IX International Conference
Mechanisms of Catalytic Reactions

ABSTRACTS

Saint Petersburg 2012

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

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MECHANISMS OF CATALYTIC REACTIONS

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PLENARY LECTURES

PL-1 ÷ PL-5

Elucidating the Mechanism of Heterogeneously Catalyzed Reactions through Combined Experimental and Theoretical Studies

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Knowledge of the mechanism of reactions occurring on the surface of heterogeneous catalysts is sought for the purpose of understand what aspect of catalyst composition and structure limit catalyst activity, selectivity, and stability. The first step is measurement of the reaction kinetics in order to understand how the rate of product formation depends on the reaction temperature and the reactant and product partial pressures. Such data can provide useful clues as to the mechanism by which the reaction proceeds. In the next step various spectroscopic techniques are used to probe the nature of adsorbed species and the relationship of their surface concentrations to the kinetics of product formation. In situ (or operando) IR or Raman spectroscopy are most often used for this purpose. Since both the bulk and surface composition and structure may change with reaction conditions, these properties are also probed using techniques such as UV-Visible spectroscopy, XANES, EXAFS, and in situ XPS. The deductions drawn from measurements of reaction kinetics and the characterization of adsorbed species are used to develop proposed reaction mechanism, which can be used to derive and an expression for the reaction kinetics. Agreement between the derived rate expression and the experimentally measured kinetics provides support for the proposed mechanism but does not prove that it is correct. Additional verification of deductions drawn from experimental findings is provided by the use of first principles theory to determine rate parameters for proposed elementary steps. If the activation energies and preexponential factors determined from theory agree with those deduced from experimental measurement, further confidence in the physical correctness of the proposed mechanism is gained. This talk will illustrate how experimental and theoretical methods can be used in conjunction to develop a better understanding of reaction mechanisms and the how catalyst composition and structure affect the kinetics of reactions catalyzed by heterogeneous catalysts. The examples considered will include the thermal dehydrogenation of alkanes, the carbonylation of olefins and ethers, and the electrochemical splitting of water. As a part of this discussion, we will also show how newly emerging experimental and theoretical techniques contribute to developing a deeper insights into the mechanism of catalyzed reactions.

PL-2

Thermodynamics of Operating Catalyst: Some Approaches and Findings

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In contrast to chemical kinetics, thermodynamics is so far not very actively used for describing the state and behavior of operating heterogeneous catalysts. The reason is indeed the non-equilibrium state of operating catalysts that does not allow common equilibrium thermodynamics to be used. In the last decade, however, there was a progress in understanding how the approaches of non-equilibrium thermodynamics could be applied to operating catalysts.

The presentation gives few examples of such applications. There are, first of all, explanation of superlow temperature of melting nanoparticles of metal catalysts active in carbon nanofiber production, semiquantitative description of the size effect for at least metal catalysts, possibility to couple or even convert direction of undesirable processes with the desirable ones, as well as ideas about possibility to change the stationary phase state of the operating catalytically active components via controlling the composition of the surrounding reactive mixture. It is also shown that a quite typical situation for catalytic processes is not coincidence of the rate-controlling step and the “bottle neck” (limiting step) of the overall process.

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Bio-Inspired Hydrocarbon Oxidations by Nonheme Iron Catalysts

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Inspired by the versatile oxidation chemistry catalyzed by nonheme iron enzymes, we have been investigating the iron-catalyzed oxidations of hydrocarbons. Highly stereoselective *cis*-dihydroxylation of olefins has been observed with the use of nonheme iron(II) complexes with H_2O_2 as oxidant. Insights into the catalytic mechanism have been obtained from a combination of product distribution studies, ^{18}O labeling experiments, and kinetic analysis as well as DFT calculations. These results implicate a high-valent iron-based oxidant. Hydrocarbon oxidation can also be observed for iron complexes supported by tris(pyrazolyl)borate ligands that activate O_2. A high-valent iron-based oxidant is also postulated for these reactions, which exhibit shape selectivity. The unusual shape selectivity observed suggests that substrate recognition can be elicited even in a biomimetic complex of relatively simple design.

PL-4

Catalysis & Complexity: From Mechanism to Function

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Catalysis is at the heart of chemistry and disciplines that directly depend on it, for harnessing the complexity of catalytic processes offers unprecedented potential for making them useful on both laboratory and industrial scales. Investigation of complex catalytic systems requires methods that examine these processes under true bench top conditions in real time and throughout their course. This global profiling approach allows us to study critically important events, such as activation and deactivation of catalysts, unproductive off-cycle pathways, and provides insights into the dynamics of the changing environment of a catalytic reaction. We then use the resulting data-dense reaction profiles for the development of most efficient reaction conditions.

A key lesson that emerged from our work during the last decade is that one can achieve near perfect selectivity without relying on the classical lock and key enzymatic catalysis paradigm because highly dynamic mixtures of complexes that exist in rapid equilibria with each other can actually serve as exquisitely selective catalysts. A single, well-defined catalyst is not always required and may, in fact, be counterproductive. If allowed, the system will select, and will inescapably form, the right catalyst – and it does not need to dominate as far as population goes – as long as there is enough of it to effect the fastest catalytic turnover.

This approach will be exemplified using several case studies of the catalytic reactions of alkynes. Alkynes are among the most energetic hydrocarbons, and transition metals enable selective and controlled manipulation of the triple bond, opening the door to the wealth of reliable reactivity: transformations of alkynes into heterocycles and into a variety of molecules with new carbon–heteroatom bonds. The combination of catalytic alkyne functionalization followed by manipulation of the resulting products allows one to proceed from a system with high energy content to a system of lower energy in a stepwise fashion, thereby enabling controlled introduction of new elements of diversity in every step. Various architectures prepared using these methods are finding increased use in organic synthesis, nano- and biotechnology, and materials science.

From Mechanistic and Kinetic Understanding of Heterogeneously Catalyzed Reactions to Tuning Catalysts Performance

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Heterogeneous catalysis is the basis of the majority of chemical processes in modern industry and affects our life in myriad ways. It helps to convert readily available raw materials to higher value-added products. Due to the scarcity of these materials and the requirements for treating/removal of side products, there is a high demand for more efficient and environmentally benign catalytic technologies. Yet, catalytic materials are too complex to predict their behaviour and to develop novel catalysts with desired performance (activity, selectivity, time-on-stream stability). Therefore it is highly desired to elaborate fundamental principles enabling to couple molecular knowledge about the structure and functioning of catalytically active sites with the reaction kinetics on the level as elementarily as possible. The relationships between the individual rate constants and catalytic sites can provide guidelines for the rational catalyst design and for the optimization of reactor operation.

To accomplish these objectives, various approaches are applied. This paper demonstrates the potential of steady-state, transient methods operating with sub-millisecond time resolution, time-resolved operando catalyst characterization and DFT calculations for monitoring and molecular understanding of various heterogeneously catalyzed reactions. The importance of micro-kinetic analysis will be especially highlighted. Finally, it will be shown that the sophisticated fundamental knowledge does really enable to tune catalysts performance for a number of gas-phase catalytic reactions such as functionalization of natural gas, Fischer-Tropsch, Ostwald and Deacon processes. This was, however, possible owing to the development of methods for controlled synthesis of catalysts with the uniformity of catalytically active species and their distribution on the support surface. Particularly the role of well-defined metal nanoparticles for establishing explicit structure-performance relationships will be discussed in this contribution.

KEYNOTE LECTURES

KL-1 ÷ KL-9

The Mechanism of the Fischer-Tropsch Reaction

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Due to the increasing detailed molecular information on the energetic and kinetics of elementary surface reactions that are part of the Fischer-Tropsch catalytic reaction cycle, the kinetics and selectivity can be probed in great detail. Using computational catalysis tools the relation between overall kinetics and structure of the catalytic reactive center can be probed in detail. The mechanism of the reaction is found to change with structure, which has important consequences for overall chain growth probabality. We will illustrate the state of affairs in detail for catalysis by Ruthenium.

To predict chain growth parameter and consumption rate, next to elementary kinetics data, available from first principle quantum-chemical data, microkinetics simulations are necessary. We will present a comparison of microkinetics simulations and Kinetic Monte Carlo simulations. Results of quantum-chemical calculations will be reported that are used as input to the kinetic simulations.

Three specific questions are addressed:

- the relation between activation energy of CO dissociation and chain growth probability;
- consequences to overall activity and selectivity of reaction centers with different CO dissociation sites and chain growth centers;
- the prediction of differences in CO consumption rate and selectivity for Ru and Co.

Most of current evidence indicates that the carbide mechanism is the most relevant for Fischer-Tropsch catalysis by metals as Co and Ru. It turns out that sites at the surface are selective that provide low energy paths to CHx intermediate formation. Such sites are similar to the step-edge sites known from transition metal surfaces that provide low barriers for CO dissociation.

Water removal and chain growth have to be fast reactions, whereas methane formation and also chain growth termination have to be slow.

KL-1

The detailed mechanism of chain growth depends on the structure of the catalyst. We will discuss several possibilities.

We find that the optimum chain-growth probability not only requires a step-edge type of reaction center, but also a site that has a dual reaction center. In the latter case CO dissociation and chain growth do not interfere. A necessary condition is that Cads is generated initially in a four fold site and upon hydrogen addition moves to a three fold site.

Whereas overall kinetics according to the single site model is limited by chain termination as slow step, in the dual site model the chain growth reaction has to be the slower elementary reaction step. This is in line with the general observation that chain growth parameters are different for the formation of short hydrocarbon chains versus the longer ones. Since particle size and shape will affect the relative stability of reactive centers, these results have important consequences for particle size dependence.

We predict low chain growth probabilities on the terraces, where formation of intermediate CH_x species is relatively slow. The dominant chain growth sites will be the step-edge type centers with efficient CH_x formation rates. When one compares the relative consumption rates of different metals it is important to establish whether comparisons are made for surfaces with CO dissociation as the slow step versus the rate of chain growth termination or the elementary rate of chain growth. In the comparison of Ru and Co, the terraces are found to be more reactive for Ru, but the step edge sites give the higher selectivity for Co.

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Catalysis from First Principles: Is it Crucial to Account for the Effects of Nanostructuring?

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Difference in the complexity of single crystal surfaces and "real" catalysts causes a problem known as material gap in catalysis. This major obstacle hinders the extension of profoundly understood processes on single crystal surfaces to equally good understanding of heterogeneous catalysis. Indeed, active components of most working catalysts are nanoparticles exposing defects and irregularities that often control the reactivity. To understand the reactivity of such systems, it is crucial to go beyond the still common single-crystal description. For that, model metal catalysts formed of well-characterized supported nanoparticles have been proven experimentally very fruitful [1].

Computational strategy to model experimentally studied catalysis-relevant nanoparticles will be outlined. Applications to metal [2-5], oxide [6, 7] and metal/oxide [8, 9] nanostructures will be discussed.

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KL-3

Catalytic Oxidation Mechanism Based on the High-Dimensional Structure of Mo_3VO_x

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Mo-V-O-based complex oxides are one of the most important solid-state oxidation catalysts. However, it has been hard to understand the origin of catalytic function of these catalysts in molecular level. Now, we have two new crystalline solids of Mo_3VO_x with unique crystal structures, orthorhombic phase and trigonal phase. Both of the Mo_3VO_x catalysts have the same structure units of pentagonal ring, 6-membered ring [1-5], and 7-membered ring with different arrangements in *a-b* plane and in addition showed extremely high catalytic activities for the selective oxidation of acrolein to acrylic acid and the oxidation of ethane to ethene with molecular oxygen. Catalytic results indicated that the structural unit arrangement [2,4,5] in the *a-b* plane of the catalysts was dominant in the genesis of the oxidation activity and showed that the existence of the 7-membered ring site in the Mo_3VO_x catalysts was indispensable for the oxidation activity. It is proposed that the bridged lattice oxygen between highly distorted Mo and V octahedra forming the 7-memebered ring unit [2] is responsible for the catalytic oxidation, and the ring with Redox tunable pore diameter of about 0.4 nm [3,6] can capture the reactant molecules for effective oxidative activation.

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Mechanistic Aspects of Hydrogenation and Oxidation of Sugars

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In recent years, exploitation of renewable sources has gained considerable attention. In particular polyols and acids derived from respectively hydrogenation and oxidation of sugars are versatile molecules with a variety of applications. In the lecture these reactions occurring in the aqueous phase will be discussed.

Extensive kinetic studies on oxidation of arabinose, galactose and glucose combined with electrochemical potential measurements along with investigations of structure sensitivity and catalyst characterization were conducted over supported gold catalysts for the interpretation of the reaction mechanism [1]. The influence of the reaction parameters such as pH, temperature, and oxygen flow rate was investigated. In-situ catalyst potential measurements during oxidation gave information about the extent of the oxygen accumulation on the metal surface and a correlation to activity was obtained. An oxidative dehydrogenation mechanism was proposed and a kinetic model taking into account the catalyst potential changes was developed.

Hydrogenation of D–maltose, D–galactose, L–rhamnose and L–arabinose and some of their binary mixtures to corresponding polyols was carried out on a finely dispersed Ru/activated carbon catalyst with the objective of studying the kinetics and the reaction mechanism [2]. This work was supplemented with DFT investigations of five L-arabinose tautomers adsorption on a ruthenium surface allowing advancing a reaction mechanism. In particular it could be suggested that conformers of sugars are mostly adsorbed keeping the conformational properties and the most abundant tautomer, perpendicularly interacting with the metal surface, is the one, which is probably hydrogenated.

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KL-5

The "True" Explanation is Typically rather Simple

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We all know examples for that: people come up with models explaining mechanisms of surface reactions and, sometimes, the models may be rather fancy. When further results disagree with the originally proposed and disseminated model, the model is modified to become even more complex. However, in many cases, the original model may simply be wrong. The current contribution discusses 4 examples of this "phenomenon":

i) the structure and selectivity of PdZn surface alloys [1,2], ii) hydrogen adsorption on Ga_2O_3 and reactions on PdGa-Ga_2O_3 [3,4], iii) CO dissociation on noble metals [5,6], and iv) CO oxidation on metallic vs. oxidic surfaces [7,8].

We show how a surface science approach utilizing *in situ* surface spectroscopy [9,10] and surface microscopy [11,12] on model catalysts, together with corresponding studies of technological catalysts, hopefully provides the right answers. Does it ?

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Understanding Thermal and Photocatalytic Chemical Routes for NO_x Storage at the Molecular Level: From Advanced Realistic Catalysts to Planar Model Catalysts

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In this talk, two different genres of TiO_2-promoted $DeNO_x$ catalysts with NO_x storage capabilities will be discussed. The first genre of catalysts to be discussed is TiO_2-promoted NO_x-Storage Reduction (NSR, or Lean NO_x Traps, LNT) catalysts which function through thermally activated surface processes. NSR catalysts are based on solid state storage of $NO_x(g)$ in the exhaust stream on a catalytic component within a thermal window of 250 - 350 °C under oxidizing (lean) conditions followed by the reduction of the stored NO_x during a short fuel-rich period. $BaO/TiO_2/Al_2O_3$ based ternary mixed oxide NO_x storage materials synthesized via sol-gel techniques reveal advantageous NO_x storage and sulfur tolerance characteristics. Although the conventional BaO/Al_2O_3 binary mixed oxide system is prone to sulfur poisoning where it loses a significant portion of its NO_x storage capacity in an irreversible fashion due to the formation of thermodynamically stable surface and bulk sulfate species, $BaO/TiO_2/Al_2O_3$ ternary system displays significantly superior thermal regeneration characteristics at low temperatures and resists sulfur poisoning. This behavior can be attributed to the presence of small TiO_2 surface domains functioning as anchoring sites for BaO clusters, preventing the sintering of BaO sites and impeding the formation of large $BaSO_4$ clusters that cannot be thermally regenerated efficiently. Along these lines, surface functionalization with TiO_2 is presented as an effective strategy to *"fine-tune"* the surface dispersion of a particular oxide domain (i.e. BaO) on a complex mixed oxide system. These arguments are supported with experimental results obtained via XRD, BET, Raman spectroscopy, in-situ FTIR, TPD, XPS, TEM, SEM and EDX techniques.

In order to shed light on the fundamental surface phenomena taking place during the NO_x storage processes on NSR catalysts at the molecular level, planar model catalysts were prepared in the form of $BaO/BaO_2/Pt(111)$ and $BaO_x/TiO_2/Pt(111)$. Structural characterization of these relatively well-defined model catalysts was performed via LEED and XPS while NO_x adsorption characteristics were studied via XPS and TPD. It is observed that BaO_2 sites play a crucial role during the uptake and release of NO_x species where the presence of exposed (open) Pt sites significantly enhance the BaO_2 formation and catalytically decrease the NO_x desorption temperatures. Two different NO_x desorption mechanisms were proposed for model catalyst surfaces containing exposed Pt sites and surfaces lacking any exposed Pt sites. Furthermore, a mechanistic explanation was also provided for the thermally induced deactivation and the structural integrity loss of TiO_2-promoted NSR catalysts at elevated temperatures which include the formation of $BaTiO_3$ domains, sub-surface diffusion of BaO sites and the surface segregation of underlying TiO_2 domains. Influence of BaO domain size on the NO_x storage was also studied as a function of BaO surface coverage.

Inspired by the thermally-activated automotive catalysts given above, a second genre of photochemically-activated TiO_2-promoted $DeNO_x$ catalysts in the form of X/TiO_2, and $X/TiO_2/Al_2O_3$ (X=Li, Na, K, Cs, Ca, Sr or Ba) were also prepared via sol-gel techniques for indoor air purification purposes. These photochemically activated systems operate under ambient conditions (25 °C) and offer a hybrid platform combining photocatalytic $NO_x(g)$ oxidation and solid state NO_x storage. Performance and the structural properties of these hybrid “Photocatalytic NO_x Oxidation and Storage” (PNOS) systems will also be discussed in the final part of the talk.

KL-7

Transition-Metal-Catalyzed Carbon-Carbon and Carbon-Heteroatom Bonds Formation in Organic Synthesis

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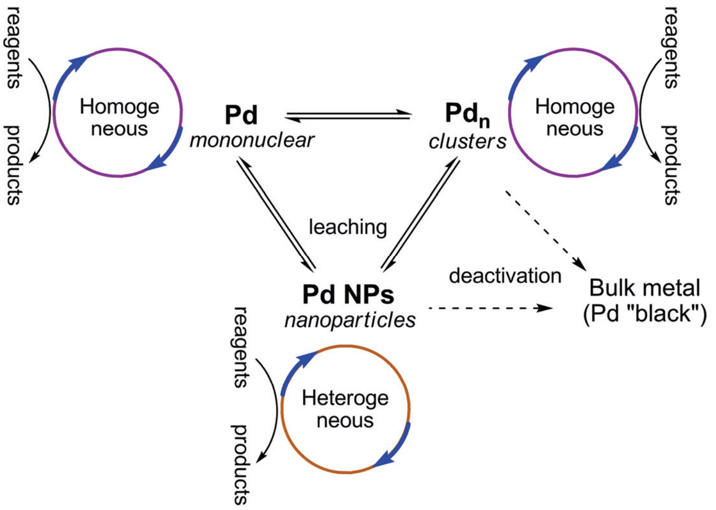
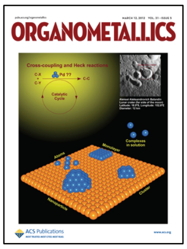
Carbon-carbon and carbon-heteroatom bonds formation are well-established and outstanding tools utilizing homogeneous catalysis in the areas of organic synthesis, pharmaceutical and medicinal chemistry, natural product synthesis, material science, and several other fascinating applications. Homogeneous catalysis in cross-coupling, Heck, carbonylation reactions, and also carbon-heteroatom bond formation has shown tremendous recent growth. Rapid methodology development in the areas of selective construction of C-C and C-Heteroatom bonds revealed unique features on the nature of metal catalysis: adaptive interconverion of different active species taking place during the catalytic transformation.

In the present study, the mechanism of transition-metal-catalyzed reactions are discussed in view of evolution of active species in solution and finding the relationship between the nature of catalyst active species to the efficiency and selectivity of the reaction (Scheme 1) [1].





Scheme 1. An example of interconversion of Pd catalyst active species in solution.

