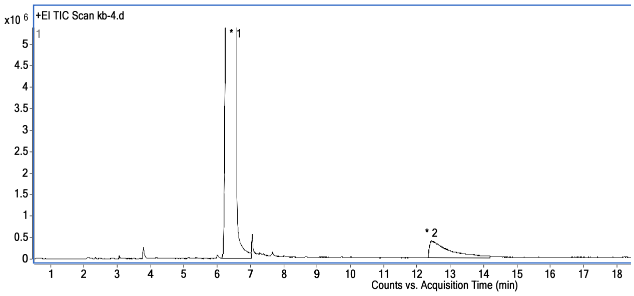

Fig. 1. GC analysis: C4 alcohol (1) condensation to 2-ethyl-1-hexanol (2) over 3%Pt/C (0.1g)@ NaOH (0.1 g), 180°C, 10 bar H_2.

Ir/CeO_2, Ir/ZrO_2, and IrRe/SiO_2 as well as Pt/C doped by CeO_2 were shown to be little active in C4-C5 alcohols condensation while Pt/C complemented with small amount of NaOH (0.1 g) resulted in targeted 2-ethyl-1-hexanol with 98% selectivity (Fig. 1). Ten-fold increase of NaOH (1.0 g) resulted in appearance of unsaturated 2-ethyl-3-hexen-1-ol and 2-ethyl-2-hexen-1-ol indicating acceleration of aldol condensation rate compared to hydrogenation of C=C double bond of intermediate C8-C10 unsaturated alcohols. Kinetic regularities of C4-C5 alcohols condensation are discussed.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 15-03-09329.

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PP-143

Kinetic and Mechanism of Stearic Acid Hydrodeoxygenation Catalyzed by Pd Impregnated in HPS

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Nowadays there are many investigations in the field of hydrodeoxygenation reaction focused on the search of high efficient non-sulfurized catalysts allowing production of sulphur free biofuel with high quality. The most investigated catalysts are Ni and Pd supported on inorganic materials [1-3]. Current work is devoted to the study of kinetic and mechanism of stearic acid catalytic hydrodeoxygenation reaction.

The kinetic experiments were carried out in stainless steel temperature-controlled autoclave reactor Parr – 4307 in the presence of 1%-Pd/HPS. The following parameters were varied: catalyst loading $[cat]_0$ ($1.6\cdot10^{-4}$ ~ $3\cdot10^{-4}$ mol(Pd)/L), initial concentrations of stearic acid $[C]_0$ (0.05 ~ 0.2 mol/L), temperature (230 ~ 260°C), and hydrogen partial pressure (0.2 ~ 1.8 MPa). N-dodecane was used as solvent.

Basing on the kinetic curves obtained for both of stearic acid (substrate) and n-heptadecane (main product) it was founded the hydrodeoxygenation process remains 3 stages: (i) the increase of reaction rate at low substrate conversion; (ii) the constant reaction rate in the conversion range 10-90%; and (iii) the decrease of reaction rate at high substrate conversion. The process scheme can be presented as following: an equilibration between the substrate and catalyst active sites and further substrate conversion into reaction product.

$$SA + \mathrm{Cat} \xleftrightarrow{K_p} [SA - \mathrm{Cat}] \xrightarrow{k_1} n - HpD + \mathrm{Cat}$$

SA – stearic acid; n-HpD – n-heptadecane; Cat – active site concentration on the catalyst surface; K_p – sorption constant; k_1 – reaction rate constant.

The kinetic equation of proposed scheme taking into account the percent of activated catalyst can be presented as:

$$\frac{d[SA]}{dt} = -\frac{\alpha \cdot k_1 \cdot K_P \cdot [SA]}{(1 + K_P \cdot [SA])},$$

$$\alpha = \frac{[Cat^*]_i}{[Cat]_0};\; k_1 = \left(\frac{1.5 \cdot 1.5 \cdot \sqrt{P_{H_2}}}{1 + 1.5 \cdot \sqrt{P_{H_2}}}\right) \exp\left(10.473 - \frac{2404}{T}\right) \cdot k_{01}$$

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Ethanol Conversion into Butadiene over Solid Catalysts: from the Reaction Mechanism to the Catalyst Design

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The increasing demand in the synthetic rubber attracts great attention to the development of novel routes of butadiene synthesis, which is a strategically important monomer for the production of rubbers, plastics and chemicals. In this contribution we report on the main routes of butadiene synthesis from ethanol.[1-3] Different zirconium containing silver promoted solid catalysts including molecular sieves, supported and bulk oxides are studied. The target reaction pathway leading to butadiene is demonstrated to include five consecutive reaction steps: 1) ethanol dehydrogenation into acetaldehyde; 2) aldol condensation of acetaldehyde; 3) dehydration of 3-hydroxybutanal; 4) MPVO reduction of crotonaldehyde with ethanol; and 5) dehydration of crotyl alcohol into butadiene. The main attention is focused on the investigation of the main reaction steps including ethanol dehydrogenation, aldol condensation and MPVO reduction using the SSITKA approach, label tracing experiments and in situ spectroscopic studies.The results obtained allow to determine the active sites of the main reaction steps and to elucidate the mechanisms of these steps over various catalysts. It has been demonstrated that over the metal containing catalysts the key reaction step is aldol condensation of acetaldehyde. The mechanism proposed shows the way for the design of efficient solid catalyst for one-step selective synthesis of butadiene from ethanol and to select the optimal conditions for this reaction.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-23-00094.

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PP-145

Methane Combustion over Mn-containing Cordierites

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Manganese oxide catalysts were found to show a good performance for catalytic oxidation reactions such as oxidation of methane, different organic compounds, CO, ammonia, soot and others. The activity is associated with the capacity of manganese to form various oxidation states (Mn^{2+}/Mn^{3+} or Mn^{3+}/Mn^{4+}) and show good redox properties. However pure and supported manganese oxides lose their catalytic activity in reactions at high temperatures (> 500 °C) due to the reduction to less selective species, sintering and interaction of active oxides with support materials. On the other hand, manganese-containing catalysts with the structure of perovskite, spinel or hexaaluminate have sufficient heat resistance for high-temperature applications.

Cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) is widespread commercial material for high temperature catalyst applications due to very low coefficient of thermal expansion, high resistance to thermal shock and good mechanical properties. A frame structure allows to obtain modified materials with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+} cations instead of Mg^{2+}. In this work we studied the formation of Mn-containing cordierites, the state and distribution of manganese cations in the catalysts and their activity in methane combustion reactions.

The series of Mn-containing cordierites were prepared from natural components (talc, clay, alumina) and Mn oxides (MnO, Mn_2O_3, MnO_2). Prepared catalysts were studied with XRD, DDPA, XPS, BET, TPR, TPD-O_2 methods in order to correlate surface and bulk properties with catalytic activity in methane combustion.

It was found that calcination at 1050-1150 °C leads to the crystallization of Mn-substituted cordierite where Mn^{2+} cations are introduced into the cordierite structure while Mn^{3+} cations are distributed between the catalysts surface and cordierite channels. The amount of Mn^{3+} cations on the catalysts surface depends on the preparation conditions: the type of manganese oxide, calcinations temperature, preliminary mechanical treatment.

The methane combustion was carried out at 650–900 °C, atmospheric pressure, gas mixtures 1% CH_4 + 10% O_2 in He, space velocity about 60000 h^{-1}. The catalytic activity of Mn-containing cordierites seems to be related to the reduction/oxidation behavior of surface Mn^{3+} cations: the most active catalyst is related the highest superficial Mn concentration and Mn^{3+}/Mn^{2+} ratio. Long-live test confirms the high stability of Mn-containing cordierites under reaction conditions.

Acknowledgement. This work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (project V.44.2.5).

PP-146

Biomimetic Catalytic Oxidation of Water with $Ru(bpy)_3^{3+}$ in the Presence of Colloidal Cobalt (III) Hydroxide. Kinetics and Mechanism Study

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In any artificial photosynthetic system the oxidation of water to molecular oxygen provides the electron needed to the reduction of proton or carbon dioxide to a fuel. Understanding how this for-electron reaction works is important for development of the improved catalysts made of Earth-abundant materials, like transition metal hydroxides (Co, Mn, Fe). This work we studied the kinetics of reaction (I) as well as the yields of oxygen in the presence of colloidal cobalt (III) hydroxide catalyst stabilized by modified starch [1].

$4\ Ru(bpy)_3^{3+} + 2\ H_2O \rightarrow 4\ Ru(bpy)_3^{2+} + O_2 + 4\ H^+$; here: bpy – bipyridyl (I)

$Ru(bpy)_3^{3+}$ is one of the most promising water oxidant which can be produced from $Ru(bpy)_3^{2+}$ by UV-radiation. We studied the kinetics using a stop-flow UV-spectrometer. The O_2 yields were measured by oximeter with Clark electrode.