KL-7

The questions of particular importance are catalytic properties related to mononuclear metal complexes and metal clusters in solution, interconversion between homogeneous and heterogeneous catalytic systems, leaching, and stability/recycling of the catalysts. The optimal strategy to select efficient catalytic system for C-C and C-Heteroatom bonds formation will be presented and discussed.

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Selective Oxidation Catalysis with Non Porphyrinic Fe and Mn Complexes that Support High Oxidation States

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The formation and cleavage of the O-O bond is arguably the most important reaction in living organisms. Reductive O-O breakage takes place in cytochrome C oxidase, during cellular respiration in aerobic organisms. [1] O-O cleavage also takes place in oxygenases, [2] and this reaction results in the generation of highly electrophilic high valent metal-oxo species, responsible for oxidative transformations. On the other hand, O-O bond formation takes place at a Mn4Ca cluster in the Oxygen Evolving Center of Photosystem II (PSII) of green plants. In both oxidative and respiration enzymes, metal ions adopting high oxidation states result from reductive O-O cleavage reactions, while in PSII they are responsible for O-O bond formation. [3] Selected coordination complexes catalyze analogous reactions, and some of these complexes have turned into very attractive tools for organic synthesis. [4] The study of the mechanisms of action of these catalysts has shed light into the molecular details of enzymatic systems. Our research group undertakes this approach and aims at studying the chemistry of iron and manganese coordination complexes which can sustain high oxidation states and that can act as catalysts for challenging oxidation reactions, such as the selective oxidation of alkyl C-H bonds, [5] the cis-dihydroxylation of alkenes, [6] stereoselective epoxidation [7] and the oxidation of water. [8] Recent progress from our group will be discussed.

Acknowledgements: Generalitat de Catalunya (ICREA Academia and SGR 2009-SGR637), MICINN (CTQ 2009-08864 and Consolider Ingenio CSD2010-00065), ERC-StG-239910.

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KL-9

Active Species of Nonheme Iron- and Manganese-Catalyzed Oxidation

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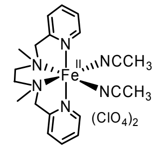
Within biomimetic oxidation catalysts, aminopyridine complexes of such biologically important elements as Fe and Mn attract particular attention.[1] These complexes have been found to efficiently catalyze olefin epoxidation with percarboxylic acids or H_2O_2/AcOH in a chemo- and sometimes enantioselective fashion.[1,2] Electron paramagnetic resonance (EPR) spectroscopy has been used to characterize oxidizing species in the catalyst systems **1**-**4**/H_2O_2. It was found that very unstable intermediates **1c**-**4c** exhibiting similar rhombic S = 1/2 EPR signals and active towards epoxidation of olefins are formed in these systems.[3] Costas, Cronin, and co-workers have used cryospray-assisted variable temperature mass spectrometry (VT-MS), to detect an elusive HO–Fe^V=O intermediate in the catalyst system **4**/H_2O_2.[4] Direct correlation of VT-MS and EPR data shows that S = 1/2 intermediate **4c** well corresponds to the oxoiron(V) species identified in the same system by VT-MS. Apparently, complexes **1c**-**4c** are similar oxoiron(V) species. Comparative studies of asymmetric olefin epoxidation by Fe and Mn catalyst systems **3**/H_2O_2/RCOOH and **5**/H_2O_2/RCOOH have shown that **3** and **5** conduct enantioselective epoxidation of prochiral olefins with H_2O_2 in the presence of carboxylic acids, manganese catalyst **5** demonstrating much higher efficiency (1000 vs. 100 TON) and enantioselectivity (up to 93% *ee*: the highest value ever reported for aminopyridine manganese catalysts). The enantioselectivity drastically increases with rising steric bulk of the acid, thus indicating the presence of the carboxylic moiety in the active species. On the basis of EPR and enantioselectivity data, the active species can be assigned to complexes $[LM^V{=}O(OC(O)R]^{2+}$ (where M = Fe or Mn, R = alkyl, L = aminopyridine ligand).



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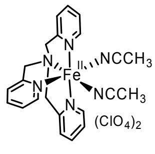

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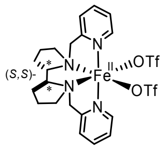

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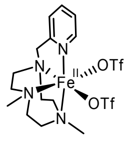

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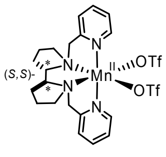

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ORAL PRESENTATIONS

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Section II. Mechanisms of homogeneous catalysis

OP-II-1 ÷ OP-II-8

Section III. Mechanisms of heterogeneous catalysis

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Section IV. Catalytic processing of renewables

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Section V. Electrocatalysis, photocatalysis, biocatalysis

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Section of the young scientists

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OY-IV-1 ÷ OY-IV-7
OY-V-1 ÷ OY-V-4

Particle Size Effect in CH_4 Oxidation over Noble Metals: Comparison of Pt and Pd Catalysts

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One of the most important factors influencing the efficiency of noble metal catalyst is the size of metal particles. High metal dispersion improves utilization of noble metal. On the other hand, turnover rates of oxidation reactions may depend significantly on the size of metal particles (particle size effect). As a result, overall activity of the catalyst becomes a function of metal dispersion (fraction of exposed atoms) and the particle size effect, and careful management of metal particle size is required for achieving optimal performance and/or minimization of noble metal loading. In this study, we carried out the detailed comparative study of the particle size effects for Pt and Pd catalyst in the total CH_4 oxidation. Catalytic tests were complemented by *in situ* XPS study of the oxidation state of Pt and Pd particles under reaction conditions for revealing the nature of the observed catalytic effects.

Catalytic studies revealed different dependencies of TOF on metal particle size for Pd and Pt catalysts. Particle size effect for Pd catalysts is much more pronounced than for Pt catalysts: TOF increases by more than order of magnitude with increase in *d* Pd from 1 to 22 nm. Therefore, the most favorable performance is observed for the catalyst with Pd particle size ~ 4 nm. For Pt catalysts TOF increases only by ~ 2-3 times with increasing particle size from 1 to 3-4 nm, and remains essentially constant when *d* Pt exceeds 4 nm. As a result, the sample with maximal Pt dispersion (*d* Pt = 1.2 nm) demonstrates the best overall activity in CH_4 oxidation among Pt catalysts.

Results of in-situ XPS studies indicate that Pd particles remain in oxidized state in the course of the reaction within the whole range of particle sizes (1 – 22 nm). For Pt catalysts it was found that 1-3 nm Pt particles are easily oxidized under reaction conditions. Note, that the pronounced particle size effect is observed for the particles of this size range. On the other hand, for Pt catalysts with bigger metal particles, XPS data showed that Pt remains mainly in the metallic state. These data suggest that the observed dependence of the catalytic activity on metal particle size may be associated with the change of the reaction pathway from Mars–van Krevelen mechanism to Langmuir–Hinshelwood kinetics.

OP-I-2

Computational Insights into Aqueous Phase Processes for Biomass Reforming

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Energy efficient conversion of plant and municipal solid waste material (biomass) into easy useable energy carriers or fine chemicals is one of the major challenges for a sustainable future. Aqueous-phase reforming processes (APR) facilitate not only the energy-efficient conversion of biomass to alkanes [1], but also the production of hydrogen [2] and light alkanes, along with CO_2 and CO.

We carried out electronic structure calculations on periodic slab models at the DFT level using the program VASP, employed the plane-wave-based projector augmented wave approach and the gradient-corrected exchange-correlation functional PW91. The systems studied consist of 1- and 2-propanol as model hydrocarbons adsorbed on either flat Pt(111) or stepped Pt(221) surfaces [3].

We examined the reaction pathways for the formation of H_2 and alkanes. On the Pt surface hydrogen formation is favored over alkane formation in agreement with experimental results [4]. We focused on the dissimilar behavior of primary and secondary alcohols in the formation of H_2. Hereby, the resulting CO_2 can be directly released or formed in a subsequent water-gas shift reaction after decarbonylation. Our calculations also show that the propensity for the species that undergoes C-C bond cleavage depends on the catalyst size. The formation of alkanes, involving the cleavage of the alcohol C-O bond on the Pt surface, can proceed by various pathways. We present the most likely one, a dehydration-hydrogenation mechanism via propylene as intermediate, which is able to compete with H_2 formation.

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Activation of Oxygen on Microclusters of Silver Anchored on SiO_2 and Al_2O_3 Surfaces. Embedded Cluster Scalar-Relativistic and Periodic Pseudopotential Density Functional Calculations

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In continuation of our previous investigations of coinage metal microclusters on oxide supports, [1-4] we investigate structure, stability and reactivity of silver trimers and tetramers supported on α-alumina(0001) and model amorphous silica surfaces. Silver clusters of such small nuclearity supported on alumina, in particular, are expected to be active centers of catalytic propylene epoxidation [5] and NO selective catalytic reduction with hydrocarbons [6].

We consider electron-deficient silver species bound to non-bridging oxygen centers (NBO), ≡Si–O• of MCM-41 silicalite wall and substituting protons of μ_3-OH groups of partially hydroxylated alumina surface. Different structures of adsorption complexes of these species with O_2 and NO molecules, which feature on top of silver atom and bridging to two silver atoms, are compared. On alumina, bridging adsorption mode with respect to Ag atom and Al cations are considered as well. Reaction of surface NO oxidation connected with O-O bond splitting is considered as a probe for O_2 activation. Barrier heights for this reaction on alumina are consistent with the idea of moderate activation consistent with selective oxidation of reducing agents.

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OP-I-4

Theoretical Insight on Catalytic Activity of Bimetallic Gold Catalysts

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The study of catalytic properties and structure of bimetallic clusters contained gold and platinum group atoms is the promising field. Here we present the new results of quantum-chemical investigation of Ni and Pd influence on active sites formation in small gold clusters. Simulation of ligand effects and ensemble effects has been performed in Au_nNi and Au_nPd bimetallic systems. The possible reaction pathways of H_2O_2 formation (reaction 1) and hydrocarbons isomerization (reaction 2) on Au_7Pd and Au_3Ni have been studied in details and compared with those on the pure gold clusters Au_8 and Au_4.

Scalar-relativistic DFT with modified Dirac-Coloumb-Breit Hamiltonian and the nonempirical local PBE functional have been applied. In some cases, plane-wave basis set and ultrasoft pseudopotentials in periodic boundary conditions have been used. Firstly, the models of bimetallic catalyst have been selected. The calculation involved the optimization of Au_nX structures (X=Ni, Pd, n=2÷7) in the various spin multiplicities, analyses of average Au-X and Au-Au distances, atomic charge (AC), molecular orbitals (MO) as well as cluster's binding energies and ΔG_T in cluster's formation process. It was obtained that (*i*) in Au_nNi the distances increased versus Au_{n+1}, (*ii*) binding energies per atom increased when the *n* increased, (*iii*) the sole role of Au atoms in clusters is to shift the d states of the Pd, (*iv*) Pd and Ni influences significantly the charge redistribution in Au_nX. From all bimetallic systems, Au_3Ni and Au_7Pd have been chosen for further investigation.

Based on AC and MO analysis of bimetallic clusters, it is supposed that $Au^{\delta+}$ site is the most active in unsaturated hydrocarbons adsorption, while $Au^{\delta-}$ is active in oxygen adsorption. The simulation of mechanism of the reactions 1 and 2 confirmed our assumption.

This work was supported by grants RFBR 11-01-00280-a, 10-03-00999-a, 11-03-01011-a, Grant of the President of the RF for state support of young Russian scientists MK-107.2011.3, and Grant of state support of leading scientific schools of RF NSh-2724.2012.3. The calculations were performed using the SKIF MSU «Chebyshev», «Lomonosov».

Oxidation of Alkanes: In Silico Catalyst Design

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Alkane C-H activation and, in particular, selective oxidation under mild conditions is an enduring challenge in catalysis. In an effort to match the in vivo effectiveness of metallo-enzymes such as cytochrome P-450, much attention has been paid to metal-oxo systems that can mimic enzyme reactivity [1]. The selective oxidation of alkanes into various oxidized products employing a transition metal catalyst together with an oxidative agent (i.e. hydrogen peroxide in Fenton chemistry processes) has been thoroughly investigated by computational means [2]. Various metal-centred catalysts have been proposed for the above functionalization with a documented large dependence on the choice of the transition metal and the ligand environment. These range from $[FeO(H_2O)_5]^{2+}$ and the ammonia substituted equivalent [2,3] to Mn-heme containing systems [4]. A plausible mechanism that governs the C-H bond activation is the oxygen rebound mechanism [5], which applies to remarkably diverse systems.

Theory can assist in tailoring an efficient catalyst, finding the optimum compromise between a fast H-abstraction/O-rebound step but also a facile regeneration of the iron-oxo active site. The latter part of the catalytic cycle is often neglected in the literature but represents a determining factor for the functionality of the catalyst. In the present DFT study, the complete catalytic cycle is considered, so that complexes that are known to perform well in the H-abstraction/O-rebound step are also assessed at the regeneration step. Heme and non-heme containing systems such as the ones mentioned above are included in the study. Furthermore, the effect of the equatorial or axial position of the ligands on the spin state and reactivity of the species is also taken into account, throughout the catalytic cycle.

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OP-I-6

Self-Induced Electric Fields in the System of Supported Metal Nanoparticles: The Impact on Heterogeneous Catalysis

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External electric fields are known to affect the catalytic processes [1]. In general, application of the electric field can result in significant enhancement of the catalytic reaction rate if the field intensity is high enough, comparable with intramolecular fields. In practice, however, application of such strong field may cause undesirable heating or even breakdown of the reaction area. In case of heterogeneous catalysis the reasonable solution would be concentration of strong electric field in close vicinity of the catalyst surface.

In a system of supported metal nanoparticles, electrons can jump between the neighboring particles or between the particles conducting support giving rise to the appearance of fast-fluctuating charge dipoles [2]. Associated with such dipoles local electric fields may have peak intensity up to 10^7 V/cm with life span in a wide range from 10^{-8} s to 10^{-13} s. These fields persist in rather small area, within particle-particle or particle-support gaps. For typical supported metal nanocatalysts the size of this area is still bigger than the size of reacting molecules. This consideration suggests that the property of supported metal catalyst will essentially depend on the surface density of nanoparticles. One can expect such dependence because in a given system the particle density determines both the field strength and the possibility for the reacting molecules to enter the field area.

The experiments were performed with the catalysts comprising supported amorphous metal nanoparticles. Specific features of these particles are fixed size and enhanced coagulation stability which opens the possibility to thoroughly trace the catalytic activity against particle density. At certain densities, when the field effects are expected to be most pronounced, unusually high catalytic activity was observed in different reactions with the use of different metals and corresponding supports. This clearly shows that the impact of self-induced electric fields on the properties of supported metal catalysts is very general phenomenon.

This work was supported by RFBR (№ 10-03-00372, 11-03-00403).

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Low Temperature Decomposition of Hydrogen Sulfide into Hydrogen and Diatomic Gaseous Sulfur

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A new catalytic reaction of hydrogen sulfide decomposition is revealed, the reaction occurs on metal catalysts in gas phase according to equation

$$2\ H_2S \leftrightarrow 2\ H_2 + S_2^{\ (gas)}$$

to produce hydrogen and gaseous diatomic sulfur, conversion of hydrogen sulfide at room temperature is in vicinity of 15%. When considering temperature dependence of the reaction discovered, conversion of hydrogen sulfide decreases with rising temperature and at 250°C the reaction is almost stopped. The thermodynamic driving force of the reaction is the formation of chemical sulfur – sulfur bond between two hydrogen sulfide molecules adsorbed on two adjacent metal atoms in the key surface intermediate and elimination of hydrogen into gas phase. Hereby, the solid catalyst ensures possibility to realize surface reaction, which is thermodynamically prohibited in gas phase. The reaction mechanism of hydrogen sulfide decomposition on solid catalysts at room temperature is experimentally substantiated.

“Fingerprints” of diatomic sulfur adsorbed on the solid surfaces and dissolved in different solvents are studied. In closed vessels, this molecule is stable for a long period of time (weeks). A possible electronic structure of diatomic gaseous sulfur in the singlet state is considered. According to DFT calculations, energy of the singlet state of S_2 molecule is over the ground triplet state energy for 10.4 kCal/mol. Some properties of gaseous diatomic sulfur are also investigated. Catalytic solid systems, both bulk and supported on porous carriers, are developed. The supported catalysts are prepared by impregnation of a carrier with aqueous solution of cheap and nontoxic metal salts; the technology of catalyst preparation can be easily realized at any catalytic manufactures.

When hydrogen sulfide is passing through the solid catalyst immersed in liquid solvent which is capable of dissolving sulfur generated, conversion of hydrogen sulfide achieves 100 % producing hydrogen in gas phase. This gives grounds to consider hydrogen sulfide as an inexhaustible potential source of hydrogen – very valuable chemical reagent and environmentally friendly energy product. Sulfur from solution can be recovered by simple technological methods as solid sulfur.

OP-II-1

Direct Synthesis of Dimethyl Carbonate from CO_2 and MeOH Catalyzed by $Sn(Ot\text{-}Bu)_4$ with Acid-Base Additives, and its Reaction Mechanism

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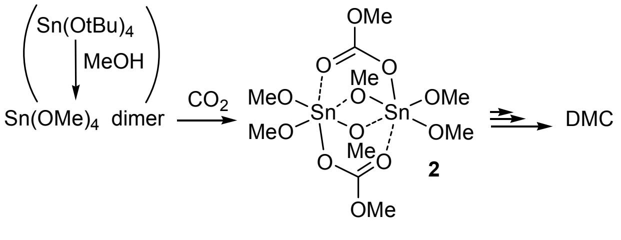
The conversion of abundant CO_2 into industrially valuable chemicals, such as dimethyl carbonate (DMC), is an imperative research theme from the viewpoint of green-sustainable chemistry. Although DMC has been practically synthesized using highly toxic agents, such as phosgene and CO, a more environmentally friendly process using CO_2 and MeOH producing water as the sole by-product is strongly desired.

Recently, we discovered that $Sn(Ot\text{-}Bu)_4$ is a user-friendly precatalyst for the direct synthesis of DMC from CO_2 and MeOH. It is far more active than the conventional $Bu_2Sn(OMe)_2$ catalyst. The addition of acid and/or base cocatalysts as well as optimization of the CO_2 pressure improved the catalytic activity [1].

The higher catalytic activity of $Sn(Ot\text{-}Bu)_4$ than $Bu_2Sn(OMe)_2$ and the effects of the reaction conditions on the catalytic activity were explained on the basis of the quantum chemical calculation. The reaction mechanism of the conventional $Bu_2Sn(OMe)_2$ has been already proposed with DFT calculation, claiming that the reaction proceeds through five-coordinated dimeric tin complexes [2]. However, our $Sn(Ot\text{-}Bu)_4$ catalyst system is proposed to proceed through the formation of intermediates composed of dimeric, six-coordinated tin carbonate complexes. The existence of the μ-carbonate structure in the intermediates was also confirmed by FT-IR. It is also proposed that the reactant MeOH should behave as a co-catalyst and play an important role in the reaction mechanism.



Scheme 1. Plausible reaction scheme for direct DMC synthesis using $Sn(OtBu)_4$ catalyst.

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OP-II-2

Living Olefin Polymerization with Post-Titanocene Catalysts Containing *o*-Fluoroaryl Substituents: Role of Noncovalent Interactions

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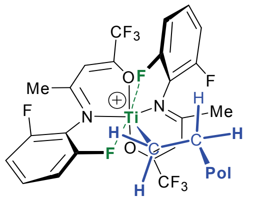
Titanium(IV) complexes with bidentate *N*,*O*-donor ligands have attracted great attention as catalysts for olefin polymerization,[1] especially with regard to their potential to induce living polymerization of ethylene, yielding PE with narrow molecular weight distributions (down to M_w/M_n 1.01[2]) and high molecular weights (M_n 10^5-10^6 g mol^{-1}). The mechanisms responsible for living polymerization in the presence of *o*-fluorine substituents are still being debated.