The oxidant was found to disappear in accordance to the first order kinetics. The effective first order rate constant of the process (k_{eff}) obeys the linear dependence on the catalyst concentration. The plots of $1/\ k_{eff}$ vs. the initial concentrations of the oxidant and its reduced form were found to be linear. A formal scheme of the reaction corresponding to the observed kinetics was proposed. From this scheme, the adsorption constants of the oxidant and its reduced form onto the catalyst surface as well as the rate constant of the first electron transfer from the catalyst to the oxidant were calculated. At wavelength ~550 nm an intermediate of reaction was found. This absorbance was attributed to peroxocomplex of Co in the composition of catalysts. The dependencies of the oxygen yield on pH, as well as on the catalyst and oxidant concentrations were evaluated. The oxygen yield was found to depend on the ratio of the oxidant to catalyst concentrations, showing the maximum at the ratio (10-100):1. Lower ratios results in decreasing of the oxygen yields and increasing the concentration of the intermediate. The results allow us to propose an overall mechanism of the process including the formation of: 1) a terminal peroxocomplex as an intermediate of the water oxidation; 2) a bridged peroxocomplex as an intermediate of a side reaction of the bipyridyl ligands oxidation.

Acknowledgement. This work was supported by Russian Foundation of Basic Research (project No.15-29-01275).

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PP-147

Nickel Ziegler Systems in Arenes Hydrogenation Catalysis

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The possibility of arenes hydrogenation on Ziegler systems has been described in several articles [1, 2]. The other fundamental research about this topic are practically absent in the literature.

The report presents the results of kinetic studies of benzene and its methyl homologues hydrogenation on nickel Ziegler systems $Ni(acac)_2$ – Red (Red = $AlEt_3$ or $AlEt_2(OEt)$).

It has been found that acceptable hydrogenation rates for the study are observed in the temperature range 80 – 150 °C. Magnitude of turnover frequency (TOF) of arenes hydrogenation is determined primarily by molar ratio Red/$Ni(acac)_2$. This dependence is characterized by a sharp peak at Al/Ni = 4 for the system based on $Ni(acac)_2$ – $AlEt_3$ and TOF is maximal at a ratio of Al/Ni = 4 ÷ 10 for the $Ni(acac)_2$ – $AlEt_2(OEt)$ system. Thereby careful observance organoaluminium compound concentration in the catalyst formation step is unnecessary.

It is shown that TOF of aromatic molecules hydrogenation decreased in the order of benzene > toluene > *p*-xylene > *m*- xylene ≥ *o*- xylene > mezitilene over the entire studied temperature range. The results of competitive hydrogenation of benzene with toluene or with three xylene isomers was obtained at T = 120 ^{0}C and $P_{H2\ initial.}$ = 15 atm in the presence of two catalytic systems $Ni(acac)_2$ – Red (Red = $AlEt_3$ or $AlEt_2(OEt)$). It was found that the ratio $[TOF_{benzene}]/[TOF_{alkyl\ substitution\ arene}]$ significantly higher than those values for the hydrogenation of individual arenes. The relative ratio of the equilibrium constant of benzene complexation (adsorption) to a similar quantity of alkyl substituted arenes were calculated by Smidt method [3]. The results are explained in terms of the arenes hydrogenation mechanism including the steps of forming π-complex arene with a nickel surface, its isomerization to π/σ-complex of benzene with several nickel atoms and the stage of the sequential addition of H_2 to arene-bound complex. The mechanism of heterogeneous arenes hydrogenation on nickel systems is compared with mechanism of homogeneous arenes hydrogenation on cobalt systems [4].

Acknowledgement. This work was supported by a base part of Government Assignment for Scientific Research from the Ministry of Education and Science, Russia (№2014/51,project code: 627).

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PP-148

Catalysis of Benzene Hydrogenation by Phosphine Cobalt Complexes

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The report presents a new experimental fact that we found in the study of the effect of the Co(acac)$_2$ catalytic systems composition on the catalytic activity nature in the hydrogenation of alkenes and arenes and conjugated hydrogenation of alkenes with arenes.

It was found that the benzene hydrogenation is observed when Co(acac)$_2$ react with organoaluminium or organomagnesium reducers (Red = AlR$_3$, MgRX, where X = halogen) in the presence of PBu$_3$ (or P(OEt)$_3$) in benzene and in hydrogen atmosphere (2 atm.) (tabl.). Depending on the time of benzene hydrogenation both expected cyclohexane and cyclohexene are present in reaction products. It was shown that the 1,5-hexadiene is generated by interaction of components of Co(acac)$_2$–3PBu$_3$–C$_3$H$_5$MgBr system, and its yield might achieve about 80% of the quantity of C$_3$H$_5$MgBr introduced into the reaction. These results as well as increasing of amount of hydrogenated benzene at lower process temperature (see tabl, pt. 6 and 7) confirm our previous proposal [1]. Namely, transition alkyl, allyl, benzyl complexes formed by the interaction of system components or products of its transformations under the hydrogen action are responsible for the catalysis of benzene hydrogenation under mild conditions.

Table. The effect of composition of catalytic system Co(acac)$_2$–3PBu$_3$–Red on the its quantitative parameters in benzene hydrogenation: $C_{Co} = 1\times10^{-2}$ mol/l, reaction time – 30 min, V_{system} = 20 ml, T = 30 °C.

№	Organometallic Compound	Red/Co	T, °C	Product, mol		TON, (mol H$_2$)·(mol Co)$^{-1}$
				Cyclohexene	Cyclohexane	
1	Al(C$_2$H$_5$)$_3$	4	30	-	1.5×10^{-5}	0.45
2	C$_3$H$_5$MgBr	2	8	0.8×10^{-6}	9.2×10^{-5}	3.30
3		6	8	0.6×10^{-6}	1.2×10^{-4}	5.40
4	C$_6$H$_5$CH$_2$MgCl	2	8	-	3.4×10^{-5}	1.0
5		4	8	-	4.2×10^{-5}	2.2
6		6	8	1.0×10^{-5}	2.0×10^{-4}	6.3
7		6	25	-	3.2×10^{-5}	0.98
8	C$_3$H$_5$MgBr – P(OC$_2$H$_5$)$_3$	2	8	2.0×10^{-5}	1.1×10^{-4}	3.7

Acknowledgement. This work was supported by a base part of Government Assignment for Scientific Research from the Ministry of Education and Science, Russia (№2014/51,project code: 627).

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PP-149

Catalyst Systems of Desulfurization of Motor Fuels Based on Vanadium and Molybdenum Oxides

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The global trend of the refining industry is aimed at improving the environmental performance of motor fuels, thus tightening the quality requirements for them. One of such parameter is the sulfur content in diesel fuels. According to international environmental standards «Euro-5» sulfur content in diesel fuel must not exceed respectively 10 ppm [1]. For removal of sulfur compounds from the diesel hydrotreating process is widely used. Despite the high efficiency, hydrotreating still has certain drawbacks, the main of which is the high cost of hydrogen and H_2S disposal problem [2]. In this regard, of new desulfurization methods are actively developed, based on the oxidation of sulfur-containing compounds. Oxidation takes place under homogeneous conditions and oxidation products are valuable chemicals - sulfoxides and sulfones. However, these methods have drawbacks related to the use of oxidizing reagents and the difficulty of separating the catalyst from the products.

This paper presents the results obtained using the new method essentially oxidative desulfurization air oxygen over heterogeneous catalysts, which are used as individual and mixed oxides of vanadium and molybdenum. This approach to oxidative desulfurization is effective as a method of removing hydrocarbons thiophene series, which does not require costly reagents, and simplifies the separation of the reaction products from the catalyst.

A fundamental possibility thiophene oxidation by air oxygen in a model mixture of dodecane with vanadium-molybdenum catalysts is shown, as well as oxidative desulfurization of diesel fuel.

A significant decrease in the content of organic sulfur compounds in the straight and hydrotreated diesel fuel was found after the oxidative desulfurization of atmospheric oxygen on vanadium-molybdenum catalysts. The optimal conditions were found for the catalytic oxidative desulfurization.

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PP-150

Preparation of Different Palladium Supported Catalysts for Partial Hydrogenation of Sunflower Oil

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During partial hydrogenation plant oils occurs some of the *cis* double bonds are isomerized to *trans* double bonds, mainly trans fatty acids (TFA) formed [1]. Recent studies have shown that TFA have negative effects for human health [2]. So, nowadays real challenges is seeking ways to reduce the level of TFA in hydrogenated fats and preparation of new active catalyst for hydrogenation of edible oils to obtain healthy food.

The aim of this research is to study influence of the supports on the activity of palladium catalysts in the partial hydrogenation of sunflower oil. This work is to use diatomite (d), kaolin (k), vermiculite (v), glauconite (g), bentonite (b) as a catalyst supports. Palladium chloride was used as the palladium precursor and palladium was loaded at 0.2wt. %. The activity of these catalysts are studied during the hydrogenation of sunflower oil at 90°C, P_{H2} = 5atm and stirring rate-800 rpm, catalyst/oil weight ratio = 1/1000. Analysis fatty acid composition of the hydrogenated oils was determined by capillary gas chromatograph (Chromos 1000) according to ISO 52677 method. Table 1 shows the results of the changes of fatty acid composition and physical properties in hydrogenated oil.

Table 1. Changes in chemical composition of fatty acid in hydrogenated sunflower oil

Fatty acids (wt%)	Sunflower oil	Pd/(d)	Pd/(V)	Pd/(b)	Pd/(k)	Pd/(g)
C14:0 - Myristic acid	0.07	0.08	0.08	0.07	0.07	0.09
C16:0 - Palmitic acid	6.48	7.18	7.46	6.45	7.43	7.33
C18:0 - Stearic acid	4.03	9.65	9.42	9.35	8.40	11.79
C18:1c - Oleic acid	24.65	59.65	54.52	61.71	32.86	56.03
C18:1t - Oleic acid	1.31	18.63	25.07	15.83	26.51	18.53
C18:2c - Linoleic acid	61.62	2.05	1.97	1.63	0.62	1.75
C18:2t - Linoleic acid	0.35	1.47	0.326	2.49	0.92	1.60
C20:0 - Arachidic acid	0.25	0.29	0.29	0.31	0.32	0.32
C22:0 - Behenic acid	0.70	0.74	0.80	0.789	0.81	0.75
Total *trans%*	1.7	20.10	25.39	18.32	27.43	20.13
Iodine value	130.08	73.19	71.95	75.78	74.17	72.62
Melting point (°C)	-16.3	32.3	33.7	31.0	34.0	31.6

Table 1 shows the fatty acids composition of produced by hydrogenating sunflower oil over the different Pd supported catalysts are high activity and selectivity lower temperature. The levels of TFA in hydrogenated oils were decreased using Pd/(b), Pd/(d) and Pd/(g) catalysts.

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PP-151

Catalytic Conversion of Aliphatic Alcohols over Carbon Materials: The Effect of Functional Groups and Carbon Matrix Structure on the Reaction Mechanism

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Metal-free materials based on carbon nanostructures are promising catalysts in acid catalysis. In the current work we have studied the effect of structure and surface functional groups of carbon nanotubes (CNT) on the mechanism of catalytic conversion of aliphatic alcohols: ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol and t-butanol. The reaction was studied using an impulse microcatalytic method on pristine and oxidised CNT catalysts. A sample of the catalyst (50 mg) was placed between two layers of glass wool into a reactor tube. Alcohol vapours (5 μmol) were injected and the products were analysed by an online gas chromatograph.

An XPS study of the catalysts showed a vast difference in oxygen content: 0.6% and 9.4% for pristine and oxidised CNTs, respectively. However, both materials were active in alcohol conversion showing various conversions and selectivities. The main product of alcohol conversion over pristine CNT was aldehyde with the selectivity decreasing with the number of carbon atoms in the alcohol. Oxidised CNT also preferentially formed aldehydes in case of ethanol and 1-propanol, but it substantially decreased in the conversion of 1-butanol falling from 71 to 48 %. A much smaller difference in catalytic behaviour between the oxidised and pristine CNT was observed in the conversion of secondary alcohols. A high conversion of 2-propanol (70 %) and 2-butanol (88 %) towards dehydration was observed on both catalysts studied.

High catalytic activity of the pristine CNT suggests an important role of the carbon structure on catalytic activity. Its activity was likely caused by the presence of surface defects because the curved shape of CNT is formed by the presence of 5- and 7-membered carbon rings in the graphene structure [1]. However, the comparison of oxidised and pristine CNT shows a substantial increase in the selectivity towards dehydration, which indicates an important role of surface oxygen groups in the reaction. Hence, the mechanism of the conversion of aliphatic alcohols over carbon nanotubes is determined not only by the structure of the carbon matrix, but oxidation state of the surface functional groups.

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Effect of Hydrophobicity of TS-1 Titanosilicate on Its Oxidation Activity

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TS-1 titanosilicate materials exhibit high activity in a number of oxidation reactions such as alkene epoxidation, phenol hydroxylation, ketone ammoxidation *etc.* Its attractive advantage as a catalyst for these reactions is the use of hydrogen peroxide as a "green" oxidation agent. This unique feature of TS-1 materials is due to rather specific interaction of H_2O_2 molecules with their catalytic sites the role of which play Ti atoms replacing Si atoms in zeolitic framework. Besides, the hydrophobic properties of TS-1titanosilicates are also crucial factors that determine their high efficiency in oxidation catalysis [1,2,3].

The oxidation reactions that occur under various conditions (solvent, pH value) with different substrates were shown to require an optimum hydrophobicity of titanosilicate catalyst used [2,3]. In this connection, we have undertaken the experimental study aimed to clear out how various synthetic approaches, namely, using the seeds, mixing the stock solutions during the hydrothermal synthesis *etc.,* affect the physico-chemical properties of the end titanosilicate products.

The catalysts prepared by different ways were also used to study kinetics of phenol hydroxylation, cyclohexane epoxidation and cyclohexanone ammoxidation.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-23-00094.

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PP-153

Performance of Modified Nickel Catalysts in a Catalytic Membrane Reactor for Partial Oxidation of Methane

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Natural gas is broadly used as a feedstock in the production of liquid hydrocarbons via synthesis gas (syngas) as an intermediate step [2]. The industrial reforming of natural gas to syngas is dominated by catalytic steam reforming [3], which requires a large excess of the gas supply for heating. The catalytic partial oxidation (CPO) allows the energy efficiency to be improved due to the using of the heat evolved in the CPO reaction. Further advancement in the overall performance of the gas to liquid process can be achieved by combining CPO with oxygen separation from air in a membrane reactor [4]. The long term stability and selectivity toward products of partial oxidation, i.e. CO and H_2, greatly depend on the catalyst used at the permeate side in the membrane reactor. Therefore, the aim of this work was to study the behavior of Ni based catalysts in the membrane reactor for partial oxidation of methane.

It was observed that simple Ni/Al_2O_3 catalysts degrade rather quickly because of the soot formation. In order to suppress this undesirable reaction we modified the catalysts by adding M_2O_3 oxides, where M = Mn and Cr.

The preparation of the catalysts was based on co-impregnation of industrial γ-Al_2O_3 support with solutions of Ni, Mn nitrates and ammonium dichromate. The BET surface area was determined by N_2 adsorption at -196°C with the help of a Micromeritics Gemini VII device. Prior to measurements the samples were pre-treated in vacuum at 300°C for 5 h. The catalytic tests were carried out in a fixed-bed flow reactor operated at atmospheric pressure. The outer shell of the reactor was made of a quartz tube. The ferrous oxygen separating membrane [4] was set inside the quartz casing in between alumina tubes that served also as in- and outlet air ducts. The membrane sizes were 1, 10 and 30 mm for wall thickness, diameter and length, respectively. The space between the membrane and the casing was filled with the catalyst. The methane conversion X_{CH_4} and selectivity S_{CO} for CO were calculated as:

$$X_{CH_4} = \frac{CH_4^{in} - CH_4^{out}}{CH_4^{in}} \times 100\% \tag{1}$$

$$S_{CO} = \frac{CO^{out}}{CO^{out} + CO_2^{out}} \times 100\% \tag{2}$$

The atmospheric pressure experiments were carried out at 850-950°C for over 200 h. The selectivity attained 96 - 98% for both Cr and Mn modified catalysts at methane flow values 70 – 75 ml/min whereupon a steady state was achieved. The methane conversion over modified catalysts was about 99 %. The after test inspections of the catalysts did not reveal any significant formation of soot or/and coke.

Acknowledgements. The work was done with the equipment of Siberian Synchrotron and Teraherz Radiation Center, Novosibirsk, Russia and carried out under financial support of the Presidium of UB RAS (grant No. 15-05-3-27).

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Determination of Platinum by Hydrogen Peaks Using Stripping Voltammetry

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The method of stripping voltammetry refers to a highly sensitive instrumental methods of analysis. However, in determining the platinum (II, IV) by this method is subject to certain difficulties.

It was shown [1,2] that fix on the current-voltage curves of platinum ions (II, IV) recovery processes and processes the electrochemical precipitation of platinum on the surface of graphite electrode is not possible.