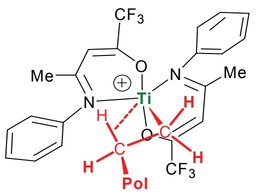
In this work, formation of ion-pair intermediates of the type $[L_2TiMe]^+[MeMAO]^-$ upon the interaction of the titanium pre-catalysts L_2TiCl_2 with methylalumoxane (MAO) has been followed by multinuclear NMR for various post-titanocene catalysts based on bis(salicylaldimine), bis(pyrrolylaldimine), and bis(enolatoimine) ligands. In some cases, propagating species of the type $[L_2TiP]^+[MeMAO]^-$ (where P is the growing polymeryl chain) have been detected in the presence of ^{13}C-enriched ethylene, and characterized spectroscopically.[3] For the bis(enolatoimine) system, weak non-covalent interaction of the *o*-F substituents with the metal center in the active sites could be documented. This interaction is likely to trigger living olefin polymerization by *o*-F substituted bis(enolatoimine) and structurally related Ti catalysts (via suppression of *β*-hydrogen transfer and of chain transfer to $AlMe_3$), while catalysts without *o*-F substituents do not exhibit living character.

living system



free-chain, interacting-ligand

non-living system



interacting-chain

This work was supported by Russian Foundation for Basic Research, grant 12-03-00133.

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OP-II-3

Mechanism for the Reduction of Dioxygen by Diethylhydroxylamine (DEHA) Organocatalyzed by Natural Polyphenols

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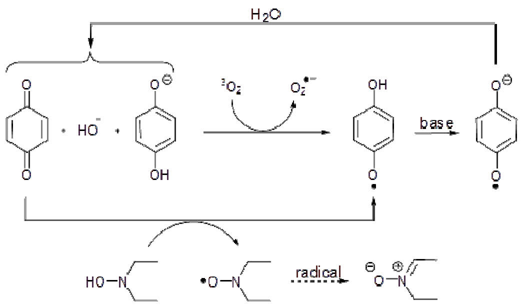
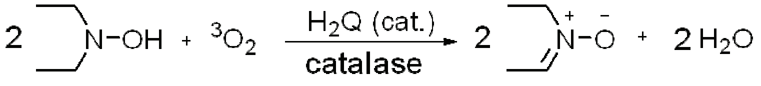
A reduction of dioxygen dissolved in water by diethylhydroxylamine (DEHA) in the presence of hydroquinones or quinones as organocatalysts was investigated with regard to reaction rate and catalyst turnover. Eleven p-benzoquinone derivatives bearing various electron-donating, electron-withdrawing and bulky substituents were studied. The catalytic activity of four benzenediols (hydroquinone, resorcinol, catechol and 4-tert-butylcatechol) and of four benzenetriols (hydroxyquinol, phloroglucinol, pyrogallol and 5-tert-butylpyrogallol) is compared.

Mechanistic and kinetic studies indicate that the rate-determining step is the regeneration of hydroquinones through the reduction of the corresponding benzoquinones by DEHA.



Then, eight natural polyphenols were tested as alternative catalysts to the potential carcinogen hydroquinone. Four of them (purpurin, myricetin, gallic acid and propyl gallate) exhibited some catalytic activity and gallic acid was shown to be even more efficient than hydroquinone itself.

A further improvement of the catalytic system was achieved by adding catalase to disproportionate the generated hydrogen peroxide, which is detrimental for the catalyst. Thus, the oxygen scavenging system DEHA–gallic acid–catalase has been found to be not only greener but also more efficient than the current system DEHA–hydroquinone since it gives water instead of hydrogen peroxide as the final reduction product of dioxygen.



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Green Chem. (2012) DOI: 10.1039/C2GC16503A

OP-II-4

Diphenylphosphinoferrocenyl Thioether Diene Rh(I) and Ir(I) Catalyzed Ketone Hydrogenation: Turning Precatalysts into Active Species

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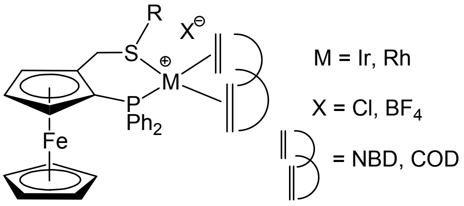
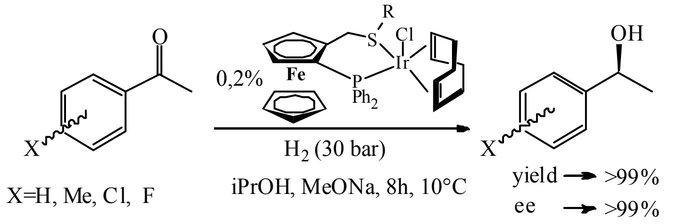
Iridium diene complexes with diphenylphosphinoferrocenyl thioether ligands (Scheme 1) are effective catalysts for ketone asymmetric hydrogenation (Scheme 2) [1]. The analogues rhodium complexes synthesized for the first time [2] are good structural and functional models of these catalysts.



Scheme 1



Scheme 2

The hydrogenation of these precatalytic species under stoichiometric conditions (1-3 bars H_2) was studied by NMR and UV/Vis spectroscopy. The reaction does not proceed in CH_2Cl_2 when well dried hydrogen is used and features an induction period in the presence of alcohol (MeOH, iPrOH) or H_2O. The use of ROD or D_2O shortens the induction period and reduces the hydrogenation rate. The effect of the diene ligand and anion, solvent and added base (pyridine, MeONa) on the hydrogenation rate was also investigated. The reaction generates a dihydride species, which is stabilized in the presence of pyridine as shown by parahydrogen NMR measurements. Combined with DFT calculations these experimental data contribute to elucidate the precatalyst activation mechanism.

Acknowledgment: We thank the CNRS and the RFBR for support through a bilateral grant, the GDRI “Homogeneous Catalysis for Sustainable Development”, and the French Embassy in Moscow for the financial support of joint PhD thesis for EMK.

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OP-II-5

Mechanisms of Catalytic Reactions of Norbornadiene

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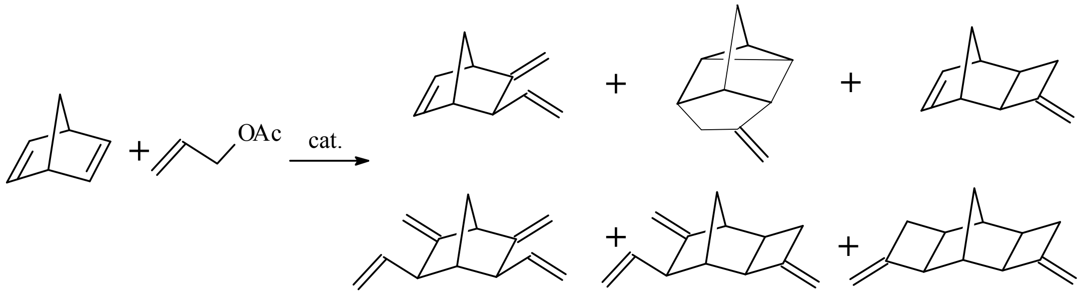
Catalytic processes with participation of norbornadiene (NBD) offer unique opportunity for synthesis of broad range of polycyclic hydrocarbons. Effective usage of such synthetic methods as homodimerization, codimerization and nonconventional allylation of NBN and NBD derivatives allows developing a unique strategy of preparation of carbocyclic structures containing methylene, vinyl and methylenecyclobutane functionalities.



Problems of selectivity in multi-reaction pathways for NBN, NBD and their derivatives are of great importance. Both rate and selectivity of NBD and NBN reactions with allyl esters can be controlled. Mechanism of formation of nickel and palladium catalysts as well was extensively studied by a number of spectral and kinetic methods, key intermediates were identified, and consistent mechanisms were proposed. Moreover, reaction pathways of NBD have been simulated in the frame of DFT method. Factors influencing on selectivity have been revealed, what allowed synthesizing individual stereoisomers quantitatively. Both selectivity and TON depend on composition of catalytic system and effective charge on the metal. A raw of new unsaturated compounds having double bonds of different reactivity is of interest for derived rubber production.

Comparative study of effectiveness of the usage of heterogeneous and homogeneous organometallic catalysts was pursued. Common features and differences in the reaction mechanisms have been revealed.

This work was financially supported by RFBR (# 11-03-00662-a).

Mechanism of the Dimerization of Propene in the Presence of the Ziegler-Natta Catalyst Based on Nickel and Aluminum Alkyl Halides

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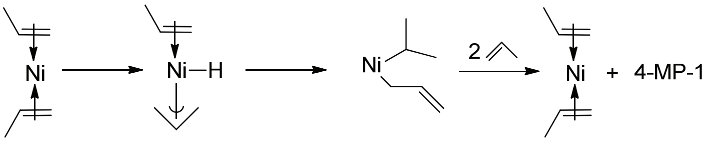
The dimerization of propylene in the presence of the Ziegler-Natta catalyst based on nickel and aluminum alkyl halides leads to three types of structural isomers: linear hexenes, methylpentenes, 2,3-dimethylbutenes. The composition of catalyst system substantially influences on the ratio of the structural isomers. But the most interesting fact is the composition of methylpentenes when dimerization of propene occurs with $Ni(acac)_2/Al(i\text{-}Bu)_2Cl/PPh_3$. In this case the content of 4-MP-1 is 24%, which is of two orders of magnitude higher than the thermodynamically equilibrium amount. The dimerization of propylene by nickel hydrides assumes formation of the intermediate with Ni-alkyl bond. The Ni-C bond breaking via the β-hydride elimination mechanism should lead to the formation of 4-MP-1 and 4-MP-2 (cis + trans). Their ratio should be close to thermodynamically equilibrium. These data can be considered as the experimental reasoning for activity of the reduced forms of nickel in the catalytic cycles, which are included on the first stage oxidative addition of substrate to transition metal and on the terminal stage reductive elimination of 4-MP-1:



To elucidate the probable nature of the catalytic action of Ni(0) complexes in alkenes (ethylene, propylene) oligomerization, the model compositions containing mainly nickel complexes NiP_4 ($P = PR_3$, $P(OR)_3$) and boron trifluoride etherate have been studied. Study of interaction of formed complexes of Ni(0) has shown oxidation (NiP_4) to Ni(I) by injection to the system $BF_3{\cdot}OEt_2$. Treatment of the reaction mixture containing Ni(I) complex $[(PPh_3)NiL_2]BF_4$ with propylene showed it's high activity in the dimerization of propylene. Activity of the Ni(I) in the dimerization of propylene assumes dissociative oxidative addition of propylene and formation of Ni(III) on the first stage of catalytic cycle. This assumption was supported by model reaction of phenylacetylene oxidative addition to Ni(I) monitored by ESR which resulted in the formation of Ni(III) complex.

OP-II-7

Catalytic Conversion of Phenol on Peroxo Edta-Type Titanate

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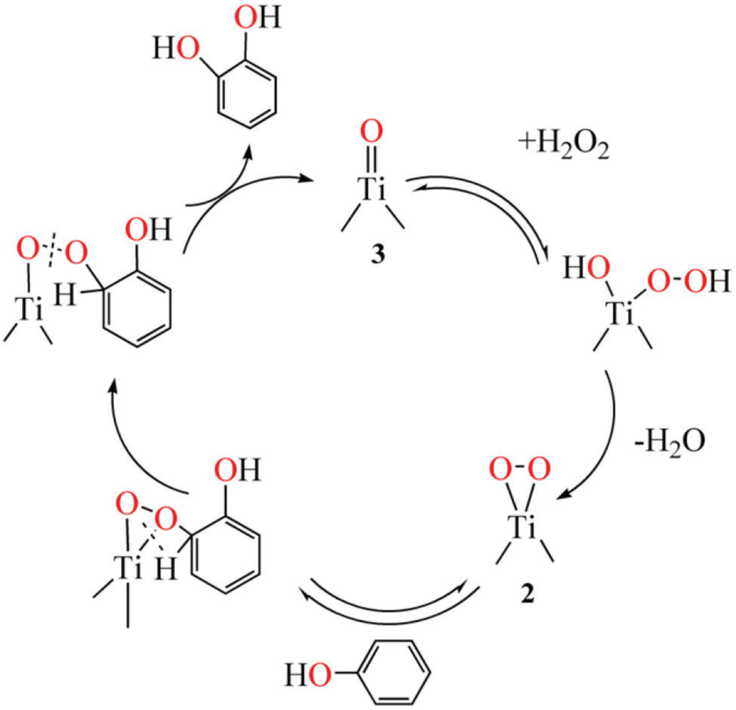
A series of peroxo edta-type titanates have been isolated and characterized in solid and solution, where hexadentate chelated *trans*-1,2-cyclohexanediaminetetraacetato titanate(IV) was used as a catalytic Ti(IV) species similar to the constrained environment of TS-1 (H_4cdta = *trans*-1,2-cyclohexanediaminetetraacetic acid, $C_{14}H_{22}O_8N_2$; TS, titanium silicalite). Octadentate cdta peroxo titanate(IV) $Na_2[Ti(O_2)(cdta)]\cdot 2H_2O$ was obtained quantitatively from the reaction of the hydrated titanium cdta complex with hydrogen peroxide. The bond distances between O–O and Ti–(O_2) are 1.464(3) and 1.908(2) Å, respectively. Heating transformation of the peroxo titanium(IV) complex with excess H_4cdta results in the formation of an interesting oxotitanate in H_2O–H_2O_2 solution. The catalytic activity of the peroxo titanate was studied for phenol hydroxylation using 30% H_2O_2. This was monitored by ^{1}H and ^{13}C NMR techniques. The main product of the reaction is catechol.



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Chiral Ionic Liquid/ESI-MS Methodology as an Efficient Tool for the Study of Transformations of Supported Organocatalysts

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An efficient approach to the study of transformations of supported organocatalysts in asymmetric organocatalytic reactions by modifying them with ionic-liquid (IL) fragments followed by the ESI-MS analysis of recovered catalyst samples has been proposed. The ESI-MS(+) spectra of IL-modified catalysts contain mainly peaks of the catalyst and of ionic compounds formed from the catalyst, whereas the molecules that do not contain ionic groups give much lower peaks. This approach was successfully applied to the study of deactivation pathways of O-TMS-prolinol [1] and primary amine-derived [2] chiral organocatalysts in asymmetric Michael reactions of nucleophiles (dialkylmalonates, nitroalkanes, hydroxycoumarin, or protected hydroxylamines) with α,β-unsaturated carbonyl compounds that involved an iminium-ion formation step. The products of these reactions are used as intermediates for the synthesis of important chiral medications paroxetine, phenibut, baclofen, rolipram for curing CNS disorders, clinically useful anticoagulant warfarin and β-aminoacide enantimers. This methodology allowed us to reveal undesirable side reactions that poisoned the catalysts and found solutions (inert atmosphere or acidic reactivation) to increase their operation period. The proposed approach may be useful for the study of transformations of other types of organocatalysts and for the development of new robust catalysts and processes that would be suitable for large-scale industrial applications.

The work was financially supported by the President of the Russian Federation (grant for young Ph.D. No. 3551.2012.3), the Russian Academy of Sciences (Basic Research Program No. 1 of the Department of Chemistry and Material Sciences) and the Russian Foundation of Basic Research (project 12-03-00420).

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OP-III-1

Mechanism of CH_4 Dry Reforming on Nanocrystalline Doped Ceria-Zirconia with Supported Pt, Ru, Ni and Ni–Ru

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This work presents results of elucidating specificity of CH_4 dry reforming mechanism for Pr, Sm-doped ceria-zirconia catalysts with a high oxygen mobility using combination of transient kinetic methods (including pulse TAP and SSITKA studies) with microcalorimetry.

The rate constants of CH_4 consumption estimated by SSITKA and TAP correlate with catalytic activity (Pt~$LaNiO_3$ <Ru < Ru+Ni), while constants of CO_2 transformation exceed those by an order of magnitude. The strength of oxygen bonding with the ss surface corresponds to bridging M_2O forms (heat of O_2 adsorption ~ 600 kJ/mol). CH_4 transformation in pulses fed to ss surface proceeds with the rate and products selectivities close to those in CO_2+CH_4 pulses without coke deposition until up to 30% of oxygen monolayer is removed. Reoxidation of ss surface by CO_2 yielding CO proceeds with nearly constant heats of reaction (from – 60 to – 30 kJ/mol CO_2) corresponding to replenishing of bridging oxygen forms. Kinetics of reoxidation is described by the model of uniform adsorption surface sites with the density up to 50% of monolayer. The specific rate constants of CO_2 consumption are close for Pt or $LaNiO_3$ –supported samples while being an order of magnitude higher for Ni+Ru- active component due to participation of Ni-Ru alloy nanoparticles in CO_2 activation. Hence, for nanocrystalline oxide supported catalysts with a high oxygen mobility, steady-state reaction of CH_4 dry reforming is described by a simple redox scheme with independent stages of CH_4 and CO_2 activation. This is provided by easy CO_2 dissociation on reduced sites of oxide supports followed by a fast oxygen transfer along the surface/domain boundaries to metal sites where CH_4 molecules are transformed to CO and H_2.

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The Mechanism of Oxidative Conversion of Methane

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Great attention is paid in catalysis over the last 10-15 years to the processes of production of synthesis gas by reaction of selective catalytic oxidation (SCO) of methane and other alkanes. We have carried out investigation on low-percentage nanosized Pt-Ru and NiCuCr catalysts in these processes.

The selective oxidation of CH_4 on catalysts begins in the first few minutes and takes place practically without the formation of CO_2; the contact time does not affect on composition of the formed products. This suggests that the reaction proceeds through the dissociative adsorption of CH_4. Activation and dissociation of CH_4 on Pt^o for the Pt-Ru catalysts (or Ni^o for Ni-Cu-Cr samples) with the formation of $H_{at.}$ and fragments of CH_x either C_x, followed by recombination of the atoms of $H_{at.}$ into the H_2 molecule and the oxidation of C_x to CO due to surface oxygen or bulk oxide RuO_2 (or copper oxide, TPO and TPD of O_2), which immediately forms in the presence of O_2 in the mixture even at 573K, was carried out. Ru at the reduced state conducts also the dissociation of CH_4, but at a slower rate, partially oxidized to RuO_2 even at 373K which reduces the selectivity of process. At the same time RuO_2 easily reduced to Ru^o according to TPR at 373-453K, and the copper oxide - to copper metal. Ru (or Cu) was injected into the catalyst for the oxidation of C_x to CO in order to equalize the rate of formation of C_x with velocities of oxygen activation. As the copper is predominant in the composition of Ni-Cu-Cr contact, the rate of oxidation of carbon particles exceeds, apparently, the rate of their formation, and thereby the accumulation of carbon does not occur. The presence of PtRu and NiCu clusters in Pt-Ru and Ni-Cu-Cr contacts facilitates the interaction of CH_4 with O_2 because of the possible separate adsorption and activation of components in different parts of the cluster: CH_4 - on Pt^o (Ni^o), and O_2 - on Ru^o (Cu^o), and the fact that the exchange and transfer of electrons in the clusters occur at high speeds.

OP-III-3

Sulphur Ageing Mechanisms on Pd/$BaCeO_3$·$2ZrO_2$ Catalyst for Methane Combustion

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The ageing effect induced by S-compounds (added as odorants in the natural gas network for safety purposes) over 2% Pd/$BaCeO_3$·$2ZrO_2$ catalysts for CH_4 combustion was studied. The catalysts were prepared by solution combustion synthesis [1], starting from metal nitrates/glycine mixtures. Basic characterization (XRD, BET, FESEM, TPD/R/O analysis), FT-IR studies and catalytic activity tests were performed in fresh status and after accelerated ageing carried out up to 500 h (hydro-thermal treatment at 800 °C under a flow of 9% CO_2, 18% H_2O, 2% O_2 in N_2, including 200 ppmv of SO_2 to emphasize any poisoning effect).

With ageing, TPO analysis demonstrated that the catalyst was heavily poisoned after 170 h (T_{50} from 512 to 628 °C); then it recovered the catalytic activity after 340 h, with a resulting performance better than in the fresh status (T_{50} equal 443 °C). Finally, after 500 h the catalyst resulted poisoned again, by reaching a T_{50} of 595 °C. Skeletal spectra of the fresh and 170 h aged catalysts showed carbonate species on the perovskite structure. With prolonged ageing, bulk sulphate species appeared, affecting mostly the support, namely the ceriate structure, forming Ba sulphate, due to diffusion mechanisms in the catalyst structure [2]. Pd deposition increased bulk sulphate formation during ageing with respect to the support. Prolonged ageing also leaded to the disappearance of the perovskite structure. Low temperature CO adsorption experiments allowed the characterization of Pd state. The main bands of the fresh sample spectra were assigned to CO coordinated over Pd ions highly dispersed and strongly interacting with the support and Pd metal particles [3]. Following prolonged ageing, the behavior of the catalysts significantly differed: all IR bands were strongly reduced in intensity, with a main peak likely due to CO coordinated over Pd ions [4]. Prevailing ageing mechanisms resulted in the oxidation of the surface Pd metal particles and surface-bulk sulfates formation, the latter destroying the starting crystallographic structure.