This is due to the process of flowing the catalytic reduction of hydrogen ions, which overlaps the electroreduction process of the platinum ions (II, IV). The process of the electrochemical precipitation of platinum takes place at potentials more positive than 1 V, and overlaps the process of oxygen evolution from water.

The purpose of this paper is to develop a methodology for the platinum determination in the tailings using stripping voltammetry by the catalytic waves reduction of hydrogen.

The catalytic reduction of hydrogen ion passes by the scheme:

$2H^{+} + 2\bar{e} = H_2$

The escaping hydrogen may improve recovery of platinum. The process of electrochemical reduction of platinum ions (IV) with hydrogen is shown in Figure 1.

The figure 1shows that in addition to the background (curves 1) of platinum ions (IV) (curves 2) there is a change of the current-voltage curves. The curve 2 is shifted by -0.3 V relative to the curve 1. This is due to the fact that the addition of platinum ions (IV) in solution catalyze the hydrogen recovery process according to the scheme above.

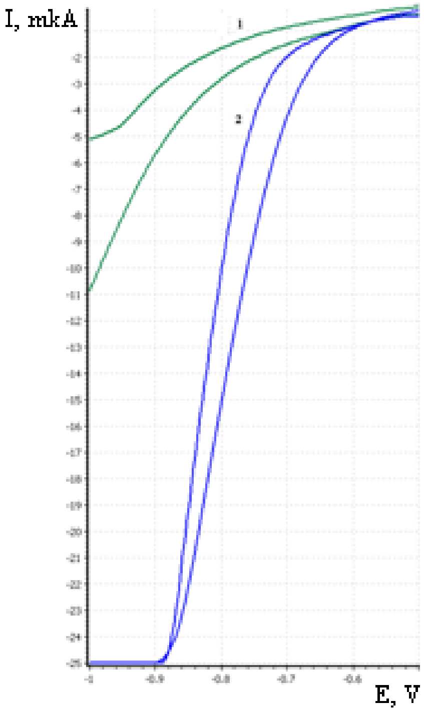

Fig. 1. Cyclic voltammetric curves of processes the electroreduction the platinum ions (IV).

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PP-155

The Reactivity of the Double Bonds Tricyclo[5.2.1.$0^{2.6}$]decadiene-3,8 in the Process of Saturation with Hydrogen in the Liquid Phase

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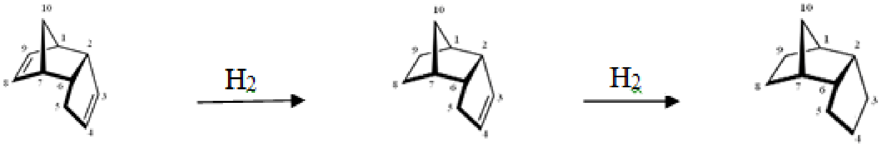
General trends and specific features of the reaction of dicyclopentadiene (tricyclo[5.2.1.$0^{2.6}$]decadiene-3,8) hydrogenation to dicyclopentene (tricyclo[5.2.1.$0^{2.6}$]decene-3) with hydrogen in the liquid phase at atmospheric pressure over a finely divided 1% Pd/C catalyst have been studied [1, 2]. By vigorous agitation, the three-phase gas–liquid–solid catalyst system is maintained in a pseudo-homogeneous state, which ensures the kinetic regime of the reaction.

Using of amorphous carbon as a catalyst support provides a nano-sized metal particles because the carbon matrix prevents their agglomeration.

Only by the successive saturation of the double bonds of diene will be possible is selective formation dicyclopentene as the target reaction product.



Tricyclo[5.2.1.$0^{2.6}$]decadiene-3,8 Dicyclopentadiene
Tricyclo[5.2.1.$0^{2.6}$]decene-3 Dicyclopentene
Tricyclo[5.2.1.$0^{2.6}$]decane Dicyclopentane

To substantiate the sequence of the saturation of double bonds of dicyclopentadiene their reactivity at using solvents of different nature (2-propanol, toluene, *ortho*- and *para*-xylenes) under mechanism of geterogeneous catalysis have compared.

In the process hydrogenation of dicyclopentadiene in 2-propanol the saturation double bonds is implemented successively at a high rate, but continuously giving dicyclopentane, what is indicate on equal to their reactivity in this solvent.

The toluene solution and its homologues give the differentiation in the reactivity of of double bonds dicyclopentadiene at saturation with hydrogen in the presence of finely divided 1% Pd/C. The rate of hydrogen uptake in process of the hydrogenation of the double bond of norbornene fragmente exceeds the rate of hydrogen uptake the hydrogenation fragment cyclopentene, depending on the nature of the aromatic solvents in 7 – 9 times.

Possibility for the selective formation of dicyclopentene (98%) appears [1] in result of equilibrium in competition during the adsorption of the solvent and the substratum on the surface of palladium, having high affinity for electrons double-bond and for the electrons the aromatic ring.

The structure of the dicyclopentene (tricyclo[5.2.1.$0^{2.6}$]decene-3) confirmed by spectroscopic methods (1H NMR, COSY-spectroscopy).

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PP-156

Non-oxidative Conversion of Methane and n-Pentane in the Presence of Supported Oxide Catalysts

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Activation of C-H bond in the methane and the mechanism for the transformation of molecules is the subject of numerous studies. Interest by methane is due to the possibility of its use as a raw material for the petrochemical industry.

Adsorption of methane at T=20-550 °C on supported monometallic catalysts (Me/Al_2O_3 and Me/SiO_2, where Me - Pt, Pd, Re, Au, Ir) was studied. The catalysts activity in conversion of methane with n-pentane was installed.

It was shown that for series of catalysts Me/SiO_2 the amount of the adsorbed methane in the all temperature range lower than for samples of Me/Al_2O_3. The observed pattern is caused by the nature of the metal, and the size of supported particles. According to SEM on the alumina observe the formation dispersion particles of metals (d=0,5-5 nm). On the samples of Me/SiO_2 besides the dispersed metal particles are detected by the conglomerates with a particle size up to 550 nm.

The composition of the reaction products in the conversion of adsorbed methane ($^{13}CH_4$) and n-pentane were analyzed by isotope ratio mass spectroscopy. It was shown that to 43.1 %mol. aromatic hydrocarbons contain carbon ^{13}C. This indicates on high selectivity of transformation of molecules at relatively low reaction temperatures.

Acknowledgement. Physico-chemical studies were carried out in the Center of Collective Usage of the Omsk Scientific center SB RAS.

PP-157

Photocatalysts Based on Glass-Fiber Materials for Cleaning Dyed Aqueous Solutions

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The problem of cleaning dyed aqueous solutions remains unresolved to date. Now, a large number of diverse methods of discoloration and degradation of dyes developed and successfully applied. Along with the known coagulation, flocculation, flotation etc. is photocatalytic oxidation.

In modern industry used photocatalysts on different carriers, such as: powders, granules, aluminum oxide, silicon (silicagels), zeolites and others with the put active components: the oxides of titanium, copper and its oxides, it is shown that the most reactive is an oxide Cu (I). With relatively recently gaining popularity carriers based on fiberglass and silica materials in view chemical inertness and ability to accept any geometric shape.

The proposed photocatalysts obtained method of magnetron dispersion of the titan in low-temperature plasma with a further application of the copper oxide in the glass fiber material.

A series of experiments carried out in a reactor with an UV light at $\lambda = 254$ nanometers has shown sufficient activity at the level of 60% for the first hour of reaction and almost complete decomposition of dyes for 4 hours.

The X-ray diffraction analysis allowed determining forms of presence of the titanium and copper on the carrier.

It revealed a synergistic effect of copper and titanium oxide as compared with single catalysts with the same reactants.

Based on experimental data calculated kinetic parameters reaction of the discoloration solutions in the destruction chromophore of groups of dye, namely: orders and constants of reactions, the degree of transformation.

The conclusions about the advisability of further studies photocatalysts for cleaning of industrial discharges and emissions.

Features of Formation and Mechanism of Propane Conversion over the Active Sites of Elementoaluminosilicate Catalysts

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The priority direction of basic research in the field of catalysis is the study of the mechanism of catalytic reactions at the atomic and molecular level. The main objective in this case is to understand the nature of the states of active sites through which their structure forms and transforms. The purpose of this paper is to establish the effect of the nature of the active centers in modified zeolite catalysts on their reactivity in the course of propane conversion into aromatic hydrocarbons. The elementoalumosilicates (E-AS) with the structure of ZSM-5 zeolite containing Zn, Zr, and In were the objects of investigation.

The catalytic studies have shown that zeolites with additions of modifying elements exhibit relatively high reactivity in the process of propane aromatization, the zeolite catalyst system with addition of zinc being the most selective and active. A more than 0.81% increase in the concentration of zinc oxide contained in the catalyst results in a slight decrease in conversion and increase in its aromatization activity. In the presence of Zr-AC sample as in the case of Zn-aluminosilicate a noticeable formation of aromatic hydrocarbons from propane is observed at temperature 550 °C and above. However, unlike the Zn-containing zeolite the increase in concentration of zirconium in a catalyst results in a decrease not only of total activity but also of aromatization activity, so the selectivity towards formation of aromatic hydrocarbons over the 3.64% Zr AC sample at 600 °C is 7.2% for a propane conversion 54%. The reaction products formed over this catalyst contain a large amount of lower C_2-C_4 olefins. Of all catalysts under study, the In-AC sample exhibits the lowest activity the catalysts under study during propane conversion.

Using data of structural and morphological studies of elementoalumosilicates it was found out that the introduction of Zn, Zr, and In into a zeolite results in a partial morphological change.

Investigation of the electronic state of active sites has shown that In and Zn cations are fixed to oxygen ions in the channels of zeolite, In being partially localized on the outer zeolite surface. The high value of the Zn3d binding energy explains the low mobility of zinc in a catalyst during the heating with a beam of electron microscope. Relatively low Zr3d and In3d binding energies cause clustering of zirconium and indium ions when heated by an electron beam, which occurs simultaneously with the destruction of zeolite channels.

The analysis of the data obtained indicates that the introduction of various modifying additives into a zeolite at the step of hydrothermal synthesis results in a yield of catalysts with different functional properties.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 15-33-51297.

PP-159

Quantum Mechanical Study of the Mechanism of Surface Stages of Catalytic Oxidation of Methylpyridines

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The Density Functional Theory method has been applied for the simulation of the mechanism of surface stages of catalytic oxidation of isomeric methylpyridines into pyridine carboxylic acids on individual V_2O_5, binary and triple vanadium-oxide catalysts, modified by Ti, Sn and Zr dioxides. Bi-exponential basic set LanL2DZ with an efficient core potential has been used. The calculations have been made with the help of Gaussian 09W program.

The initial compounds possess basic properties and are able to react with the Lewis acidic sites of the catalyst surface (the Lewis acidic sites, vanadium ions). On the other hand, methylpyridines are related to weak CH-acids and are prone to a heterolytic breaking of the C-H bond of the methyl group under the effect of a proton acceptor (for example, vanadium oxygen). First, chemosorption of isomeric methylpyridines by a nitrogen atom at the Lewis acidic sites of individual V_2O_5 has been simulated. It has been established that upon the transfer of a proton to vanadium oxygen and formation of a new O−H bond energy is released, at whose expense the energy consumption for the heterocyclic breaking of the C-H bond is compensated. As a result the methyl substituent deprotonation enthalpy (DPE, $kJ \cdot mol^{-1}$) significantly lowers and decreases in the row of 3-MP (238,5) > 2-MP (176,3) > 4-MP (155,7). Upon the simulation of chemosorption of substrates by the ring plane at LAC with the transfer of a proton to V=O, close DPE values have been obtained: 3-MP (239,4) > 2-MP (173,9) > 4-MP (163,5). According to the experimental kinetic data a relative reactivity is increasing in the indicated row of the initial compounds.

Modifying of V_2O_5 by Sn, Ti and Zr dioxides results in an increase of activity of the binary contacts in the oxidation reaction of methylpyridines. Quantum chemical simulation of chemosorption of methylpyridines at the Lewis acidic sites of the binary catalysts has been carried out. It has been established that the promoting activity of the enumerated oxides is stipulated both by the increase of affinity to the vanadium oxygen proton ($PA_{V=O}$) under the effect of the above oxides, and decrease of DPE of the oxidized methyl substituent of the chemosorbed substrate. Upon the transfer from the binary clusters to the triple V-Ti-Sn- and V-Ti-Zr-oxide systems a synergy effect is observed. A summary effect of the two oxides-promoters upon $PA_{V=O}$ significantly surpasses the effects of each separate promoter in the form of their simple sum. The results of the calculations agree with the experimental data by the effect of the oxides-modifiers upon the activity and selectivity of the studied catalysts in oxidation of methylpyridines.

PP-160

Initiation of Directed Crystallization of New Formations in Cement Matrix with Multi-walled Carbon Nanotubes Dispersion

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The work presents the results of the studies of cement binding matrix in terms of modifying the morphology of crystallohydrates based on calcium hydrosilicates (CHS) by means of adding multi-walled carbon nanotubes (MWCNT) dispersion to the setting cement matrix. While modifying the cement matrix with MWCNTs, one of the main issues is the directed regulation of polycondensation processes of silicon-oxygen anions in order to strengthen the borders of contact zones. Using nanodispersed modifier provides the control of interaction kinetics between cement minerals and mixing water, the influence on the composition and the structure of CHS, and the increase of polycondensation of silicon-oxygen anions in the CHS composition.

Many researchers [1] limit the role of carbon nanotubes to nanoreinforcement of the set cement structure, the content of nanotubes exceeding 0,05% from the mass of the binder. The main fact causing the absence of the structuring effect in the modified cement matrix is insufficient dispersion of MWCNTs despite using various dispersion methods and using surfactants in aqueous dispersions. The study shows the nature of self-organization of the microstructure of cement binding matrix when adding minute amounts of MWCNT dispersions.

A scanning electron microscope with the attachment for X-ray microanalysis, IR spectrum and differential thermal analysis have found that the main effect of the cement matrix modification in case of adding MWCNTs dispersions is due to accelerating influence on the hydration processes and the initiation of directed crystallization of new formations. It is shown that, carbon nanotubes dispersion being added in the amount of 0,001% from the mass of the binder, there is structural modification of the binding matrix and formation of defect-free dense shell from crystallohydrate new formations on the surface of solid phases. This shell provides high strength binding matrix in the set cement. At that, the strength of cement concrete increases up to 40%, water resistance up to W14 and frost resistance up to F400, which leads to a significant increase of durability of modified cement concrete products [2].

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Chemical Aspect of Regulation of Active Site Structure in Cu-ZSM-5

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Cu-ZSM-5 catalysts possess unique properties in DeNOx processes [1, 2] and other redox reactions [3]. For the most reactions, a nonlinear dependence of the Cu-ZSM-5 activity versus its copper content was revealed [2, 3], but sometimes the catalytic activity of Cu-ZSM-5 with the same copper loading may differ greatly. Unfortunately, available literature data on the chemical aspects of the formation of catalytically active states in Cu-ZSM-5 are fragmentary, which does not allow regulating the catalytic activity.

In this communication chemical factors which have a major influence on the formation of catalytically active states from copper cations during the Cu-ZSM-5 preparation by the ion-exchange mode with subsequent thermal treatment are examined.

Sorption of Cu(II) ions by H-, Na- and NH_4-form of ZSM-5 (Si/Al = 17) during the ion-exchange with aqueous and water-ammonia solutions of copper acetate and copper chloride are well described within the Langmuir monomolecular adsorption [4]. At the ideal ion exchange conditions, the increase of the copper salt concentration in the solution results in an increase of its content in the zeolite as well as the formation of structures of Cu(II) ions with the extra-framework oxygen in addition to the isolated Cu(II) ions located in the zeolite channels. A number of the isolated Cu(II) ions sorbed by the zeolite is limited to the ion-exchange sites in the zeolite, dynamic equilibrium, the presence of competing ions (NH_4^+) in solution and the stoichiometry of the ion-exchange (Cu/2Al). Adding ammonia to aqueous solutions of copper salts has a nonlinear effect on the copper content in the Cu-ZSM-5, which is due to hydrolysis, polycondensation, and complexation reactions in the solution.

The genesis of various electronic states of Cu(II) ions in the air-dried Cu-ZSM-5 samples during their thermal treatment in oxygen-containing environment is analyzed using DTA-TG-MS, UV-Vis DR, ESR, FTIR, TPR by hydrogen and TPR by carbon monoxide.

The structures of Cu(II) ions with the extra-framework oxygen forming in the water-ammonia solutions of copper salts at moderate ammonia concentrations (NH_4OH/Cu = 6-15) are more active in the DeNOx [4] than the isolated Cu(II) ions and CuO nanoparticles on the surface of the zeolite crystallites.

Acknowledgement. This work was supported by Russian Science Foundation (project 14-13-01155).

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Effect of the Method of Catalysts Preparing for Their Activity in the Fischer –Tropsh Synthesis

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Fischer -Tropsh Synthesis (FTS) is currently one of the most promising methods of obtaining components of motor fuels. The value obtained on the basis FTS fuel fractions is largely due to their high environmental characteristics [1].The catalysts used for the implementation of the FTS are complex systems containing the active component, one or more promoters and a carrier. As the active catalyst component mainly used cobalt or iron. Cheapness of iron catalysts compared with cobalt to a certain extent compensated by the greater stability of a cobalt-based catalysts. Investigations of cobalt catalysts are engaged by many scholars, the works are in search of the optimal carrier providing stabilization of cobalt nanoparticles with a size of 6-9 nm, as well as a method of activation of the cobalt catalyst excluding high-temperature reduction [2].