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OP-III-4

Effect of Metal-Support Interaction in Ni/ZSM-5+Al_2O_3 Catalysts on *n*-Paraffins Transformation

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Catalysts NiO(8%)/Ni,H-ZSM-5+Al_2O_3 (1:1) differing in metal-support interactions, which influenced the metal-to-acid ratios, were examined. Interactions were controlled by the method of zeolite and aluminium hydroxide combining and the method of Ni incorporation. Nickel(II) nitrate was used as a metal precursor. The catalysts were characterized by ICP, XRD, N_2 sorption, SEM, TEM, NH_3-TPD, PY-IR, TPR, H_2 chemisorption and XPS. The effect of metal-support interaction was determined during *n*-C_6 conversion in a continuous system (H_2:CH = 7:1 Nm^3/m^3, 0.1 MPa and LHSV=$1h^{-1}$).

Table 1. Catalysts under the study.

Catalyst code	ZSM-5 & Al_2O_3	NiO deposition	nNi_a/n ${}^{x}10^{2}$
A/F+I	A	F+I	4,8
A/F	A	F	1.2
E/I	E	I	2.7
E/F+I	E	F+I	3.2
E/F	E	F	1.8

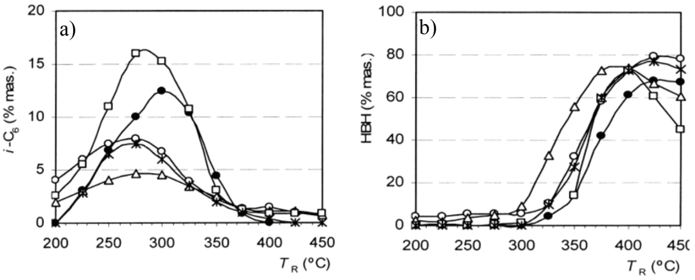

Fig. 1. Yield of *i*-C_6 (a) and HBH (b).
Catalysts: A/F+I (●), A/F (○), E/I (Δ), E/F+I (□), E/F (×)

The activity results showed that the conversion of *n*-C_6 over the all investigated catalysts was similar (not show). Over the catalysts with a larger metal to acid ratio (n_{Ni_a}/n – note: n_{Ni_a}, amount of accessible nickel atoms; *n*, amount of acid sites), where Ni was incorporated by method F+I (catalysts E/F+I and A/F+I), the yield of isomerization products was by 5–10 wt. % higher, and the yield of HBH (above *n*-C_6) by 10–30 wt.% lower than over the catalysts with a lower n_{Ni_a}/n ratio, where the whole amount of Ni was incorporated before the step of catalyst forming (F) (catalysts E/F and A/F). It can be assumed that at a larger number of Ni atoms, the isomerised carbenium ions can be hydrogenated and leave the catalyst surface prior to *β*-scission. Despite the fact that E/I catalyst is characterized by relatively high nNi_a/n ratio, the yield of isomerization product was low, while yield of HBH products was high, because dehydrogenation and cyclization of *n*-C_6 occurred over the "isolated" metal centers.

Slightly higher yield of HBH over A/F (up to 300 °C) may be due to its lower reducibility, because of strong metal-support interaction. Synergetic effect between Ni^{2+} ions (acting as Lewis sites) and Brønsted sites increases the catalyst activity in aromatization of *n*-C_6.

OP-III-5

Effect of Carbonization on Dry Methane Reforming over Ni Catalysts

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Dry methane reforming (DMR) is a promising process of the production of synthesis gas using CH_4 and CO_2 as initial reagents, and Ni-containing systems are the effective catalysts of this reaction. It is known that during the DMR reaction CH_4 decomposes on metal surface giving surface carbon, which is an intermediate in CO production, but also can be a poison of the DMR process [1, 2]. Carbonization of Ni catalysts is one the main problems of industrial application of dry methane reforming, but details of carbon state, formation and removal during DMR are still not clear. In this study, carbonization of supported Ni catalysts was investigated using thermogravimetry and mass-spectrometry. Samples containing Ni particles of different sizes were prepared and a redox thermogravimentric method for determination of Ni particle size was proposed and applied to the samples. Accumulation and removal of carbon during interactions of the catalysts with CH_4, CO_2, H_2, O_2 as well as CH_4-CO_2 mixtures were measured at temperature programmed and isothermal regimes.

It was found that accumulation of carbon proceeds in CH_4 or CH_4-CO_2 flow and the rate of C accumulation depends on Ni particle size, nature of alumina support, gas phase composition, temperature and also, in some cases, a direction of temperature variation. Minimal C accumulation was found for catalysts containing the smallest and biggest Ni particles, 2 and 30 nm, respectively. It was shown that the catalyst with the large Ni particles 30 nm, due to lower carbonization and despite of lower area of Ni surface, demonstrated the same catalytic activity as the samples with 2-5 nm Ni particles.

The rate of C accumulation in Ni/Al_2O_3 was maximal at 600-650°C. So, it was shown that a higher catalytic activity at 700°C can be observed for the catalyst, which was not preheated in the reaction mixture from the room temperature.

Experiments on removal of accumulated carbon by CO_2, H_2 and O_2 allowed to compare different states of the carbon in the catalysts. In particular, it was shown that all carbon accumulated in Ni/α-Al_2O_3 can react with CO_2 giving CO, but only part of carbon accumulated in Ni/γ-Al_2O_3 is reactive with CO_2.

This work was supported by the Russian Foundation for Basic Research (grant no 10-03-00715).

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Self-Oscillations in the Methane Oxidation on Ni: Mathematical Modelling

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Studying nonlinear dynamics of heterogeneous catalytic reactions attracts a great attention. One of the reasons is the possibility to study the reaction mechanism when the catalyst activity changes under the reaction conditions. There are many experimental data demonstrated oscillatory behaviour in the methane oxidation on Ni catalysts. The oscillations are observed of both concentrations of products and reactants and catalyst temperature under certain conditions. It is suggested that the oscillations appearance is related to the reversible oxidation of Ni to NiO.

In this work, we apply the methods of mathematical modelling to study the self-oscillations in this reaction. We consider the reaction mechanism of Langmuir type, taking into account the CH_4 dissociative adsorption that lead to formation of different CH_x species, carbon and hydrogen adsorbed on the Ni surface. Oxygen also adsorbs and dissociates on the Ni surface and then can transform into NiO. Adsorbed C, H, and O can react to form CO, CO_2, H_2, and H_2O. Reduction of the Ni surface is considered to proceed mainly via the NiO interaction with adsorbed carbon. Using the method by Shustorovich [1], we specify the activation energies as well as thermal effects of some steps corresponding to the species interactions on the metal surface. The parameter values for the other steps are taken of [2].

The developed mathematical model describes the dynamics of the concentrations of different surface species, partial pressures of methane and oxygen in the gas phase, and temperature. We show that the model predicts the oscillatory behaviour under isothermal conditions. Moreover, using the bifurcation theory and numerical methods, we specify the ranges of the inlet partial pressures and initial catalyst temperature, for which non-isothermal self-oscillations occur.

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OP-III-7

A Single Model of Oscillations in the NO+H_2 Reaction on Noble Metals

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Non-linear kinetic behavior has been revealed for numerous heterogeneous catalytic reactions. Regarding the topic, amazing phenomena of “surface explosion” followed by the sustained traveling waves were observed by Field Emission Microscopy, and regular rate oscillations at fixed experimental conditions were reported for the NO+H_2 reaction on various single crystals of noble metals [1]. Each of known mathematical models fitting experimental data has obvious shortcomings, and therefore the detailed mechanisms of spatiotemporal and reaction rate oscillations are still points for discussion [2].

The study presents the qualitative and quantitative description of oscillation phenomena in the reaction of NO+H_2 on noble metals within a single model originated from experimental and theoretical regularities in a set of transition metal surfaces. The model consists of the permanent reaction root complemented with the temporal one. The latter provides the fast removal of the adsorbed nitrogen atoms from saturated layer under certain conditions using an intermediate NH_{ad} species as a catalyst. The driving force of oscillations is a drastic difference between activity of nitrogen atom N_{ad} adsorbed at perfect terraces and at surface defects in hydrogenation reaction to form NH_{ad}. Besides that, a considerable advantage of generated NH_{ad} species over N_{ad} in the diffusion rate provides the sharpness of recurrent surface waves. The wave nucleation visually proceeds at the grain boundary.

Mathematical simulations were performed by the Euler method and revealed three kinetic region-attractors: of the steady-state rate, of sustained oscillations in partial coverage and reaction rate, and of the complete reaction inhibition by the adsorbed oxygen atoms. The regular oscillations are obtained at fixed elementary step constants within the interval of allowed values typical for the Pt(100) single crystal surface, taken for matching as the most studied. The calculated characteristics of oscillations related to the total reaction rate, the selectivity, the temperature effect, and the work function change are in complete agreement with experimental observations. No external means of the reaction rate control such as surface reconstruction, reactant diffusion or coverage dependent elementary step constants were used in simulations.

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Does the Bulk Matter? Methane and Ethylene Oxidation on Palladium

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According to the traditional understanding, heterogeneous catalytic chemical reactions occur on the surface and the reaction rate mainly depends on a surface composition and a surface structure. However, dissolution of small molecules such as hydrogen, oxygen, carbon might take place and this might result in the changes of electronic and structure property of the surface. As the consequence, catalyst behavior could change. This was demonstrated for methane and ethylene oxidation over palladium. It was found that dissolution of carbon and oxygen could change catalytic activity of palladium, leading to passivation or activation of the catalyst.

We have shown that the reaction of combustion of methane over Pd is not sensitive to the structure. This finding implies that industrial catalysts should be prepared to maximize the Pd surface area without consideration of the cluster shape. On the other hand, the reaction rate shows hysteresis behavior, which relates to palladium oxidation. It was found that the palladium oxidation is controlled by oxygen dissolution and the oxidation is triggered when super saturated solid solution of oxygen is achieved. The *in situ* XPS highlighted that appearing PdO nucleus is an active phase for methane oxidation.

A carbidic-like phase forms during ethylene oxidation through carbon dissolution in the palladium bulk. The reaction is catalyzed by both the pure metallic and the carbon modified phase, but the temperature/selectivity performance of the catalyst changes significantly. At low temperatures, the clean Pd (111) surface mainly runs the reaction of complete oxidation with a low activation barrier. However, dissolution of carbon in the bulk occurs during this stage and once the reaction is catalyzed by the new carbon-containing phase, the selectivity shifts towards CO and the activation energy increases.

Dissolution of small molecules/atoms such as carbon and oxygen can change catalytic activity of palladium, leading to passivation or activation of the catalyst. Dissolution is the important step of the reaction mechanism.

OP-III-9

In Situ X-ray Studies of Model and Real Catalysts: Bridging the Complexity Gap

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In the last decade, there was a surge in advancing synchrotron-based characterization methods to study catalytic materials. Most notable innovations include combining the X-ray absorption and scattering methods, and coupling one or both of them to vibrational spectroscopies. For example, in situ XAFS-XRD combination enables complementary studies of short and long range order in the same system, a great tool when multiple spatial dimensions evolve in a certain process, such as: modifications of both the catalyst and the support during catalytic reaction, the nucleation and growth of a nano-catalyst, oxidation/reduction of a bulk oxide. Combining in situ XAS or XRD with infrared or Raman spectroscopy is critical for understanding how the structural and electronic properties of a catalyst relate to its reactivity [1]. I will report on recent developments at the Synchrotron Catalysis Consortium (SCC) at Brookhaven National Laboratory (BNL) on combining these measurements in the same experiment for investigations Water-Gas Shift reaction catalysts.

While well-defined, *model* catalysts can be characterized by ensemble-average methods, new methodologies are sought to study *real* catalysts that possess broad compositional and structural distributions. Average methods (XAFS and XRD) are not sensitive to local fluctuations in size, shape, structure and composition of nanomaterials, and the local information, such as one provided by electron microscopy, is needed. I will present recent developments at the SCC in combining the local and average information by coupling the in situ XAFS to in situ environmental transmission electron microscopy. The use of these methods will be demonstrated on the example of supported Pt clusters that exhibited unique thermodynamic properties, such as negative thermal expansion, anomalous lattice dynamics, broad amorphous-to-crystalline transition zone, large surface strain, as well as the charge exchange with support and adsorbates. I will present recent developments that demonstrate the feasibility of conducting *in situ* and *in operando* catalytic experiments on the same system by XAS and TEM techniques using a specially designed environmental cell that is compatible both with X-ray absorption and electron microscopy probes.

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FTIR Spectroscopy in the Studies of Catalytic Reaction Mechanisms

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The paper deals with the advances in the studies of mechanisms, establishing the structure of intermediates and the nature of active sites of the reactions catalysed by oxides and zeolites using FTIR spectroscopy at variable temperatures.

Spectroscopy at low and variable temperatures broadens the number of test molecules for acid sites and besides ammonia, pyridine and nitriles, to use CO, NO, H_2 or other molecules that are not adsorbed at 300 K. Low-temperature adsorption of weak CH proton-donating molecules such as CHF_3, enables one to characterize semi-quantitatively the basicity of surface electron-donating sites. The strength of surface sites is affected by lateral interactions between the adsorbed species, which modify the catalytic properties of solids and shift the bands of test molecules, distorting the data on surface acidity.

Some diatomics, such as CO, reveal linkage isomerism and form with the cations or OH-groups in zeolites, besides the usual C-bonded complex with the frequency shifted to higher wavenumbers, the energetically unfavorable O-bonded with the frequency lowered with respect to gas phase. The latter species have the excess of energy and can be considered as an activated state, which can play a role of intermediate in catalytic reactions. Surface isomeric states were established for some other adsorbed species, such as cyanide ion CN^- produced by HCN dissociation. The linkage isomerism can be explained by an electrostatic model, which also predicts formation of side-on complexes of CO and N_2 with surface anions.

Spectra evolution with temperature provides information on the chain of reactant transformations and clarifies the mechanism of catalytic processes. This could be illustrated by surface ozone reactions, CO or thiophene isotopic scrambling over activated CaO, which occur below 200 K on the same basic sites that account for ‘carbonite’ CO_2^{2-} formation. Quantitative spectral analysis of surface sites is not possible without the knowledge of absorption coefficients of test molecules. Quantum chemical calculations and electrostatic approach predict the correlation between the frequency shifts on adsorption and the absorption coefficients, in a fair agreement with recent data on CO adsorption on ionic surfaces.

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OP-III-11

Decomposition and Oxidation of Methanol on Pt and Pd: *In situ* XPS and Mass-Spectrometry Study

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Decomposition and oxidation of methanol on Pt(111) and Pd(111) single crystals were examined between 300 and 650 K in the mbar pressure range using *in situ* X-ray photoelectron spectroscopy and temperature-programmed reaction spectroscopy. It was found that even in the oxygen presence, the methanol decomposition on both Pt and Pd proceeds through two competitive routes: fast dehydrogenation to CO and H_2 and slow decomposition of methanol via the C-O bond scission. In contrast to ultrahigh vacuum conditions, in the mbar pressure range the rate of the second route is significant, which leads to a blocking of the catalyst surface by carbon and to a prevention of the further methanol conversion [1-2]. These carbon deposits are very active toward adsorbed oxygen species and, as a result, in the presence of oxygen, fast methanol oxidation occurs at temperature above 450 K [3]. 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 methanol conversion as well as in CO_2 and H_2O selectivities. For example, a change in the O_2/MeOH molar ratio from 0 to 2 leads to an increase in methanol conversion rate (in turnover frequency, TOF) on Pt(111) at 650 K from 0.3 to 20 s^{-1}; CO selectivity decreases from 100 to 6 %. It means that the main route of methanol reforming is the methanol dehydrogenation, while in the presence of oxygen, CO is oxidized to CO_2, and H_2 is oxidized to water. According to XPS in all used conditions, Pt and Pd are in the metallic state. Using "perfect" and "defect-rich" single-crystal surfaces, we found that the methanol oxidation is a structure-sensitive reaction on Pt. In our experiments, the "defect-rich" surfaces were prepared by long Ar^+-bombardment of the "perfect" single-crystal surfaces [1]. It was found that at 550 K, the methanol conversion rate on the "defect-rich" Pt(111) surface is a few times higher than on the "perfect" Pt(111) surface. Moreover, the CO selectivity at low oxygen content is also higher on the "defect-rich" Pt(111) surface. At 650 K, these effects fade out due to annealing defects. Such effects were not observed on Pd. The mechanism of decomposition and oxidation of methanol on Pt and Pd is discussed.

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Different Carbon Species and Deactivation of Alumina Supported Cobalt Fischer-Tropsch Catalysts in Slurry Reactor

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Supported cobalt catalysts are generally preferred for synthesis of clean fuels from natural gas, coal or biomass via Fischer-Tropsch (FT) synthesis due to their high activity and selectivity to long-chain linear paraffins. Unfortunately, the catalyst activity decreases with time-on-stream. Cobalt catalyst deactivation appears to be a combination of several phenomena such as: surface reconstruction, sintering, attrition and carbon deposition. Carbon deposition seems to be one of the major deactivation mechnisms especially in long term operations [1]. Our work focuses on the identification and characterization of carbon species in cobalt catalyst, which form during FT reaction in a slurry reactor under different operating conditions and their role in catalyst deactivation. A 15 wt% Co supported catalyst on alumina carrier was prepared by incipient wetness impregnation with cobalt nitrate, then calcined and reduced. The catalytic performance was evaluated in a CSTR slurry reactor of 100 cm^3 at 20 bar, at 220°C and stirring rate of 1000 rpm with H_2/CO ratios adjusted between 1-3 and different syngas velocities (GHSV). The duration of catalytic tests was beyond 2-3 weeks. Carbon species and catalyst structure in wax-coated catalysts and after dewaxing were investigated using a wide range of techniques: XRD, TEM/SEM, XPS, TPH/TPR, XANES/EXAFS, TOF-SIMS. Cobalt oxidation was insignificant during the catalytic runs, while HAADF-TEM showed limited cobalt sintering. Temperature programmed hydrogenation coupled with mass spectrometry (TPH-MS) showed the presence of three types of carbonaceous species. XPS showed that the nature of the resilient carbons could be: (i) polymeric carbon, (ii) long chain hydrocarbon products remaining after wax extraction. The time of flight secondary ion mass spectrometry (TOF-SIMS) pointed out the presence of several hydrocarbon species probably related with remaining wax, polymeric carbon and cobalt carbides. The concentration of these species correlates with the deactivation rate and is a function of reactor operating conditions.

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OP-III-13

Heterogeneous Hydrogenation Reaction Mechanism Evaluation by Using Parahydrogen

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Parahydrogen-induced polarization (PHIP) phenomenon has become one of the very important tools for the investigation of homogeneous hydrogenation or hydrogen activation reactions mechanisms. The polarization providing by the using of parahydrogen in the catalytic hydrogenation reaction is orders of magnitude higher than thermal one, therefore due to the significant signal enhancement it is possible to study the fast reactions and identify intermediates of the catalytic reaction even that presented in the low concentration in reaction solution. Industrial catalytic processes are predominantly heterogeneous, and the studies of the nature of active sites and of the mechanisms of heterogeneous catalytic reactions represent an extremely important area of research that could benefit from the utilization of PHIP effects. In this work it was shown that it is possible to observe PHIP effects in heterogeneous hydrogenation reactions catalyzed by immobilized as well as supported metal catalysts. The PHIP effects were demonstrated for heterogeneous hydrogenation reactions carried out in both liquid and gas phases. These results constitute the direct confirmation of the mechanism of the hydrogenation reaction [1]. The observation of PHIP indicates that hydrogen addition is pairwise. A plausible explanation of the experimental results relies on the concept of static or dynamic isolation or localization of catalytic sites by various adsorbates which partition the metal surface into smaller regions [2]. The resulting hyperpolarized fluids may be successfully utilized for gas phase MRI studies of microreactor loaded with the catalyst.