In this work we investigate the effect of catalyst preparation methods on the activation regime of 10% Co/Al_2O_3 catalyst in FTS. The catalysts were prepared by impregnating the carrier on wetness (IC) and method solution combustion "SC". The results represented that the catalyst 10% Co/Al_2O_3 synthesized by "SC" method CO conversion reaches 94%, whereas for the catalyst prepared by impregnating a carrier on wetness CO conversion was 71%. The same changes take place with the selectivity to liquid hydrocarbons. Synthesis of catalyst by "SC" method allows to increase the selectivity to liquid hydrocarbons up to 44% compared to the impregnation method wherein the selectivity is 35%. Liquid hydrocarbons by 96 - 100% consist of a narrow fraction of C_5-C_8 hydrocarbons. The effect of the catalyst preparation method on the formation of the active sites of cobalt catalysts was studied by thermal programmed reducing method (TPR). In the TPR spectrum of 10% Co/Al_2O_3 (IC) catalyst before reaction are two peaks with maxima at $T^1_{мах}$ =411 и $T^2_{мах}$ = 583°C. On the spectrum of 10% Co / Al_2O_3 (SC) before the reaction observed four peaks with maxima at $T^1_{мах}$ =175, $T^2_{мах}$ =340, $T^3_{мах}$ =499 and $T^4_{мах}$ = 707°C. Such a change indicating the formation of cobalt oxides with different sizes. Compared with the catalyst 10% Co / Al_2O_3 (IC) synthesizing catalyst by SC method leads to a decrease of the reduction temperature from 617 to 503°C and increasing the peak intensity. These changes may indicate that synthesize of 10% Co / Al_2O_3 by SC leads to the formation and increase the number of easy reduced form of cobalt oxide. The method of catalyst preparation "SC" in comparison with the method of impregnation facilitates recovery of cobalt oxide, which favorably affects the hydrogenation ability of a catalyst, the conversion of CO increases up to 96%. Also, catalyst preparation method "solution-combustion" will increase the economic efficiency of the process by reducing the time and cost of pre-activation of the catalyst.

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PP-163

Composite Materials for the Conversion of Methane to Synthesis Gas

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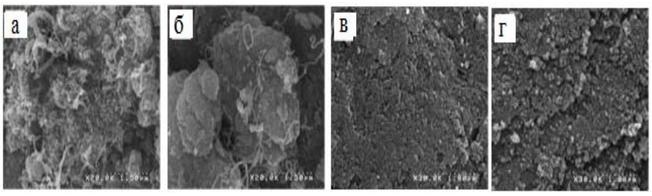
The potential raw material for production of valuable chemicals is associated gas. The main component of the associated gas is methane. By the catalytic oxidation of methane can be produced synthesis gas, which is a raw material for the production of chemical and petrochemical products (methanol and other oxygenates, the products of the Fischer-Tropsch process) [1]. It is known that the synthesis gas from methane is obtained mainly by partial oxidation, steam-oxygen and carbon dioxide conversion of methane. All these methods occur with catalysts. The most popular for the processes of partial oxidation of methane are the nickel catalysts. However, in the presence of oxygen, there is the possibility of oxidation of metallic nickel, in which take place the activation and subsequent dissociation of methane [2]. Also, there is its agglomeration because of local overheating, which along with coking leads to reduced activity. Solving of these technological problems is possible by the introduction of modifying additives. In the present work we investigated the stability of Ni / ɣ - Al_2O_3 catalyst in partial oxidation of methane, as well as the effect of modifying additives Ce, La and Co on the catalytic activity and resistance to coking. The catalysts were prepared by co-impregnating the carrier with solutions of nitrates and dispersant compound.

After testing the catalysts during the process they were investigated by scanning electron microscopy, the data shown in Fig.



a - Ni/γ-Al_2O_3; b- NiCo/γ-Al_2O_3; c - NiCe/γ-Al_2O_3; d-NiLa/γ-Al_2O_3
Figure. The micrographs of the catalysts.

As seen from the figure, after the test in the oxidation of methane on the surface of the catalyst Ni / γ-Al_2O_3 is formed of carbon filaments. Modified by cobalt sample was also subjected to carbonization as evidenced by the SEM data. Modification of nickel catalyst by cerium and lanthanum causes an increase of dispersion of the catalyst surface, and also to reduce of carbon deposition.

Catalyst NiLa / γ -Al_2O_3 showed high catalytic activity and stability. When process conditions T = 750°C, ratio of CH_4: O_2 = 2: 1 and τ = 3.8 sec. catalyst has worked in the laboratory more than 100 hours without loss of catalytic activity and methane conversion reached 97%.

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PP-164

Ionic Liquid-catalyzed Carbon Dioxide Fixation. Quantum-Chemical Study

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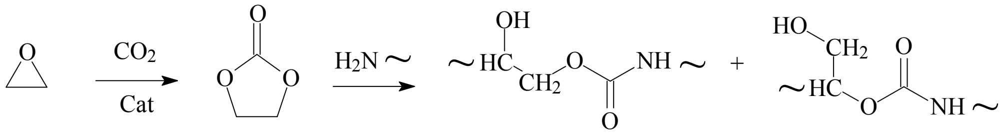
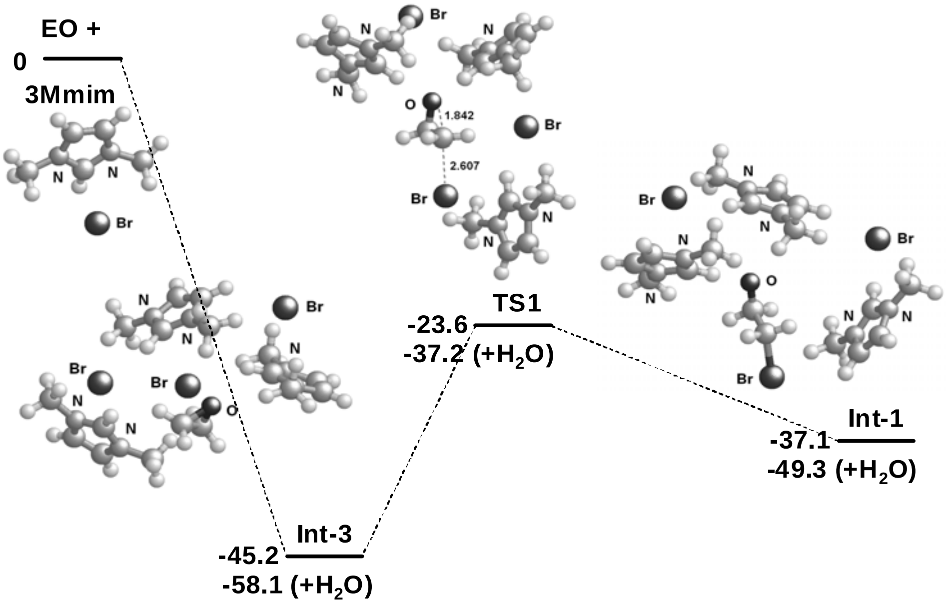
Emissions of greenhouse gases, the most important from which is CO_2, are a very acute problem of the modern world. The most promising recycling methods include the using of CO_2 as a carbon source for the production of chemical compounds. Among these methods the synthesis of organic cyclocarbonates looks the most attractive. Cyclocarbonates are used in the new synthesis of polyurethanes, which eliminates the usage of toxic reagents (phosgene, isocyanates). This is a new direction in Green Chemistry of polymers which has been developing for the last years.



We have studied the mechanism of the reaction of ethylene oxide with CO_2 using DFT method (PBE/TZ2P) in the presence of various catalysts (BF_3, $SbCl_3$, $SbCl_5$, H_2O, Py, Py/H_2O, Py/PhOH, Py/$ZnBr_2$, Py/Py_2ZnBr_2, PMe_4Br, PMe_4Br/H_2O, MmimBr, MmimBr/H_2O). The most effective catalyst, according to the calculation, was the combination of ionic liquid with water (MmimBr/H_2O).



The calculated activation energies are in good agreement with the experimental relative activity of the catalyst, which is derived on the basis of reactions conditions (temperature, pressure, time, yield). It allows to predict theoretically the most effective catalyst in this process.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, Grant 14-03-00026-a.

PP-165

Selective Oxidation of Ammonia Vapor on Industrial Catalysts

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The studies of possible mechanisms of selective oxidation of ammonia to molecular nitrogen and water vapor, not only led to an understanding of the chemical nature of this process on the molecular level, but to the development of new types of catalyst systems.

For many systems for the selective catalytic oxidation of ammonia mechanism is considered conventional i-SCR (internal selective catalytic reduction) [1].

In accordance with the mechanism i-SCR in the first stage of the ammonia present in the reaction mixture, it is oxidized to NOx, a second step is reduced NOx NH_3 (unreacted in the first stage of the reaction). Therefore, the catalysts employed in accordance with the mechanism i-SCR, must contain catalytically active components in the oxidation of ammonia to NOx (selective catalytic oxidation - SCO) and the components that are active in the process of NOx reduction to N_2 c using NH_3 (selective catalytic reduction - SCR).

For realization of the mechanism of i-SCR ammonia in the selective oxidation system can be applied in the form of a dual-layer catalyst. As such, the authors of [2] proposed a system of Fe-ZSM-5 - Pt /Al_2O_3, where the layer Fe-zeolite, the process of the ammonia selective reduction of nitrogen oxides proceeds efficiently formed in the oxidation portion of ammonia on Pt / Al_2O_3 layer that shifts selectivity of the process towards the formation of N_2.

We have investigated the selective oxidation of ammonia with atmospheric oxygen vapor on a dual-layer catalytic contact, the mechanism of implementing i-SCR and consists of manufactured on a commercial scale catalysts - iron oxide - SK-201-2 (HALDOR TOPSOE, Denmark), and aluminum-vanadium - AOK-78-55 (Novosibirsk).

Based on the results obtained by JSC «KRASTSVETMET" developed and implemented industrial installation of selective catalytic oxidation of ammonia vapor in the oxygen-containing flue gas pulse columns, consisting of two parallel operating reactors of type "KPOT" with bifilar helical coil, a capacity of 1500 m^3/ hour each.

It is found that dual-layer contact SK-201-2 and AOK-78-55 (ratio 1:2 vol.) at a temperature of the catalyst SK-201-2 $t = 350 \div 380$ °C and AOK-78-55 $t = 270 \div 290$ °C with initial concentration of ammonia vapors 15-18 g/m3 of a high degree of conversion of ammonia.

The purified gases nitrogen oxides does not exceed 5 mg / m3.

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1H NMR and Quantum Chemistry Study of Hydrolysis of Isobutylaluminium Aryloxides

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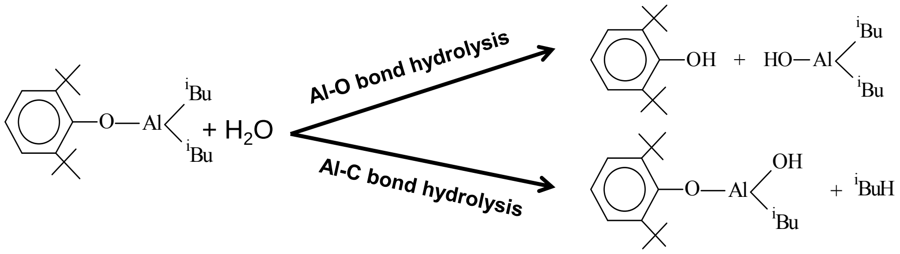
The mechanism of hydrolysis reaction for alkylaluminium aryloxides still remains unclear. The process principally may go by two ways: through the cleavage of either (i) Al-O or (ii) Al-C bond as shown on the scheme below:



Judging by the fact that Al-C bond is normally much weaker than Al-O, the reaction is expected to go through the Al-C bond, resulting in formation of isobutylalumoxane species that contain Aryl-oxo groups. As we have shown earlier, both isobutylalumoxanes [1] and isobutylaluminium aryloxides [2] are effective activators of metallocene catalytic systems for olefin polymerization. Sterically hindered aryl-oxy groups are to stabilize the alumoxanes by preventing the association (that is typical for alkylalumoxanes) and, as expected, make them useful candidates as activators of metallocene catalytic systems for olefin polymerization. However, as the presented work reports, the reaction goes the unexpected way – through the cleavage of much stronger Al-O bond.

The results of ^{1}H NMR study proves that hydrolysis of monomeric aryloxides $2,6\text{-}Bu^t_2\text{-}C_6H_3O)AlBu^i_2$ and $(2,6\text{-}Bu^t_2\text{-}4\text{-}Me\text{-}C_6H_2O)AlBu^i_2$ goes selectively through Al-O bond, yielding phenol and polyisobutylalumoxane. At molar ratio $Al/H_2O=2$ the produced phenol slowly reacts with the excess of di-isobutylalyminium mono-aryloxide ($Al[OAr]^iBu_2$), forming di-aryloxide of mono-isobutylaluminium ($Al[OAr]_2{}^iBu$). Under the similar conditions, dimeric aryloxide $[(2\text{-}Bu^t\text{-}C_6H_4O)AlBu^i_2]_2$ is shown to be completely inert to water. The NMR study is supported by quantum chemistry (DFT) modelling of the reaction, which shows that energy barrier for Al-O (14.35 kcal/mol) is significantly lower than that barrier for Al-C hydrolysis (25.76 kcal/mol), thus confirming the experimental data of hydrolysis following the Al-O bond cleavage patch.

Acknowledgement. This work was supported by the Russian Science Foundation, grants № 13-03-01281-a, 15-03-02307-a.

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PP-167

Pt-containing Catalysts for Primary Biomass Products Conversion into Hydrocarbons

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Development of alternative approaches to fuel components and basic organic synthesis precursors producing based on biomass treatment products is important objective for ecology and chemistry. In the present work a number of industrial Pt-containing catalysts samples (AP-64, R-264, IP-62, PR-56) were used as well as an original Pt-Sn/Al_2O_3 catalyst based on heterometallic precursor providing the presence of Pt-Sn bonds.

Catalysts were observed to become more selective in hydrocarbons formation after the pretreatment procedure under 50 atm of H_2 and 450 °C during 12 hours. Industrial catalysts samples AP-64 and PR-51 were found to be the most active in ethanol conversion towards C_3-C_{12} alkanes or olefins. Ethanol conversion over Pt-Sn containing catalysts led to a number of ethers formation. By adding probable intermediates into reaction zone was found that hydrocarbon chain grow via ethylene oligomerization followed by olifins reduction.

Shown that over Pt-containing catalysts rapeseed oil converts into alkanes or olefins C_3-C_{28}. By temperature tuning was found the ability to adjust hydrocarbons chain length. The highest selectivity close to 100 % during rapeseed oil conversion into hydrocarbons C_3-C_{22} was found to be over Pd-Sn/Al_2O_3 catalyst with Pt:Sn molar ratio equal to 1:5.

Structural peculiarities of catalysts were characterized with X-ray diffraction and XAS technique. Relations between Pt clusters structure and its catalytic properties were determined.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 15-13-30034.

DFT Studies of Interrelations between Structures of New Nickel(II) Complexes with N,O-coordinating Ligands and Their Catecholase Activity

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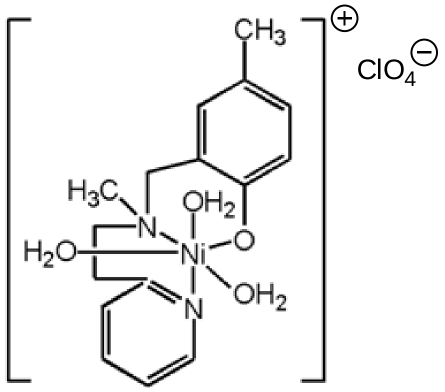
Synthetic analogues of catechol oxidase have been studied extensively in recent years in order to understand the structure-function relationships. Three newly synthesized mononuclear nickel(II) complexes **1-3** bearing Mannich-base ligands have been tested for catecholase activity in oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) in methanol under aerobic conditions. Complexes **1** and **2** appear to be catalysts of the 3,5-DTBC oxidation (**1** is more active than **2**), in contrast to compound **3**.