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Investigation on the Kinetic Behavior of Bio-Ethanol Steam Reforming over Bimetallic Catalysts Supported on Cerium Oxide

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In the last years, ethanol has become attractive as a fuel source and a possible energy carrier within the hydrogen economy for fuel cells applications. The ethanol steam reforming (ESR) reaction seems to be a very promising method, combining the renewability of the feedstock with other advantages like the possibility to easily handle, store and transport a liquid, the non-toxicity and the absence of sulphur atoms. Prior research of ESR at high temperatures (> 400°C) has identified several metallic and oxide-based catalyst systems that improve ethanol conversion, hydrogen production, and catalyst stability [1]. At low temperatures, it can be possible to reduce the thermal duty and to enhance plant compactness. But some thermodynamic limit was the main drawback: several secondary reactions maybe promoted instead of the desired process, with the formation of coke precursors, very dangerous for the catalyst stability [2].

The objective of this paper is the choice of a catalyst with by different properties: high activity in the low temperature-ESR reaction, high selectivity towards H_2, ability to promote WGS reaction for the CO removal and to minimize coke formation, high stability. Many catalysts based on Pt, Ni and Co and supported on cerium oxide were prepared, characterized and tested, in terms of activity, selectivity and stability. The results were very interesting, since the total ethanol conversion and high H_2 yield were obtained, yet at 400°C and 240 ms. The reaction mechanism was also determined for the 3wt%Pt/10wt%Ni/CeO_2 sample. The results were in agreement with the literature [3] demonstrating that the combination of sequential reactions occurs, instead of the direct desired reaction that allows the production of 6 moles of H_2 from 1 mole of CH_4.

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OP-III-15

Mechanistic Studies on the Selective Oxidation of Acrolein to Acrylic Acid on Mo/V/W-Mixed Oxide Catalysts

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Mixed oxides based on the transition metals molybdenum, vanadium and tungsten are used for the synthesis of acrylic acid from acrolein. Due to the complexity of the catalyst structure (several phases, different oxygen species), the mechanistic details are not completely understood. Particularly the enhancement of the performance with additional water in the reactor feed needs explicit investigations. Insight into the function of water on to catalytic mechanism will be given from results obtained by transient kinetic methods (e.g. TPReactions, TPR, TPO) and especially by isotope exchange methods (SSITKA). TP-reactions on catalysts with the general formula $Mo_8V_2W_cO_x$ $(0 \leq c \leq 1.5)$ [1] with and without feed water clearly showed an enhanced activity and selectivity for the "water case". Remarkably, only the selective oxidation was significantly accelerated, but combustion of acrolein or acrylic acid remained unaffected. From H_2O-SSITKA (H216O exchanged with $H_2{}^{18}O$) it could be seen that the oxygen of the water molecule is incorporated not only into the catalyst and the oxidation products, but also into acrolein. The oxygen exchange reaction between acrolein and water can already be observed at such low temperatures, where no conversion takes place. Water induces a higher coverage of surface hydroxyl groups according to results obtained by DRIFT-spectroscopy. Therefore, the probability for the formation of intermediate acetalic species on the surface increases. Furthermore, it can be shown that in a wide range the selective oxidation is independent on the oxygen concentration, but the CO_x formation is proportional to the O_2-concentration. A deeper insight into the role of the oxygen mobility could be shown in $^{18}O_2$-SSITKA experiments [2]. Especially by performing SSITKA and modeling the results, a deeper insight into the reaction mechanism can be given. The kinetics of the selective acrolein oxidation can be achieved.

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Scorpionate Gold Complexes Anchored on Nano-Size Magnetic Silica as Hybrid Catalysts for Oxyfunctionalization of Hydrocarbons

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Oxyfunctionalization of hydrocarbons (linear alkanes) into valuable product products, *e.g.* alcohols, ketones and acids, catalyzed by supported metal complex, is a topic of a high current interest [1-3]. The use of dioxygen is also preferred from the environmental point of view. In the current context, the presented here scorpionate tris(1-pyrazolyl)ethanol gold complexes $[Au\{HOCH_2C(pz)_3\}]$ (**I**) and $[AuCl_2\{HOCH_2C(pz)_3\}]$ (**II**) have been synthesized and well characterized. These complexes were covalently bond to the surface of modified nano-size magnetic silica. These catalysts showed high catalytic efficiency in the selective oxidation of *n*-pentane and *n*-hexane with dioxygen (O_2) in batch reactor. Supported catalyst **II** exhibited high TONs (*ca.* 28×10^3 to 32×10^3) and best overall yield for both *n*-pentane and *n*-hexane as well as high product selectivity under optimized conditions. Radical traps impact and detection of intermediate peroxy radical were also investigated to establish a radical mechanism.

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OP-III-17

Catalysis of Organic Reactions with Hydrogen on Graphene Activated by the Presence of Defects and Metal Sublayer

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At present, many fundamental researches are directed to investigation of graphene due to its unique properties. In this work, an attempt has been made to divide the catalytic properties in hydrogenation reactions of transition metals and graphene in model onion-like nanocomposite systems consisting of the 4-10 nm in size particles that include metal core and graphene shell of a few layers. Such systems were prepared by modified CCVD method including levitation melting of metal wire with subsequent hot nanoparticles formation, on which graphene layer was deposited by dissociation of hydrocarbons. Ni@C, Fe@C and NiPd@C systems were prepared in this work. The structure and composition of nanocomposites were irrefragably characterized with Raman spectroscopy, HR TEM, synchronic thermal analysis (TGA, DTA, MS), Mossbauer spectroscopy, XRD, XAS.

Catalytic tests in vapor-phase continuous flow hydrodechlorination (HDC) of chlorobenzene and hydrogenation of phenylacetylene (PA) on fixed bed of Ni@C, Fe@C and NiPd@C demonstrate high conversion of substrate molecules at 150-350°C. Benzene was the only product of HDC irrespective of catalyst composition; styrene as desired product of PA hydrogenation formed on Ni@C and Fe@C. TEM investigation after repeated catalytic cycles confirms the integrity of graphene shell during catalytic tests and the absence of its destruction under the reaction conditions.

The possibility of H_2 activation on graphene shell was demonstrated by various methods. DFT calculations of pristine one and three-layer graphene and the same systems activated by metal sublayer and/or Stowne-Walls defects confirmed that activation energy was significantly reduced due to both modification types. Experimental proof is the significant catalytic activity of Fe@C composite in both reactions in mild conditions. Additional proofs of the dissociative H_2 adsorption on graphene shell were found using H-D exchange method.

This work was supported by RFBR (№ 10-03-00372, 11-03-00820-a) and Leading Scientific Schools grant НШ-2724.2012.3. Results were obtained with the help of SRCCU “Nanochemistry and Nanomaterials” of Lomonosov Moscow State University.

OP-III-18

Mechanism of Tetralin Ring Opening and Ring Contraction over Bifunctional Ir/SiO_2-Al_2O_3 Catalysts

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The development of cleaner fuels from conventional resources requires finding of new hydrotreatment processes able to improve fuel combustion performances and limit undesirable emissions. In the context of gas oil upgrading *via* selective ring opening [1], we have investigated the hydroconversion of tetralin over iridium nanoparticles supported on amorphous silica-alumina. This reaction leads to hydrogenation, ring contraction, and ring opening products. The selectivity to ring-opening/contraction products (ROCPs) increases linearly with the acid-metal site ratio, which has been tuned by modifying the support composition [2], the metal nanoparticle size [3], and the metal loading [4].

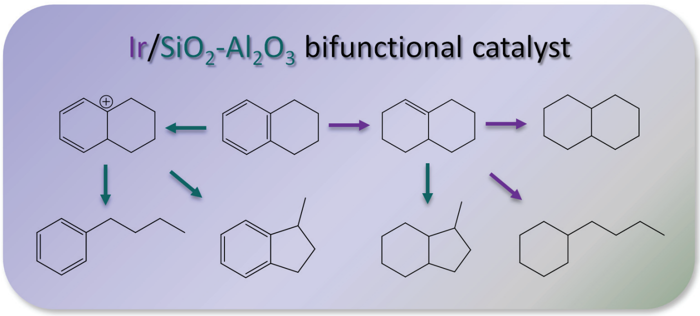

Fig. 1: Simplified scheme for catalytic hydroconversion of tetralin.
Green and violet arrows relate to acidic and metallic steps, respectively.

From the combination of catalytic tests at variable conversion and products identification by two-dimensional gas chromatography, a mechanistic reaction scheme (summarized in Fig. 1) has been established. Aromatic ROCPs are formed *via* purely acidic steps, while saturated ROCPs formation mostly involves bifunctional reaction steps. Ir-catalyzed hydrogenolysis appears to be a minor pathway with respect to Ir-catalyzed hydrogenation and Brönsted acid-catalyzed isomerization [4].

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OP-III-19

Comparative Studies of Pd, Ru, Ni and Cu Supported $ZnAl_2O_4$ Catalysts Used for Hydrogen Production from Methanol Steam Reforming

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Introduction

Intensive appreciation in prices of fuel as well as shrinking stocks of petroleum and hard coal have caused growth of interest in new source of energy [1, 2].

One of the most promising alternative fuel is hydrogen. It has the highest specific energy content of all conventional fuels being the most abundant element in the universe [3, 4].

Hydrogen can be used in fuel cells which can achieve a high electric efficiency. The total energy efficiency may even exceed 90% if the waste heat can be used [5]. Hydrogen and fuel cells are often considered as a key technology for future sustainable energy supply. In comparison to traditional methods for electric energy generation from coal, fuel cell have lower carbon dioxide emission about 40% - 60% and nitrogen oxides emission about 50% - 90%, which has significant influence on ecology.

Experimental and Discusion - The monometallic Pd, Ru, Ni and Cu (2%wt. Pd, Ru, 5% Ni, 20% Cu) catalysts supported on $ZnAl_2O_4$ were prepared by conventional impregnation methods. In order to prepare $ZnAl_2O_4$ support, zinc acetate and aluminium nitrate compounds were used. The ammonia co-precipitated mixture of zinc and aluminium hydroxides with molar ratio Zn : Al = 0.5 was dried and calcined for 4 h in air at 600 °C. The physicochemical properties of catalysts were examined by BET, XRD, XPS, TPR and TPD-NH_3 methods. Chemisorption uptakes were measured using ASAP 2020C apparatus from Micromeritics (USA). The activity tests in methanol steam reforming (SRM) and methanol decomposition were carried out over all prepared catalysts in the temperature range 160 – 320 °C in a flow quartz reactor under atmospheric pressure, molar ratio $H_2O/CH_3OH = 1$.

The formation of spinel $ZnAl_2O_4$ structure during calcination process was proved by XRD technique. Phase composition studies of monometallic catalysts supported on $ZnAl_2O_4$ spinel structure showed the appearance of appropriate oxide phases: PdO, RuO_2, CuO, $ZnAl_2O_4$ and ZnO in the case of catalysts calcined in air at 400 °C for 4 h. XRD measurements carried out for catalysts after reduction process confirmed the presence of metallic Cu, Ru, PdZn and

$ZnAl_2O_4$ phases. XRD and TPR studies confirmed the formation of $CuAl_2O_4$ spinel phase during calcination process in the case of copper catalysts. The presence of Cu^+ species on the catalysts surface after reduction in 5%H_2-95%Ar was confirmed by XPS technique for copper catalysts. Activity tests carried out for prepared monometallic Cu, Ni, Ru, Pd/$ZnAl_2O_4$ supported catalysts using impregnation method showed that all catalysts were active in methanol steam reforming reaction (SRM). The highest conversion of methanol was obtained on Cu catalyst. This result can be explained by the higher concentration of Cu^+ and Cu^0 species on the catalysts surface which are formed during reaction what confirms the redox surface mechanism. However, it is worth to note that comparison of copper to other metallic catalysts leads to conclusion that only in the case of copper catalysts carbon monoxide was not formed. However, supported palladium catalyst exhibited the best performance in hydrogen formation in comparison to remaining noble metal catalysts. From the applicability point of view, methanol steam reforming is most favorable on copper catalyst due to no CO formation and high yield of hydrogen production.

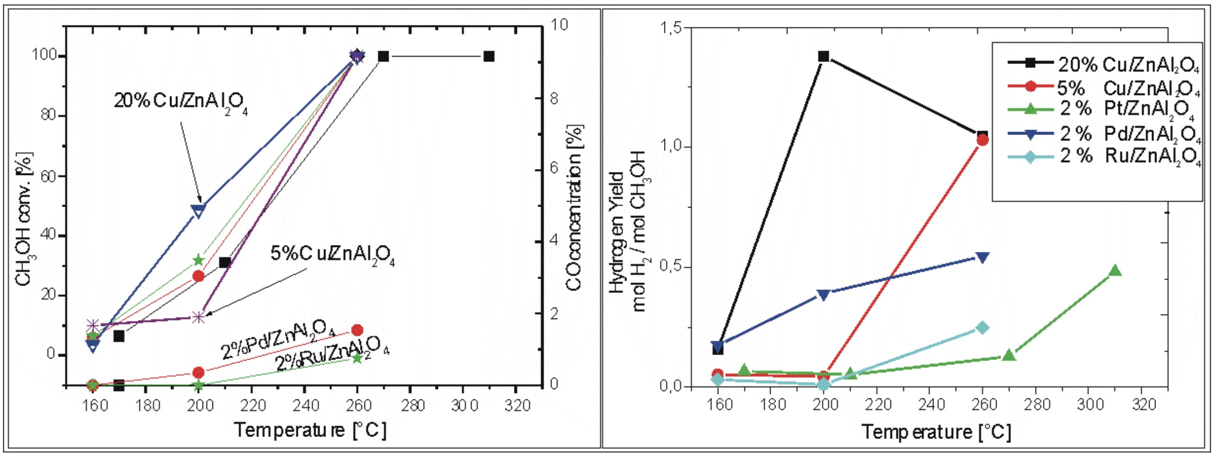

Figure 1. Methanol steam reforming over various metal catalysts calcined in air at 400°C for 4 h ($CH_3OH : H_2O = 1$).

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OP-III-20

Reactivity of Methoxy Species in the Methanol to Olefin Reactions over H-ZSM-5

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The worldwide demand for ethene and propene, building blocks for the synthetic chemicals, has increased steadily in the last decade because of the growing demand for polymer products. The methanol to olefins (MTO) process is a promising industrial route [1]. Various discussions have been made on the mechanism of the MTO reaction; one of the main discussions is devoted to the structure of hydrocarbons formed in zeolite channels, so-called "hydrocarbon pool (HCP)" [2, 3]. On the other hand, less research and discussion have been carried out on the initial C-C bond formation from the starting C_1 compound, methanol [1, 3]. MTO reactions start with the activation of methanol. The formation of methoxy species on zeolite upon exposure to methanol can be observed by infrared (IR) spectroscopy. Hunger *et al.* have recently been energetically studying the reactivity of methoxy species and claimed that methoxy groups are active species [4]. Here we closely investigated the reactivity of methoxy species on H-ZSM-5 by IR spectroscopy using isotopes [5]. The methoxy groups were supposed to migrate in the form of methyl cations in a similar manner to the motion of protons of acidic OH groups. However, we have found that the methyl carbenium cation mechanism is not applicable. The presence of carbene-like intermediate is the most likely; this reaction probably proceeds in a concerted manner.

We have also found that the reaction of methoxy species with DME is faster than that with ethane or methanol. Methoxy species react with DME directly to form propene. Furthermore, it is implied that the initial hydrocarbon product in the MTO reaction is propene. Detailed investigations into the mechanism of the initial reactions are now in progress.

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Dechlorination of Chlorohydrocarbons on Bulk Ni-Alloyed Catalysts: Mechanism of Carbon "Corrosion"

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Heterogeneous gas-phase dechlorination of chlorinated hydrocarbons into valuable chemical products (olefins [1] or carbon nanofibers – CNF [2]) is considered to be a prospective way for abatement of hazardous organochlorine wastes. Unlike other methods, including thermal oxidation, dechlorination doesn't lead to formation of secondary polluting substances, even more dangerous. Catalytic decomposition of chlorinated organic compounds usually results in formation of aggressive environment that requires the using of catalysts possessing the enhanced stability towards possible chlorination of metal particles. In this case the catalyst deactivation could be prevented by carrying out the process at temperatures above 500°C in the presence of hydrogen in reaction gas feed.

As we have recently reported [2], the catalytic particles (acting as sites for CNF growth) characterized with an optimal chemical composition and size can be spontaneously generated in situ during the decomposition of chlorohydrocarbons on bulk Ni-based alloys used as precursors. The interaction mechanism resulting in formation of high-performance self-organizing catalyst is of a great interest. The process is schematically shown below.

$$C_xH_yCl_z + NiCr \rightarrow \boxed{\begin{array}{c} NiCr + 2HCl \rightarrow Ni\text{-}Cl + Cr\text{-}Cl + H_2 \\ Ni\text{-}Cl + H_2 \leftrightarrow Ni\text{-}H + HCl \end{array}} \rightarrow Ni\text{-}CNF + Cr + HCl$$

Fig. 1. Proposed scheme of catalytic destruction of chlorinated hydrocarbons on surface of bulk NiCr alloy

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OP-III-22

Dehydration of Glycerol over Heteropoly Acid Supported Mesoporous Silica

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Various solid acid catalysts including metal oxides [1-3], mixed metal oxides, sulphates, phosphates and zeolites have been employed for the dehydration of glycerol. However, one of the main disadvantages of these catalysts lies in the formation of a large amount of by-products and the catalyst deactivation. On the other hand, heteropoly acids are strong Bronsted acids with tunable acidity but they lack thermal stability and have low specific surface area. In order to improve such problems, heteropoly acids are often supported over acidic carriers [4-6] like silica, alumina, titania and zirconia. Among the various heteropoly acids, silicotungstic acid (H-SW) is moderately strong acid with high water tolerant ability [4,6]. In this investigation, periodic mesoporous silica supported heteropoly acid catalysts were used for the dehydration of glycerol to acrolein. Among the different loading, 30 wt.% heteropoly acid supported SBA-15 was found to show better activity in terms of glycerol conversion (> 99%) and acrolein selectivity (~ 95%) at 275°C.

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Application of Model Systems for XPS Studies of the Mechanism of Interaction of Supported Metal Catalysts with Gaseous Reaction Media

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X-ray photoelectron spectroscopy (XPS) is extensively used in the field of heterogeneous catalysis for ascertainment of the nature of active sites as well as for studies the interaction of active components with supports and catalysts with reaction media. However, application of XPS method in characterization of commercial catalysts used for neutralization of noxious substances in the automotive exhaust is frequently problematic due to a low concentration of the active components that are normally platinum group metals (PGM) dispersed in a porous supporting material. An efficient way to tackle the problem is to study model objects of the chemical composition identical to that of commercial catalysts. With the model catalysts prepared in the form of thin oxide films supporting metal particles, most of the particles concentrate on the outer surface of the support and, hence, are accessible for XPS analysis.

This report presents a review of studies performed by the authors on supported platinum group metals (PGM) and gold model catalysts. The model samples were prepared in a preparation chamber of VG ESCA-3 spectrometer in the form of an oxide film (Al_2O_3, Fe_2O_3, SiO_2 and others) of ~ 100 Å in thickness grown in vacuum conditions on a substrate made of a Ta foil with following evaporation of Rh, Pd, Pt or Au on the surface of the oxide film. The average size of the evaporated metal particles was evaluated in TEM studies of model samples prepared similarly on carbon film substrates; depending on the preparation conditions, the size was varied from 2 to 10 nm. The treatment of the model catalysts in gaseous media were performed in the preparation chamber at pressures from 10^{-6} to 20 mbar and temperatures between 30 and 800°C. With no exposure to the atmosphere, the treated samples were transferred into an analyzer chamber for spectra registration. The composition of the samples and treatment conditions were as close as possible to conditions of the practical catalysis. The results obtained under studies of the reactions of the model catalysts with the following gaseous mixtures - NO_x ($NO+O_2$), SO_x (SO_2+O_2), $CO+O_2$ – are discussed in the report.