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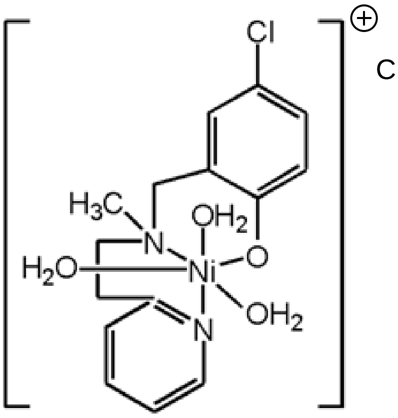

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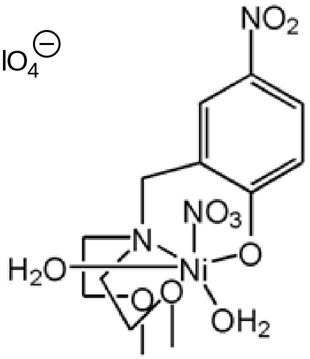

3

To explain these effects possible processes accompanying interactions between nickel complexes and 3,5-DTBC in methanol have been investigated by DFT at the B3LYP/DGDZVP level of theory. The calculated dissociation energies of complexes **1** and **2** appear to be lower than that of **3** (11.4, 11.7, and 17.3 kcal/mol, respectively). The equilibrium concentration of the ionic species should, therefore, be higher in the **1** and **2** solutions. We have simulated ionic mechanisms of catalysis. In particular, for complex **3** the first step (addition of 3,5-DTBC) is accompanied by a higher positive energy change than for **1** (11.6 and 1.8 kcal/mol, respectively). The decreased concentration of the cations derived from complex **3** and the more endothermic first catalytic step can well lead to low catalytic efficiency of this compound. The neutral catalytic path of the 3,5-DTBC oxidation for complex **3** is predicted to be much less energetically favorable as compared to that based on the cationic **1** species. The replacement of the Me substituent with Cl on going from complex **1** to compound **2** results in the more endothermic first two steps of the ionic catalytic cycle. This agrees well with the decrease of the catecholase activity observed in the experiment.

Acknowledgement. This work was supported by the Russian Science Foundation, grant 14-13-00832.

PP-169

Electrocatalytic Properties of Rhenium-Nickel Electrodes Prepared by Electrodeposition from Aqueous Solution in the Hydrogen Evolution Reaction

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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 (fuel cells, electrocatalysis, etc). The alloys of refractory metals with iron group elements 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 rhenium and Re-based alloys towards the HER

This study provides a new experimental data for the HER on Re-Ni (70-88 at.%Re) electrodes prepared by electrodeposition from citrate solution under galvanostatic conditions on cooper foil.

Mathematical processing of experimental data were proceeded by means of nonlinear regression. 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 exchange current densities of the Volmer step (~$3*10^{-7}$ A/cm^2) is significantly lower in comparison with exchange current densities of Heyrovsky step (~$7.9*10^{-4}$ A/cm^2). 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. It was shown that catalytic activity of Re-Ni 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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Theoretical Foundations Catalytic Synthesis of Aromatic Acetylene Alcohols

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Aromatic acetylene alcohols (AAA) synthesized by reacting acetylene with phenylacetylene (PhA) − croton aldehyde and ketones (acetone, methyl ethyl ketone, methyl isopropyl ketone, acetophenone and pinokalin) by the method of tabor. Scientifically proven influence of various factors-the molar ratio of the starting materials, temperature and the nature of the solvent on the yield of the product itself. The optimal conditions for the synthesis of a high yield in the process. Determined purity, structure, elemental composition, quantum chemical and physical constants of the synthesized compounds. The optimal conditions for the synthesis of a product with a high yield. The reaction mechanism based on literary sources. On the obtained results the influence of the nature of solvents on the generation of product yield has been systematically analyzed, and the most favorable homogen-catalytic state has been defined for the procedure of process. Selective family of the influence of solvents on the AAA yield has been offered in the following state: ethanol < methanol < diethyl ether < THF. And at used catalysts, and at KOH with high basicity AAA has been synthesized with maximum amount and additional products have been synthesized with minimum amount. Synthesis process of alcohols gets completive along with appearing of volume radicals around the carbon in carbonyl group and falling down of general energy in them. Consequently the heat-energy of AAA is higher, and this leads to the generation of additional products in the reaction on account of the generation of active centers.

In JSC "Navoiazot-Uzbekistan' the plant for their synthesis has been constructed and also the test samples of 1-phenyl-3-methylbutyn-1-ol-3 were obtained and also the technological regalement and economical effect of the synthesis was elaborated. Microbiological activity of some synthesised compounds were investigated. It was shown that are effective inhibitors of biocorrosion of oil-yield metallic constructions and they have been recommended for more wide investigation in industrial scale.

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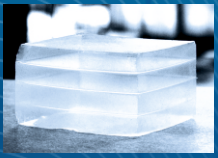

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Сегодня БФУ им. И. Канта – крупнейший образовательный, научный, культурный, просветительский центр самого западного региона России. В настоящее время в университете реализуется более 300 образовательных программ среднего, высшего, дополнительного и послевузовского профессионального образования. Всего обучающихся на программах среднего профессионального, высшего, послевузовского и дополнительного образования 14 000 человек. В структуру университета входит 9 образовательных институтов, в которых работают 2 тысячи сотрудников, из них 1000 преподавателей. Инфраструктура университета включает 53 здания, включая собственный Клинико-диагностический центр.

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БФУ им. И. Канта 3 года подряд является победителем конкурса программ развития деятельности студенческих объединений, проводимого Министерством образования и науки РФ.

БФУ им. И. Канта входит в ТОП 100 лучших вузов России согласно ведущему национальному рейтингу «Эксперт», имеет партнерские отношения с 144 ведущими университетами и научными центрами мира.

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ЛАБОРАТОРНОЕ ОБОРУДОВАНИЕ ДЛЯ ИССЛЕДОВАНИЯ КАТАЛИЗАТОРОВ

Лабораторные Каталитические Установки
Технологические Стенды

МНОГОЦЕЛЕВАЯ УСТАНОВКА ДЛЯ ПРОЦЕССОВ ПРИ ВЫСОКОМ ДАВЛЕНИИ (ДО 100 АТМ)

РИФОРМИНГ * БИФОРМИНГ * ИЗОМЕРИЗАЦИЯ

АЛКИЛИРОВАНИЕ * ГИДРОИЗОМЕРИЗАЦИЯ

КАТАЛИТИЧЕСКАЯ УСТАНОВКА ДЛЯ ПРОЦЕССОВ НЕФТЕПЕРЕРАБОТКИ ПОД ДАВЛЕНИЕМ

УСТАНОВКА ТЕРМОПАРОВОЙ СТАБИЛИЗАЦИИ КАТАЛИЗАТОРОВ КРЕКИНГА

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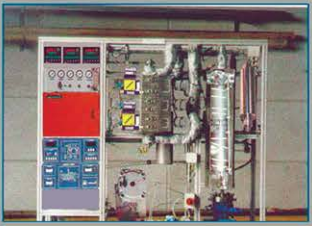

УСТАНОВКА ДЛЯ ПРОЦЕССОВ ПАРОВОЙ И ВОЗДУШНОЙ КОНВЕРСИИ УГЛЕВОДОРОДОВ ПРИ ДАВЛЕНИИ

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- ПРИ ПРОВЕДЕНИИ НАУЧНО-ИССЛЕДОВАТЕЛЬСКИХ РАБОТ ПО СОЗДАНИЮ НОВЫХ КАТАЛИЗАТОРОВ И ИЗУЧЕНИЮ КИНЕТИКИ КАТАЛИТИЧЕСКИХ ПРОЦЕССОВ
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СОРБТОМЕТР ™

АНАЛИЗАТОРЫ УДЕЛЬНОЙ ПОВЕРХНОСТИ / ТЕКСТУРНЫХ ХАРАКТЕРИСТИК ДИСПЕРСНЫХ И ПОРИСТЫХ МАТЕРИАЛОВ

(свидетельство №55098-13 об утверждении типа средств измерений)

Предназначены для исследования текстурных характеристик дисперсных и пористых материалов, в том числе нанокомпозитов, катализаторов, сорбентов, и т.д.

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(одноточечный метод БЭТ)

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СОРБТОМЕТР

СОРБТОМЕТР-М

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- Расчёт распределения мезопор по размерам

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Scientific edition

X International Conference
“Mechanisms of Catalytic Reactions” *Svetlogorsk,*
Kaliningrad Region, Russia October 2 - 6, 2016

ABSTRACTS

Editor: Professor Valerii I. Bukhtiyarov

Научное издание

X Международная конференция
“Механизмы каталитических реакций”
Светлогорск, Калининградская область, Россия
2–6 сентября 2016 года

Сборник тезисов докладов

Под редакцией проф. В.И. Бухтиярова

Составители: М.А. Клюса
Л.Я. Старцева
М.С. Суворова
Компьютерная обработка: Ю.В. Климова
А.А. Спиридонов
Обложка: Е.К. Гулина

Издатель:
Федеральное государственное бюджетное учреждение науки
Институт катализа им. Г.К. Борескова
Сибирского отделения Российской академии наук
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E-mail: pub@catalysis.ru Тел.: +7 383 326 97 15

Объём: 18,8 МБ. 1 CD-R Заказ № 55. Подписано в тираж: 23.09.2016. Тираж: 185 экз.

Системные требования: i486; Adobe Reader (чтение формата PDF)

ISBN 978-5-906376-15-2