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OP-III-24

Catalytic Purification of Exhaust Gases over Pd-Rh Alloy Catalysts: From Mechanism Understanding to High Temperature Stability

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Reducing air pollution nowadays is of the utmost importance. It is known that the mobile pollution sources (primarily motor cars) are responsible for about 60 % of total carbon monoxide releasing in the atmosphere. Exhaust gases normally contain volatile organic compounds, CO, nitric oxides and unburned hydrocarbons in various concentrations which are to be determined by the engine type. Gasoline engine exhausts can be converted to harmless nonpollutants via using heterogeneous three way catalysts (so-called TWC) in which the platinum group metals play the role of active component. The mechanism of neutralization process is rather complicated and includes a large number of elementary reactions proceeding at the same time. Understanding of mechanism is believed to be important for creation of new generation of high-performance and cost-effective catalysts.

The principle problem of catalytic converters lies in their deactivation at the evaluated temperatures. As we reported earlier [1], the rhodium (responsible for NO_x reduction) can readily diffuse from a surface inside the bulk of support (Al_2O_3) therefore initiating the phase transformation of latter into α-Al_2O_3 where Rh ions become irreversibly encapsulated. The high-T treatment of disperse Pd particles (essential for oxidation of CO and hydrocarbons) results in their significant sintering that explains the loss of activity [2]. This work concerns development of stable bimetallic catalysts based on improved action of Rh-Pd alloys.

Financial support by Russian Foundation for Basic Research (Grant 11-03-00668) is acknowledged with gratitude.

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Ce-O-Pt Active Sites in Ceria Promoted NO_x Storage Reduction Catalysis

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The NO_x emissions from automobile exhausts have serious destructive effects on the global ecosystem as well as on the human health. NO_x storage/reduction (NSR) catalysts which are used for NO_x abatement in the absence of additional reducing agents such as poly-urea are composed of precious metal nanoparticles which act as redox centres, a high surface area support material (γ-Al_2O_3) and a NO_x storage component (BaO) that interacts with NO_x in the oxidizing conditions forming nitrates and decompose under the reducing conditions releasing harmless N_2 and H_2O [1,2]. Ceria promotion leads to a significant improvement in a wide range of catalytic processes, including NSR catalysis, owing to its high oxygen storage and oxygen transport capacity [1,3]. In the current work, we investigated the nitration and the subsequent NO_x reduction by H_2 over ceria promoted NSR model catalysts ($Pt/CeO_2/Al_2O_3$ and $BaO/Pt/CeO_2/Al_2O_3$) by means of in-situ FTIR. The ceria promotion was found to facilitate the nitrate reduction process. Characterization of the synthesized catalysts by XRD, BET, XPS and Raman spectroscopy revealed the existence of a strong Pt – ceria interaction and the formation of Pt-O-Ce anchoring sites that may be responsible for the higher stability and the dispersion of Pt sites. The enhanced NO_x reduction efficiency of ceria promoted NSR catalysts can be explained by the presence of Pt-O-Ce sites operating as oxygen transport centers facilitating the oxygen transfer between the nitrate species adsorbed on the CeO_2/BaO sites and the Pt sites activating H_2. A plausible NO_x reduction mechanism is proposed in the light of the current structural characterization and in-situ spectroscopic results.

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OP-III-26

Influence of the Hydrogen Source in the Mechanism of Glycerol Hydrogenolysis to 1,2-Propanediol

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Bio-glycerol obtained as a byproduct in biodiesel production through the transesterification of vegetable oil will become a key building block in future bio-refineries. One of the most interesting routes for the valorization of glycerol is the hydrogenolysis process that leads to the formation of 1,2-propanediol (1,2-PDO). 1,2-PDO is widely used as antifreeze, or humectant in paints and cosmetics. Hydrogenolysis involves chemical bond dissociation in an organic substrate and simultaneous addition of hydrogen to the resulting molecular fragments [1]. If the process is carried out in liquid phase, high molecular hydrogen pressures are required due to the low solubility of hydrogen in aqueous organic solutions. The use of hydrogen donor molecules to generate the necessary active hydrogen species directly in the active sites of the catalysts is a promising alternative that allows working under inert atmosphere.

In this work, the effect that the source of hydrogen (molecular hydrogen or hydrogen donor molecules) has on the glycerol hydrogenolysis mechanism was studied over a sol-gel prepared Ni-Cu/Al_2O_3 catalyst. Under H_2 pressure and using bi-functional metal-acid catalysts, the most accepted mechanism in the literature consists of an initial dehydration of glycerol to acetol in the acid sites and a subsequent hydrogenation of acetol to 1,2-PDO in the metal sites [2]. Both 2-propanol and formic acid showed to be really efficient hydrogen donor molecules for glycerol hydrogenolysis, and yields similar to those obtained under H_2 pressure were reported. When acetol was used as reactant, it was readily and selectivity converted to 1,2-PDO under H_2 pressure. Nevertheless, when the source of hydrogen was formic acid or 2-propanol, negligible yields to 1,2-PDO were achieved. This clearly indicated that there are different mechanisms involved in glycerol hydrogenolysis regarding the origin of the active hydrogen species. Activity test results and deep catalyst characterization allowed propounding a direct hydrogenolysis mechanism through intermediate alkoxide formation, and to understand the role of Ni, Cu and acid sites of the Al_2O_3 support.

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Structure of Allylic Intermediates Formed from Olefins on Zinc Oxide

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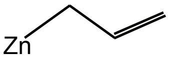
Zinc oxide is active catalyst for olefin double bond isomerization. π-Allylzinc is generally considered to be the main intermediate of the process [1–3]. However, a number of different bonding modes are possible for allyl ligand attached to zinc in zinc allyl compounds [4]: σ-allyl (**1**), σ,π-allyl (**2**), π-allyl (**3**). σ-Allylzinc was found to be intermediate of propane aromatization process on ZnO-modified zeolite beta [5]. Thus, the question arises on the structure of intermediates formed from olefins on zinc oxide. Understanding the structure of surface intermediates is the key to reveal the mechanism of the isomerization process.

1



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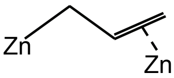

3

To inquire into the structure of the surface allylzinc, the interaction of propene and *n*-butene with zinc oxide has been monitored by ^{13}C solid-state NMR spectroscopy. The data obtained clearly prove that the surface allylzinc exists in a form of σ,π-allyl rather than exclusively π-allyl complex. Dissociative adsorption of propene on zinc oxide results in formation of two equilibrium structures: σ,π-allyl and π-allyl, the former being a prevailing species (Figure 1). On the other hand, only σ,π-allyl was detected in case of *n*-butene adsorption.

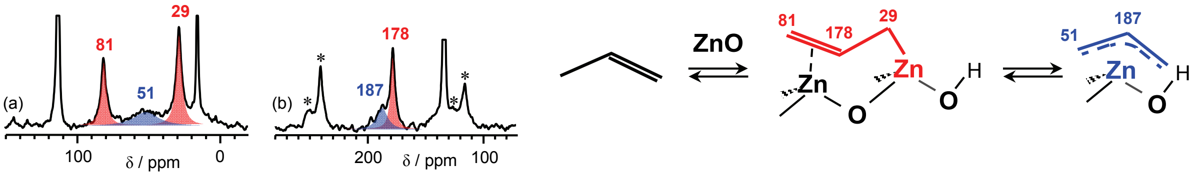

Figure 1. ^{13}C MAS NMR spectra of propene-*3*-^{13}C (a) and propene-*2*-^{13}C (b) on ZnO.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (grant no. 10-03-00555).

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OP-III-28

Mechanism of Low-Temperature Carbon Monoxide Oxidation over $PdCl_2$-$CuCl_2/\gamma$-Al_2O_3 Catalyst

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This report deals with new data on the state of active components on the surface of the $PdCl_2$-$CuCl_2/\gamma$-Al_2O_3 catalyst and the mechanism of the low-temperature oxidation of carbon monooxide. The structure of freshly prepared $PdCl_2$-$CuCl_2/\gamma$-Al_2O_3 catalyst was studied by physical metods (XAS, XRD, SEM, DRIFTS) [1]. It was shown that copper and palladium exist on the surface of γ-Al_2O_3 in the forms of crystalline of $Cu_2Cl(OH)_3$ (paratacamite) and chemisorbed mononuclear $PdCl_4^{2-}$ anions, respectively. DRIFTS spectra indicate that both linear (2114 cm^{-1}) and bridging (1990 and 1928 cm^{-1}) coordinated carbon monooxide emerge upon CO adsorption on the catalyst surface.

The kinetic regularities were studied at 18-40°C and atmospheric pressure of CO, O_2, N_2, H_2O(gas) mixture in a flow reactor (steady state conditions). The activation energy of the reaction was found to be negative (-40 kJ/mole*K). The empirically derived equation for the rate of carbon dioxide formation is presented below (1).

$$r_{CO_2} = kP_{CO}^{0.2}P_{H_2O}^{1.7}P_{O_2}^{0.8} \qquad (1)$$

The high kinetic orders for water and oxygen partial pressures allowed us to propose mechanisms with the participation of both (O_2 and H_2O) reagents in steps of carbon dioxide formation.

Alternative mechanisms of this reaction are discussed.

Acknowledgements. This work was supported by the Government of Moscow (Russia) and the Russian Foundation for Basic research (project nos. 11-03-00118 and 11-03-00820) and state contract no. 16.552.11.7003.

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OP-III-29

Enantioselective Hydrogenation of Activated Ketones in the Presence of Pt-Cinchona Catalysts. Is the Proton Transfer Concept Valid?

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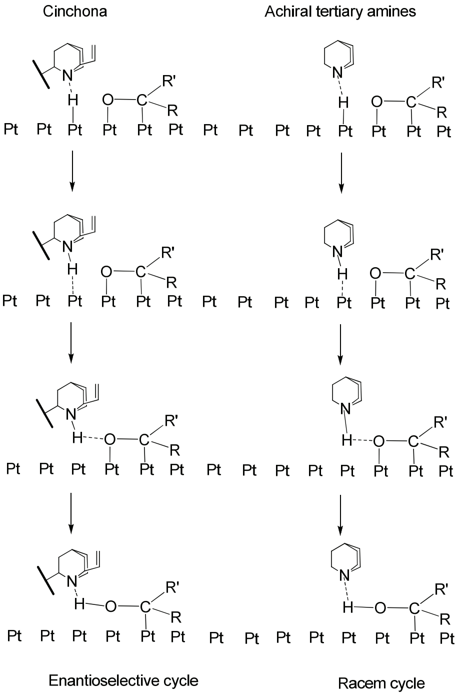
In this contribution we express our view and supporting experimental data related to the proposed hydrogen (proton) transfer [1,2], in the catalytic system Pt-cinchona alkaloids used in the enantioselective hydrogenation of activated ketones (α-ketoesters). We suggest that this scheme [1,2] does not work. Our doubts related to the scheme given in refs. [1,2] are based on various experimental facts. If we assume that the quinuclidine nitrogen in CD can perform the hydrogen transfer as described in refs. [1,2] in this case other tertiary amines have to accomplish similar job, *i.e.* they should be able to transfer hydrogen from the Pt site to the prochiral substrate. Consequently, the proton transfer should be an intrinsic property of tertiary amines. The rate acceleration observed both in the presence of cinchona alkaloids and different achiral tertiary amines [3] can be considered as a basis for this assumption. Therefore, if other tertiary amines can be involved in the above hydrogen transfer, the addition of tertiary nitrogen compounds to the reaction mixture containing CD should decrease the enantioselectivity, as in this case two catalytic cycles will operate simultaneously as shown in the scheme. However, we observed just an opposite effect. Our results clearly demonstrated that in the presence of achiral tertiary amine additives, no decrease of the enantioselectivity was found upon using ethyl pyruvate, 2,3-butanedione, 4,6-hexanedione and methylbenzoyl formate. In all cases substantial increase of *ee* and reaction rates was observed. Among the tertiary amines quinuclidine and 1,4-diazabicyclo-[2.2.2]octane provided the highest increase in the reaction rate and *ee* values. *Accordingly, the lack of the negative effect of tertiary amine additives used in the enantioselective hydrogenation of four different substrates suggests that the proton transfer mechanism is not adequate. This mechanism should be revised.*



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OP-III-30

Mechanistic and Kinetic Studies of Aromatic Carbon-Carbon Coupling (Suzuki Reaction) with Heterogeneous Catalysts

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Suzuki coupling is often a crucial step in the synthesis of many molecules like pharmaceuticals, liquid crystals, organic conductive materials and semi-conductors [1]. Indeed, this reaction allows the combination of aryl halides with aryl boronic acids to form biaryls in the presence of a Pd-based catalyst and a base. The knowledge about the Suzuki coupling mechanism with heterogeneous catalysts is relatively limited. Actually, current research leads to contradictory results which bring to a blurred situation [2]. Is it a real heterogeneous catalysis or does the active metal (Pd) have to be leached from the supports in order to perform the reaction? Furthermore, the nature of the active Pd oxidation state (Pd^{2+} and/or Pd^0) has not yet been well elucidated and investigations on this subject lead to conflicting conclusions [2]. In this context, better understanding of the Suzuki coupling would allow to improve the catalytic performances of this important and useful reaction for the construction of carbon-carbon bonds.

A methodical study of different parameters of the reaction and the catalyst, namely palladium supported on carbon black, has permitted to determine that the Pd is not leached from the carbon support. So, it is a real heterogeneous catalysis. Furthermore, the oxidation state of the active Pd species is +II. The reduced form is not active.

An experimental reaction rate expression has then been determined by varying the concentration of the reactants (4-bromotoluene, phenylboronic acid and the base (K_2CO_3)) and the reaction temperature. A theoretical rate expression has been also determined by making assumptions of the reaction pathway with a heterogeneous catalyst. The catalytic cycle is divided into 7 elementary steps. By comparing the experimental and theoretical expressions, we were able to identify that the rate limiting step of the Suzuki coupling is the transmetallation of the phenylboronic acid on an intermediate species formed by the adsorption of 4-bromotoluene onto the Pd. So, for improving the catalytic performances of the Suzuki reaction with heterogeneous catalysts, the rate of the transmetallation step has to be increased.

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On Mechanisms of Oxidation of 1,3-Butadiene on Pd-Te Catalysts in Polar Solvents

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Apart from high reactivity and wide use in polymerization, 1,3-butadiene (BD) is a convenient feedstock for obtaining variable oxygenates, such as epoxybutene, maleic anhydride, furan, 1,4-diacetoxy-2-butene. Liquid-phase oxidations of BD follow three typical mechanisms: (1) oxygenation directed to one of double bonds, (2) concert oxidative addition to 1,4-positions , and (3) radical chain mechanism. It has been shown that Pd-Te catalysts are able to participate in each single type of these reactions in appropriate solvent and conditions.

Adsorption of oxygen on well-reduced Pd-Te/C catalysts resulted in electron transfer from Pd^0 and formation of surface reactive species capable of oxidizing BD. Suspended in a polar organic solvent, the Pd-Te catalyst gave rise to formation of methyl vinyl ketone, furan and croton aldehyde, the last compound being also produced on pure supported Pd. Water was necessary for the oxidation to proceed, and acid additives accelerated oxidation with preferable formation of furan.

Stabilization of intermediate and final products are required to realize oxidative 1,4-addition to BD. 1,4-Diacetoxy-2-butene is produced on Pd-Te catalysts in acetic acid [1]. We observed formation of 1,4-dimetoxy-2-butene from BD in methyl alcohol. Application of silica support, instead of carbon, or addition of sulfuric acid to solvent gave positive effect on ether production. Optimal temperature, water and acid additives appeared sufficient for conversion of BD predominantly to 1,4-dimetoxy-2-butene and allenic alcohol methyl ether.

At a large BD loading, radical chain process is developed to form peroxides and finally 1,2- and 1,4-butenedions together with numerous secondary products. The Pd-Te/C catalyst introduced some changes into the product composition increasing portion of 1,4-oxygenates in the products.

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OP-III-32

Solid State Isotope Exchange with Spillover Hydrogen in Organic Compounds

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This report summarizes data on the theoretical and experimental investigation of high temperature solid state catalytic isotope exchange (HSCIE) that takes place in organic compounds under the action of spillover hydrogen (SH) [1]. The HSCIE reaction has been shown to proceed on Brendsted-type acidic centers formed under the action of SH. The new one-center synchronous mechanism of hydrogen substitution in organic compounds has been studied. Analysis of the kinetic isotopic effects of the HSCIE reaction were conducted for the first time. The dependence of the reaction' s activation energy on the parameters of acidic centers type $H^+(H_2O)_n$ was established. It was shown that the kinetic isotopic effect of solid state reaction of hydrogen exchange with SH is 1.2 – 1.4, which is several times lower than that of liquid state reactions of protium and deuterium transfer (equal to 3 to 30). Good agreement was observed between our experimental data and the results of quantum chemical measurements of hydrogen exchange on model acidic centers type $H^+(H_2O)_n$. By using the HSCIE reaction, highly deuterium- and tritium-labeled histamine and melatonine with a 70-95% degree of substitution of all C-H bonds were produced. By reaction HSCIE we obtained deuterium-labeled octapeptide bradikinin with 7 atoms of deuterium and labeled hexapeptide dalargin with 14 atoms of deuterium. The HSCIE reaction proceeds in the virtually complete absence of racemization, that makes this reaction a valuable preparative method of the production of evenly tritium or deuterium labeled organic compounds. Complexes of deuterium-labeled histamine with transition metals were obtained, and isotope effects in these complexes were studied by electron spectroscopy. Theoretical assessment of isotopic effect by the electron spectroscopy of the complexes of deuterium-labeled histamines with metals was performed using RB3LYP/LanL2DZ and CIS/LanL2DZ. As for the complexes of histamine with platinum and copper, the isotopic effect in UV-absorption spectra was 1600 and 1800 cal/mol, respectively.

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Kinetic Study of Aspen-Wood Delignification by H_2O_2 with Sulfuric Acid Catalyst under Mild Conditions

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Previously, it was shown that a significant intensification of oxidative delignification of wood by H_2O_2 in acetic acid–water medium at 120–130 °C and increased pressure takes place in the presence of sulfuric acid catalyst (SAC) [1]. The present communication describes the results of kinetic study of a "green" process of aspen-wood oxidative delignification by H_2O_2 with SAC under mild conditions: temperature less 100 °C, atmospheric pressure.

Kinetics of wood delignification process was investigated at variation of temperature (70–98.5 °C), concentration of H_2O_2 (2–6 wt%), acetic acid (15–40 wt%), H_2SO_4 (1 wt%), liquor ratio (5–15), time (1–4 h). The increase of temperature, concentrations of H_2O_2 and acetic acid, liquor ratio (LR) and time results in the acceleration of the rate of delignification process. Cellulose obtained under the optimal conditions (98.5 °C, H_2O_2 4 wt %, CH_3COOH 25 wt%, H_2SO_4 1 wt%, LR 10, 4 h) contains only 0.6 wt% of residual lignin. The decomposition of hemicelluloses and amorphous part of cellulose is also intensified at these process parameters. The time dependence of residual lignin content in cellulosic product and concentration of dissolved LMML corresponds to first order equation. Rate constants of aspen-wood delignification process vary from $0.25 \cdot 10^{-4}$ c^{-1} (70 °C) to $2.5 \cdot 10^{-4}$ c^{-1} (98.5 °C). The activation energy of aspen-wood delignification is 90.9 (±13.0) kJ/mol. This value points that delignification process goes predominantly in kinetic region.

The possible mechanism of wood delignification in the medium "acetic acid – H_2O_2–water–SAC" is discussed. Some dependences between the delignification process parameters and reaction ability of main wood components (lignin, hemicelluloses, cellulose) and products of their oxidative and hydrolytic depolymerization are established. Optimal conditions of aspen-wood delignification were selected which allow to obtain by "green" method at atmospheric pressure the cellulosic products with a variable content of residual lignin, hemicelluloses, amorphous and crystalline cellulose.

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OP-IV-2

Deoxygenation of Biomass-Derived Molecules over Multifunctional Polyoxometalate Catalysts in the Gas Phase

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Biomass-derived oxygenates are attractive as renewable raw materials for the production of value-added chemicals and biofuel components. For fuel applications, they require reduction in their oxygen content, i.e., deoxygenation. Here we discuss various reaction pathways of (hydro)deoxygenation of carboxylic acids and ketones in the gas phase over multifunctional catalysts based on polyoxometalates (POMs). Among the substrates are C3-C6 carboxylic acids, representing the carboxylic acids derived from carbohydrate feedctocks, and methylisobutyl and diisobutyl ketones (MIBK and DIBK) obtained by condensation of acetone, the byproduct of biobutanol production. The catalysts and catalyst precursors under study involve bulk and supported Keggin-type POMs comprising P-Mo, P-Mo-V and P-W polyanions. Their acid properties are modified by Cs^+-for-H^+ substitution and a metal functionality is provided by doping with Pd, Pt, Ru and Cu. Deoxygenation/hydrodeoxygenation reaction pathways, such as ketonisation, decarboxylation, decarbonylation and hydrogenation for carboxylic acids and hydrogenation and hydrogenation/dehydration for ketones, are identified and related to metal-acid multifunctional catalysis.

Unravelling the Structure and Reactivity of Supported Ni Particles in Ni-$CeZrO_2$ Catalysts

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The growing request for the development and diffusion of technologies based on renewable energy sources represents an important challenge for researchers working in catalysis. When coupled to water gas shift reaction, steam reforming of methane (MSR) can be employed to produce hydromethane (a mixture of hydrogen and methane) after CO_2 removal. If the temperature of the process is lowered by employing a proper catalyst, a low green-house impact fuel (which could be employed to power hybrid automotive systems) can be produced in solar powered plants, based on molten salt technology [1].

One of the most promising catalysts for low temperature MSR is based on Ni-$CeZrO_2$ mixed oxide [2], where the $CeZrO_2$ support is supposed to play an important role in stabilizing the active phase towards sintering and coke formation [3]. Thus, Ni-$CeZrO_2$ represents a challenging system for surface studies, due to the complex reactivity of both the support and the supported active phase, with particular interest in their interaction.

In this work, a one step co-precipitation/digestion method [2] was optimized to prepare a series of Ni-Ce-ZrO_2 catalysts with various Ni loading and Ce/Zr ratios, high Specific Surface Area and good metal dispersion. The structural (XRD, HRTEM) and surface properties of the samples were characterized (FTIR of adsorbed CO). Their reactivity and stability was tested in MSR reaction at 520 °C, varying steam to carbon ratio and spatial velocity, in order to obtain kinetic values for a possible upscale of the process. The results suggest good performances of the catalysts and an important effect of the support on the Ni phase performance.

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OP-IV-4

Ketonization of Valeric Acid over Metal Oxides as a First Step for Green Diesel Synthesis: Consideration from Mechanistic Viewpoint

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To produce green diesel fuel from renewable organic materials such as carboxylic acids, obtained via aqueous phase reforming of sugars and sugar alcohols, ketonization [1] followed by deoxygenation of formed ketone can be applied. Ketonization is bimolecular reaction in which two acid molecules are converted into ketone, carbon dioxide and water. The benefit of the process is safety for environment because non-polluting by-products are formed. In the current work, conversion of valeric acid into symmetrical ketone 5-nonanone has been studied over various metal oxides such as ZrO_2, CeO_2, MgO, Al_2O_3, CeO_2/ZrO_2, MnO_2/ZrO_2, CeO_2/Al_2O_3 at T= 573÷673 K under P_{H_2}=1 bar in fixed bed reactor. Before the reaction, the catalyst was heated in carrier gas stream to reaction temperature. Then pure valeric acid was fed using a syringe pump and after a certain period of time the condensable products were collected in the trap cooled with liquid nitrogen. In the case of catalytic stability tests, reaction products were analyzed every 2 hours.

The effects of temperature, residence time, nature of carrier gas on the conversion and selectivity toward the desired ketone was investigated. Selectivity toward 5-nonanone of 94% at complete conversion of valeric acid was observed over the most active ZrO_2 at 628 K. Methods of TEM, XRD, BET by Ar adsorption and XPS were applied to elucidate correlation between ketonization activity and structure as well as surface properties of the catalyst's active component. Here, we discuss possible reaction mechanism involving formation of β-keto acid intermediate [2]. First, surface carboxylates are formed, and then α-hydrogen atom is abstracted to form an anion radical which interacts with another carboxylate to give β-keto acid followed by decarboxylation to form a ketone. According to this consideration, the ratio between Lewis acid (M^{x+}) and base (O^{-2}, OH^-) sites provides catalytic activity of the metal oxides. The most active catalysts ZrO_2 and CeO_2/ZrO_2 seem to possess the optimal ratio and strength of acidic and basic surface sites.

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Selective Oxidation of Glycerol Using Au/ZrO_2 as Catalyst

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We present here a comprehensive study on the catalytic performance of Au/ZrO_2 [1,2] for glycerol (GL) oxidation in aqueous solution containing varying amounts of NaOH and discuss the reaction mechanism on the basis of detailed quantitative analyses of the product selectivity in response to the reaction variables including temperature (0−80 ºC), molar NaOH/GL ratio (0−15), oxygen pressure (P_{O_2}= 0.1−2.5 MPa) and duration of reaction.

A nanocomposite 1 wt% Au/ZrO_2 catalyst (Au: 2−4 nm, ZrO_2: 6−10 nm) was prepared [3] for this study using a batch reactor. We confirmed no reaction in the absence of the base (NaOH/GL = 0) under the most commonly used temperature (60 ºC) and P_{O_2} (1.0 MPa). Increasing the ratio up to NaOH/GL= 10 resulted in increases in both the conversion of GL and the selectivity for glyceric acid (GLA) though the increase in the GLA selectivity was less significant (57−60% on carbon calibration) at NaOH/GL= 2−10. However, a further increase of the ratio to NaOH/GL = 15 even led to much lower GL conversion. Formation of lactic acid (LA) kept on increasing at NaOH/GL > 0.1 though it was not detected in the reaction with lower NaOH/GL ratios. Significant amounts of the non-C3 products, glycolic acid (GCA), formic acid (FA) and acetic acid (AC), were formed at NaOH/GL ≤ 0.1, they all decreased in the reaction with higher NaOH/GL ratios. The oxygen pressure (P_{O_2}) had a remarkable effect on GL reactivity and product distribution. The selectivity for LA was as high as 58% at P_{O_2}= 0.1 MPa (60 ºC, NaOH/GL= 2) with a GL conversion of ca. 3% and GLA selectivity of 29%. The LA selectivity decreased to 21% but the GLA selectivity increased to 54% at P_{O_2}= 0.2 MPa. The GL conversion was retained upon raising the pressure up to P_{O_2}= 2.5 MPa but the GLA selectivity became stabilized at 60−63% at $P_{O_2} \geq 1$ MPa. The GCA, FA and AC products varied in the opposite to LA.

On lowering the reaction temperature to 0−20 ºC, GLA, FA, GCA and AC were detected as the products when the GL conversion was < 5%; the C1 product FA appeared as the main product (> 40%) at 0 ºC, far more than the C2 product (GCA + AC: < 20%), when less than 1% GL was converted. The selectivity for GLA increased while that for GCA and FA decreased when the temperature was increased from 20 to 80 ºC; LA was not formed below

20 ºC but its selectivity increased to 20% at 80 ºC. Glyceraldehyde (GLAD), which was assumed as the key intermediate in GL oxidation over the gold catalysts in literature, has been never detected in this work.

In order to avoid water involvement, we also conducted the oxidation of GL in methanol. This non-aqueous reaction (20−80 ºC, P_{O_2}= 1.0 Mpa, NaOH/GL= 2) always produced FA (45−75%) and GCA (20−30%) as the main products, making GLA a minor product (0−35%). These present data will be compared with those in literature for other gold catalysts to highlight the feature of Au/ZrO_2 catalyst. Mechanistic issues involved in the oxidative GL activation and competitiveness of the C−C breaking reactions in the oxidation of GL will also be addressed.

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Controlled Synthesis of Pt_3Sn/C Electrocatalysts with Exclusive Sn-Pt Interaction Designed for Use in Direct Methanol Fuel Cells

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High resistance to CO is one of the criteria for the preparation of efficient alcohol electrooxidation catalysts. Pt-Sn bulk alloys are among the most studied bimetallic systems for fuel cell application [1]. Exclusive formation of supported Sn-Pt alloy phases with different Sn/Pt ratios can be achieved by using Controlled Surface Reactions (CSRs) between hydrogen adsorbed on Pt sites and tetraethyltin [2]. The presence of Sn decreases not only the total number of exposed Pt atoms but also the number of extended Pt ensembles, required on the early stages of the methanol oxidation for methanol adsorption-dehydrogenation reaction. The possibility to find such Pt ensembles decreases with the increasing Sn/Pt ratio. In good accordance with this, in our recent study, it was demonstrated [3] that the performance of Pt_3Sn (fcc) phase is superior to that of the PtSn (hcp) phase for both CO and methanol electrooxidation reactions. Nevertheless, the promotional effect of Sn for the electrooxidation of CO_{ad} is to provide the necessary OH_{ad} species at less positive potentials than on Pt.

Efforts were made to adjust synthesis parameters in order to prepare carbon supported Pt_3Sn (fcc) alloy phase exclusively. As demonstrated by X-ray diffraction, the amount of the Pt_3Sn phase can be controlled by tuning the conditions of CSRs. Results of XPS after in situ treatment in H_2 at 350°C showed that the modification of Pt/C catalyst with $Sn(C_2H_5)_4$ leads to exclusive formation of Sn-Pt alloy phase without tin introduction onto the carbon support. Thus, the bimetallic catalysts prepared displayed an outstanding performance in both the CO and methanol electrooxidation reactions. Upon addition of tin, the onset potential of CO oxidation was shifted by 500 mV to more negative potentials, which indicate significant improvement in CO-resistance of tin-modified sample in comparison to the Pt/C catalyst.

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OP-V-2

Reaction Mechanism of Selective Oxidation of Alcohols and Amines over Semiconductor Photocatalysts

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Recently, we found that niobium oxide (Nb_2O_5) is an effective catalyst for the photooxidations of various alcohols and various amines to the corresponding imines under atmospheric pressure at room temperature by using molecular oxygen [1,2]. It is well known that the band structure of semiconductor photocatalysts determines the utilizable light energy, oxidizability, and reducing ability. Although Nb_2O_5 usually works only in the ultraviolet (UV) region because of the limit of its bandgap energy, Nb_2O_5 can catalyze these oxidations even under visible light irradiation up to ca. 460 nm. This suggests that these two oxidations take place by the different photo-activation mechanisms from the classical electron transfer mechanism in semiconductor photocatalysis, that is, the formation of an excited electron in the conduction band and the positive hole in the valence band.

We investigated the reaction mechanisms of the photooxidation of alcohols and amines over Nb_2O_5. A mechanistic study by UV-Vis, ESR, FT/IR, kinetic study, and DFT calculations revealed the reaction mechanisms of photooxidation of alcohols and amines, and that the surface complex consisting of adsorbed molecule and catalyst plays an important role in the photo-activation step. The surface complex is converted to the photo-activated species even under visible light irradiation, because the direct electron transition from a donor level derived from adsorbed molecule to the conduction band of photocatalyst takes place and photo-generated hole is trapped on adsorbed molecule to form the photo-activated radical species. The effective wavelength becomes longer due to the formation of donor level derived from adsorbed molecule during a chemical reaction (called here "*in situ doping"*). This unique photo-activation mechanism by "*in situ doping*" gives us attractive ways for the removing the limit of bandgap energy, and the utilization of visible light.

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RuO_x-VO_x/TiO_2 as Very Highly Selective Photocatalysts for the Oxidative Dehydrogenation of Ethanol to Acetaldehyde

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Aldehydes are important products and intermediates in the field of fine chemicals. A commonly used method for their preparation is the oxidation of the respective alcohols [1].

Ru-based catalysts are well known to oxidize alcohols. The most studies are carried out in liquid phase and discontinuous reactors, so it is necessary to separate the catalyst from reaction products after the oxidation. This operation can be avoided using a gas-solid continuous catalytic reactor. But generally, the gas phase process is carried out at high temperatures resulting in low selectivity towards aldehydes. For this reason, the use of a photocatalytic system to carry out selective oxidation of alcohols is particularly attractive because the reactions are often conducted at ambient temperature [2].

The gas-solid photocatalytic partial oxidation of ethanol to acetaldehyde on monometallic RuO_x/TiO_2 and bimetallic RuO_x-VO_x/TiO_2 catalysts has been studied in a fluidized bed photoreactor at high illumination efficiency [3-5].

For RuO_x/TiO_2, by increasing ruthenium loading, ethanol conversion decreased from 60 to 37%, while acetaldehyde selectivity increased to about 97% (0.4 wt% RuO_2 loading). With bimetallic RuO_x-VO_x/TiO_2, the selectivity to acetaldehyde on monometallic Ru-based catalysts is enhanced by the highly active V species, resulting in higher catalytic performance. By increasing the vanadium loading, ethanol conversion increased up to 100 % with almost total selectivity to acetaldehyde.

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OP-V-4

Design of the Nanocrystalline CdS/TiO_2 Photocatalyst

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Purification of air from organic pollutants is currently an acute problem. Photocatalysis on semiconductors is widely used as a purification method. The photocatalytic air treatment method involves, in most cases, oxidation on titania (TiO_2) under UV irradiation. The major drawback of TiO_2 is its rather wide band gap and, as a result, low photoactivity under sunlight, in which wavelengths shorter than 365 nm account for only a few percent. Therefore, to enhance the catalytic process efficiency, it is necessary to shift the absorption band of the TiO_2 toward longer wavelengths. In this context, the present work has been aimed at designing a complex catalyst with the use of semiconducting cadmium sulfide.

The narrow band gap CdS semiconductor is applied to the wide band gap TiO_2, and this leads to the extension of the light sensitivity range of the photocatalyst from 365 to 515 nm. Catalysts active under visible light on the basis of the composite of cadmium sulfide and titania CdS/TiO_2 were obtained in an aqueous medium by a two-stage process. The first stage was the synthesis of nanocrystalline CdS particles by chemical deposition from aqueous solutions in the presence of the complexation agents, and the second stage was the deposition of CdS on a commercially available TiO_2 powder Hombifine N and Degussa P25.

The CdS/TiO_2 catalyst activity was studied for the oxidation of ethanol to acetaldehyde in a batch system under visible light irradiation ($\lambda > 400$ nm). The catalytic activity of the CdS/TiO_2 Degussa P25, 0.34 μmol acetaldehyde per hour, turned out to be close to the values for the CdS/TiO_2 Hombifine N. The activity of CdS/TiO_2 Hombifine N without adding a complexation agent was 0.10 μmol acetaldehyde per hour, which is considerably lower than the activity of all systems containing complexation agents. The highest activity was exhibited by the samples obtained from solutions of ammine and citrate cadmium complexes where the complex ion formation constants were minimal but sufficient to prevent the formation of cadmium oxygenous impurities.

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The Theoretical Prediction of Structural and Electronic Effects of Gold-Based Systems in Selective Alkynes Activation

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Gold nanoparticles supported on metal oxides are active in the conversion of unsaturated hydrocarbons. The activation of C=C and C≡C bonds is a key step in hydrogenation, oxidation and isomerization reactions. The investigation of catalytic sites of gold nanoparticles and the evaluation of support influence on these sites is necessary for the design of new highly efficient catalysts.

In the present work, the results of simulation of the simplest unsaturated hydrocarbons C_2H_2 and C_2H_4 adsorption onto neutral and charged cluster Au_{12} (2D and 3D isomers), as well as onto the MgO(100) surface are described. The calculations were performed using the density functional theory (DFT/PBE) in the programs "Priroda 08" and "CASTEP 5.5". Relativistic effects were taken into account using a scalar-relativistic approach. MgO(100) was investigated using a plane wave basis set and ultrasoft pseudopotentials in periodic boundary conditions.

The adsorption of hydrocarbons (C_xH_y) onto Au_{12} cluster is accompanied by the formation of complexes, where C_xH_y bonded with low-coordinated atoms of the cluster. The increase of the multiple bond lengths in complexes versus free C_xH_y is an evidence of hydrocarbon activation. Molecular orbital analysis of the complexes indicates the interaction to occur via a donor-acceptor mechanism involving the HOMO of the hydrocarbons and the LUMO of the gold cluster. The preferable adsorption of C_2H_2 over C_2H_4 on 3D cluster was found out based on the calculated adsorption heats. The adsorption of hydrocarbons onto Au_{12}^+ cluster is accompanied by an increase in adsorption heats for both C_2H_2 and C_2H_4 due to effective overlap between frontier orbitals of hydrocarbon and a cluster. The Au_{12}^- cluster exhibit a pronounced selectivity for C_2H_2 over C_2H_4. It was shown that charge effect is more apparent than structural effect. Both C_2H_2 and C_2H_4 are adsorbed physically on the MgO(100) surface.

This work was funded by grant of the President of the Russian Federation for state support of young Russian Ph.D. scientists (MK-107.2011.3) and RFBR (10-03-00999). The calculations were performed using supercomputer SKIF MSU "Chebyshev".

OY-II-1

The Role of Monovalent Nickel in Metalcomplex Catalysis

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The reaction of comproportionation with the formation of complexes of Ni(I) proceed in the joint presence in the system of Ni(0) and Ni(II) as the cationic and electroneutral types of stabilized olefin or organoelement ligands, that has been shown on the basis of analysis of experimental data. The spontaneous decay of hydride and organometallic complexes of Ni(II) also leads to the formation of complexes of Ni (I), it is set on the example of individual complexes of Ni(II). The experimental data presented in this report allow us to assert that despite the established notions, the equilibrium

$$\mathrm{Ni(II)} + \mathrm{Ni(0)} \rightleftharpoons 2\mathrm{Ni(I)}$$

in nickel metal complex catalytic systems is almost completely shifted to the right and the formation of Ni(I) complexes is not out of the ordinary case.

Complexes of Ni(I) formed in the catalytic systems have several unique properties that provide them the opportunity to participate directly in key reactions of various catalytic cycles. It is shown that one of the unique properties of cationic complexes of Ni(I) is the possibility to stabilize only olefinic ligands in the solution.

Complexes of Ni(I) can be easily incorporated into oxidative addition reaction of alkenes and alkynes to form complexes of Ni(III), the catalytic transformations of olefins and acetylenes take place with the formed complexes of Ni(III). The possibility of easy transformation of cationic complexes of Ni(I) to the organometallic complexes of Ni(III) allowed for the first time to carry out the reaction of cyclodimerization of cyclooctadiene-1,5 with the formation of tetracyclic product wich had not been described before. For example, the atom-economical catalytic system $\mathrm{Ni(COD)_2/BF_3{\cdot}OEt_2}$ was developed and showed high activity in the additive polymerization of norbornene (1930(kg NB) $(\mathrm{mol{\cdot}Ni})^{-1}\mathrm{h}^{-1}$. The metallocyclic mechanism of polymerization of norbornene with complexes of Ni(I) and Ni(III) has also been suggested by us.

This work was supported by the Federal Program "Scientific and scientific-pedagogical personnel of innovative Russia" (contract number P732).

OY-II-2

Non-Heme Iron and Manganese-Catalyzed Asymmetric Olefin Epoxidations with H_2O_2: Probing the Nature of Active Species by EPR Spectroscopic and Enantioselectivity Studies

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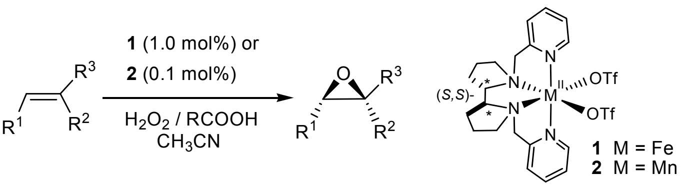
The demand for efficient and sustainable regio- and stereoselective catalyst systems for the oxidation of organic substrates is continuously growing in line with toughening economic and environmental constraints. To date, Fe complexes with polydentate *N*-donor ligands are regarded as the best models of natural non-heme oxygenases capable of catalyzing selective oxidation of inactivated aliphatic C–H bonds with H_2O_2.[1] While the nature of active species in various non-heme iron/H_2O_2 catalyst systems has been extensively studied in the last years, no mechanistic data have been reported for bipyrrolidine-based ((*S,S*)-pdp)Fe complexes of the type **1**, that have been found to be remarkably efficient and selective catalysts of C–H oxidations and asymmetric *cis*-dihydroxylations.[2, 3] For related aminopyridine-based manganese systems, very little mechanistic data is available as yet.

In this study, chiral bipyrrolidine-based non-heme iron and manganese complexes **1** and **2** have been found to catalyze enantioselective epoxidation of prochiral olefins with H_2O_2 in the presence of carboxylic acids, manganese catalyst **2** demonstrating much higher efficiency (1000 vs. 100 TON) and enantioselectivity (up to 93% *ee*: the highest value ever reported for aminopyridine metal catalysts). The enantioselectivity rises with rising steric bulk of the acid, thus indicating the presence of the carboxylic moiety in the active species at the enantioselectivity-determining step. On the basis of EPR and enantioselectivity data, the active species can be assigned to $[((S,S)\text{-pdp})M^{V}{=}O(OC(O)R)]^{2+}$ complexes (where M = Fe or Mn, R = alkyl). In the iron system, the corresponding intermediate $[((S,S)\text{-pdp})Fe^{V}{=}O(OC(O)CH_3)]^{2+}$ has been trapped by EPR at −85 °C. A consistent mechanism for the active species formation is proposed.



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OY-II-3

Highly Efficient, Regioselective and Stereospecific Oxidation of Non-Activated Aliphatic C-H Groups with H_2O_2, Catalyzed by Aminopyridine Manganese Complexes

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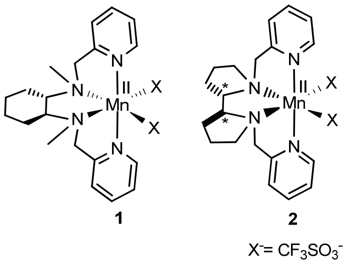
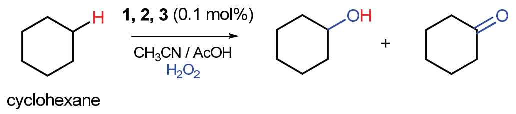
The selective functionalization of non-activated C-H groups remains one of the greatest challenges in synthetic chemistry since such reactions would disclose new and more straightforward synthetic routes towards complex organic molecules. The oxidations of C-H groups catalyzed by enzymes are widely present in nature. In contrast, very few examples of selective and environmentally benign C-H oxidations catalyzed by synthetic non-heme iron complexes are known [1, 2], albeit with low-to-moderate efficiencies (10 up to 100). Here we report the C-H oxidation reactivity of Mn complexes **1**-**3** (Scheme 1): they have demonstrated previously unachievable high site-selectivities and high efficiencies at the same time.



Scheme 1. Manganese(II) complexes considered



Scheme 2. Catalytic oxidation of cyclohexane

Mn complexes **1**-**3** were employed as catalysts for oxidation of a number of aliphatic substrates with H_2O_2 in the presence of acetic acid. Cyclohexane was oxidized (Scheme 2) with up to 5.1 A/K ratio under model conditions ($[H_2O_2] \ll [\text{substrate}]$), and with up to 84% cyclohexanone yield under practical conditions (TON up to 870). The regioselective hydroxylations of 1-substituted derivatives of 3,7-dimethyloctane were probed to reveal the effect of electron-withdrawing groups on site-selectivity. Adamantane oxidation was also found to be highly selective (3°/2° values of 40-49). Stereospecific hydroxylation of *cis*-1,2-dimethylcyclohexane proceeded with excellent RC (>99%) and TON up to 970.

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OY-II-4

Self-Immobilizing Catalysts for Ethylene Polymerization Based on Derivatives of bis(Phenoxy-Imine) Titanium Halide Complexes

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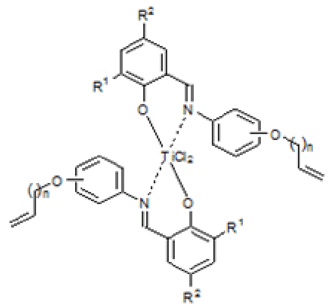
The catalysis features and ethylene polymerization mechanism are studied for the following 10 functionalized bis(phenoxy-imine) titanium(IV) chloride complexes functionalized with an oxyallyl group containing different number of CH_2 units and located in the para- (**1-6**) or meta- (**7-10**) position in the phenyl ring with respect to the imine nitrogen:



1. n=1, R^1=CMe_2(Ph), R^2=H
2. n=2, R^1=CMe_2(Ph), R^2=H
3. n=3, R^1=CMe_2(Ph), R^2=H
4. n=1, R^1= R^2=CMe_2(Ph)
5. n=2, R^1= R^2=CMe_2(Ph)
6. n=3, R^1= R^2=CMe_2(Ph)
7. n=1, R^1=CMe_2(Ph), R^2=H
8. n=2, R^1=CMe_2(Ph), R^2=H
9. n=1, R^1= R^2=CMe_2(Ph)
10. n=2, R^1= R^2=CMe_2(Ph)

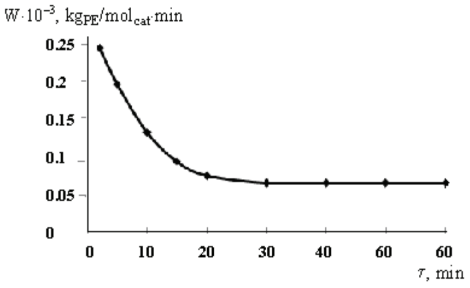


Figure 1. Kinetic plot of ethylene polymerization using the catalyst system **1.**

The kinetic plots of ethylene polymerization (Fig. 1) indicate the transition from the initially homogeneous to heterogeneous polymerization mechanism after the catalyst system immobilization on the synthesized polyethylene (PE).

The duration of the process stage following the homogeneous mechanism and the overall polymerization kinetics are determined by the bis(phenoxy-imine) complex structure. The catalyst immobilization onto the resulting polymer is experimentally confirmed by the appearance of an intrinsic band in FTIR spectra of the obtained PE.

The study of ethylene polymerization kinetic features as a function of the catalyst structure revealed a significant role of the substituents in the phenoxy-group and oxyallyl group position in the phenyl ring bound to the imine nitrogen.

GPC characterization of the progressive changes of PE obtained at the homogeneous and heterogeneous stages of the polymerization allowed us to clarify the polymerization mechanisms at these steps as a function of the applied catalyst structure.

The characterized catalyst systems demonstrated significant activity and can be effectively applied in the production of polyethylenes for various purposes.

OY-II-5

Radical Processes Catalysed by Transition Metal Complexes with Grafted Ionic Liquids

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The Cu(II), Co(II) and Mn(II) chloride complexes with immobilized N-ethyl-N'-propylimidazolium chloride ($EtPrImCl\text{-}SiO_2$), propyltriethylammonium chloride ($PrEt_3NCl\text{-}SiO_2$) and propylpyridinium chloride ($PrPyCl\text{-}SiO_2$) are efficient in two environmentally important reactions: liquid-phase oxidation of thiols with air oxygen leading to the formation of disulfides:

$$4RSH + O_2 = 2RSSR + 2H_2O$$

and in phase interaction between alkanes and carbon tetrachloride

$$RH + CCl_4 \rightarrow RCl + CHCl_3$$

The processes mentioned above are of practical significance. The first one is used in petrochemistry. The second one is a promising method for disposal of banned carbon tetrachloride (CTC), as it allows the initial organic chlorine to be fully utilized to form valuable commercial products. The effectiveness of the catalysts depends on the transition metal, the ionic liquid and the support nature. In C-Cl C-H metathesis the highest activity is shown by the complexes with alkylamines derivatives grafted on silica with wide pores. In case of thiol oxidation, complexes with heterocycles derivatives grafted on supports with narrow pores are most active. We found that transition metal complexes with immobilized on the silica gel surface thermally stable quaternary ammonium bases (QAB) should be used together with aliphatic alcohols (ethanol or propanol) to increase catalytic activity and stability. Using this approach, the yield of chloroalkanes was increased and the catalyst stability was enhanced, and thus the catalysts became suitable for repeated use without loss of activity. Complexes and their evolution were studied by means of EPR and UV-spectroscopy. Also, some organic intermediates were determined by means of GLC-MS. On the basis of experimental data, the mechanism of the process was suggested.

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OY-II-6

Catalytic Effect of Si-Containing Compounds on the C-Methylation of Indole in *sc*-MeOH

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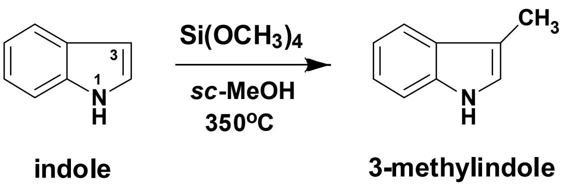
C$_3$-alkyl indole derivatives, such as 3-methylindole, 3-indolylcarbinol, 3,3'-diindolylmethane, are naturally occurring compounds and is of considerable practical significance. For example, 3-methylindole has a high biological activity. It affects the production of serotonin, can hemolyze bovine erythrocytes, activates transcription of cytochrome P450 enzymes in hepatocytes etc. The synthesis and functionalization of 3-methylindole is of high interest of synthetic organic chemists. A promising way to *C*-alkylation of various organic compounds is the use of supercritical lower C_1–C_3 alcohols as alkylating agents.



It has been shown that C_3-selective methylation of indole by *sc*-MeOH in supercritical conditions at 350ºC are promoted by different forms of SiO_2 (quartz, Pyrex glass, and wide-porous silica gel). Moreover, both indole conversion and regioselectivity to C_3-methylation increase after preliminary chemical interaction between methanol and SiO_2. It was demonstrated that SiO_2-containing materials are "dissolved" in *sc*-MeOH to form the methylated mono- and poly-orthosilicates. Additionally, C_3–selective methylation reaction of indole was studied in *sc*-MeOH catalyzed by tetramethyl or tetraethyl orthosilicates (TMOS or TEOS). It was shown that the use of these orthosilicates leads to the same result of indole methylation. The indole conversion is ~30 % after 5 hours of the reaction with and without catalysts. But catalytic reaction is more selective to the 3-methyl-1*H*-indole formation – 95–96 mol % against 60 mol % for non-catalytic methylation. Indole conversion in catalytic reaction increases by a quarter (without selectivity change), when two equivalents of water are added into reaction mixture. The mechanism of the reaction was proposed and discussed in this paper. Methylating system was assumed to be the TMOS–MeOH, and methylation proceeds *via* cyclic, multi-centered transition state (TS).

Thus, we have shown that SiO_2-containing materials (quartz, Pyrex glass, silica gel) are not inert in *sc*-MeOH at high temperature to give tetramethoxysilane (tetramethyl orthosilicate). The last has a catalytic effect on methylation reaction of indole by methanol promoting selectively the C_3-alkylation.

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OY-III-1

Methane Activation and Conversion on Ag/H-MFI Catalyst

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Ag-containing MFI zeolite is active catalyst for methane non-oxidative conversion to higher hydrocarbons [1,2]. Methane activation is considered to occur on silver cationic species by dissociation of C–H bond with the formation of silver-hydride and surface methoxide [3]. But the data obtained give only indirect evidence of this activation mechanism. Formation of the silver-hydride has been observed only for the methane dissociation on Ag-FAU zeolite, but not on MFI. The methoxide formation has not been detected at all. So the question arises on the mechanism of methane activation and conversion to higher hydrocarbons on Ag/H-MFI zeolite.

Kinetics of H/D exchange between Brønsted acid sites of pure H-MFI and Ag/H-MFI zeolites and methane (CD_4) has been monitored by ^{1}H MAS NMR spectroscopy *in situ*. Significant increase of the H/D exchange rate has been observed on the Ag-modified zeolite. The exchange reaction on Ag/H-MFI zeolite occurs 2 orders of magnitude faster as compared to that on H-MFI zeolite. Thus silver species does influence on activation of C–H bond of methane by Brønsted acid sites of the zeolite.

Conversion of pure methane and methane in the presence of co-reactant higher alkanes on Ag/H-MFI zeolite has been studied by ^{13}C CP/MAS NMR. Ethene has been observed as the product of pure methane conversion at 673 K. Further formation of aromatic hydrocarbons has been detected at 723 K. So it has been demonstrated for the first time that Ag/H-MFI zeolite catalyzes pure methane conversion to aromatic hydrocarbons. Also noticeable involvement degree of the ^{13}C-label from methane into the reaction products has been observed as the result of joint conversion of methane with co-reactants. These data prove that methane indeed converts to higher hydrocarbons in the presence of a co-reactant higher alkane.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (grant no. 10-03-00555, 12-03-91162).

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OY-III-2

Platinum-Catalyzed Asymmetric Hydrogenation: Spectroscopic Evidence for O-H-O Hydrogen Bond Interaction between Substrate and Modifier

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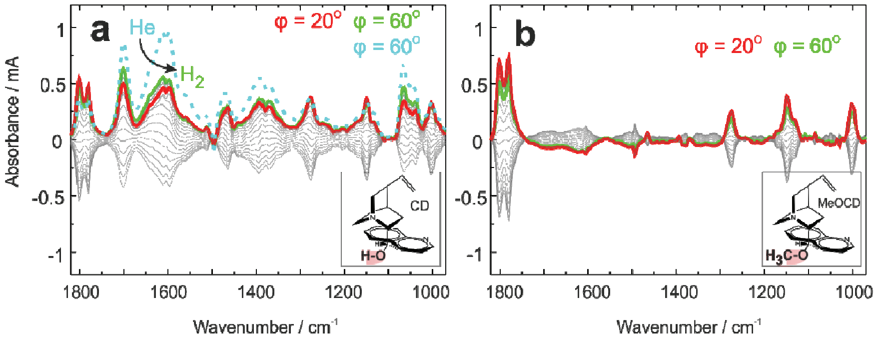
Simple addition of catalytic amounts of cinchonidine (CD) induces remarkably high enantiomeric excess (ee) in the asymmetric hydrogenation of activated ketones on chirally modified platinum (up to 98% ee). Understanding of the governing mechanism is a necessary prerequisite for the rational design of such catalytic systems. Extensive studies have led to the proposal of several different mechanistic models which commonly focus on the role of the tertiary amine functionality of the modifier.[1] In contrast, little attention has been given to the secondary alcohol group of CD, albeit blocking of this functional group leads to a significant decrease in ee for hydrogenation of some ketones.

Using in situ attenuated total reflection infrared (ATR-IR) spectroscopy in combination with modulation excitation spectroscopy (MES) and phase-sensitive detection (PSD) [2] we uncovered a new hydrogen bonding between ketopantolactone (KPL) and modifier (CD) which so far has been overlooked in the literature. This C_9-O··H··O=C hydrogen bonding together with the previously postulated N-H··O=C bonding is crucial for the formation of the intermediate enantiodifferentiating diastereomeric surface complex. The phase-resolved surface spectra (see Figure below) show adsorption-desorption cycles of KPL on Pt/Al_2O_3 modified with CD and the methyl ether derivative, MeOCD. Interestingly, formation of the complex (φ = 60°), following initially adsorbed KPL (φ = 20°), is only observed on the CD-modified surface. Additionally, experimental evidence for the particular stereocontrol of the surface complex toward the major product enantiomer indicates that for some ketones the C_9-OH group of the modifier has to be taken into account for explaining enantiodifferentiation on chiral surfaces.



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OY-III-3

Unusually Active Nanostructured Ni Catalysts with Low Metal Coverage for Chlorobenzene Hydrodechlorination

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Metal particle size and metal-support interaction are of the great importance in heterogeneous catalysis. When an isolated metal cluster is placed on the support, it could result in the electric field appearance in between. It represents an additional variable of state which, like pressure or temperature, can alter chemical equilibrium. Usually it is manifested in reagents and pruducts chemisorption parameters during surface reactions. Both the nature of a support and metal distribution influence on the strength of such interaction. Laser electrodispersion (LED) technique was successfully used for preparation of nanostructured catalysts containing highly uniform (about 2 nm) metal particles, and the particle size is constant in the wide range of metal loadings. In this work, LED prepared Ni catalysts on conductive and non-conductive supports (Sibunit and Al_2O_3) with different metal loadings (from 0,25 of monolayer to several layers, where 1 monolayer is 0.001 wt% on Sibunit and 0.005 wt% on Al_2O_3) were tested in the hydrodechlorination of chlorobenzene at 50-350°C in the gas-phase flow type system. The similar samples prepared by wet impregnation were used for comparison. Catalysts were examined by HR TEM, XPS and adsorption methods.

It was demonstrated by XPS that at low coverages, Ni in LED samples is presented predominantly in more oxidized forms than at higher contents which are close to monolayer. This dependence is more prominent for alumina supported samples, than for Sibunit supported ones. Catalytic activity of Ni on these supports is different as well. For Ni/γ-Al_2O_3, extremal dependence of catalytic activity on Ni loading with maximum at 0,001 wt% was observed ($2{,}9 \bullet 10^4$ Mol/Mol (Ni)•h), that is comparable with the values for Pd. The activity of Ni/Sibunit significantly grows with the decrease of Ni loading ($4{,}9 \bullet 10^4$ mol/mol (Ni)•h at 0,001 wt% Ni). Such unusual activity at the Ni loadings of about one monolayer could be explained in terms of charge transfer between the closely situated Ni particles or between Ni particle and support.

This work was supported by RFBR (№ 10-03-00372, 11-03-00403) and Leading Scientific Schools grant НШ-2724.2012.3. Results were obtained with the help of SRCCU "Nanochemistry and Nanomaterials" of Lomonosov Moscow State University.

Carbonylation of Dimethyl Ether on Rh/$Cs_2HPW_{12}O_{40}$: Mechanism of the Reaction in the Presence of Methyl Iodide Promoter

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Carbonylation of methanol and dimethyl ether (DME) is considered to be the main way to produce acetic acid and methyl acetate at industrial level. In recent years, the Rh–containing cesium salts of tungstophosphoric heteropoly acid (HPA) have been shown to be effective heterogeneous catalysts for halide-free carbonylation of dimetyl ether to methyl acetate [1]. We have demonstrated recently that Rh/$Cs_2HPW_{12}O_{40}$ works as a bi-functional catalyst, where the activation of DME and CO occurs at different surface centers, Brønsted acid sites of HPA and rhodium. The interaction between reaction intermediates, Rh-carbonyl and methoxy-group, gives surface acetate, the immediate precursor of methyl acetate [2].

In this paper we report that the use of methyl iodide promoter leads to a noticeable acceleration of the DME carbonylation on Rh/$Cs_2HPW_{12}O_{40}$ by opening a new reaction pathway. Using ^{13}C solid-state NMR, the main peculiarities of the reaction mechanism have been established. Methyl iodide forms rhodium-methyl intermediate, Rh-CH_3. Carbon monoxide, existing on the surface of Rh/HPA as rhodium carbonyls, is embedded into Rh-CH_3 bond, Rh-acetyl being produced. Then the migration of acetyl group from rhodium to Brønsted acid site of HPA results in the formation of surface acetate group and hydrogen iodide. The acetate reacts with DME molecule producing target product, methyl acetate. Dimethyl ether is activated at Brønsted acid sites of HPA with the formation of surface methoxy-group, from which reactive methyl iodide is restored through the interaction with HI. The latter process provides the involvement of DME into the catalytic cycle. All the stages described above occur at $\geq$ 100 °C, thus providing the decrease of the temperature required for the carbonylation in comparison with halide-free system ($\geq$ 150 °C).

Acknowledgements: This work was supported in part by Zamaraev International Charitable Scientific Foundation.

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OY-III-5

Studying the Influence of Precursor and Promoter on the Activity and Stability of Methane Combustion Catalysts

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Catalytic combustion of methane, the strongest greenhouse gas, is the most effective way to reduce the emission of CH_4 and thus fulfill the current restrictions on the methane concentrations in the exhaust of Natural Gas Vehicles (NGV). Palladium catalysts are the most perspective ones to be used as the exhaust neutralizers in NGVs. However, serious modifications of such catalysts are needed because despite of high initial activity they are easily deactivated due to high susceptibility to the concentration of catalytic poisons and water vapor in the reaction media [1-4].

It is shown in literature that the stability of palladium methane combustion catalysts can be increased via introducing of promoters, but inconsistency of literature data makes it difficult to select the optimum catalyst structure. For example, the addition of Ni, Co and Sn oxides can improve the catalyst tolerance to water [5, 6].

The aim of this work is studying the water vapor induced deactivation of the Pd-catalyst active component. To reach this goal, influence of the Pd-precursor and promoters (Ni, Co, Pt oxides) on the stability and activity of Pd/Al_2O_3 methane combustion catalysts in the model reaction mixture (CH_4+O_2+H_2O in Ar) with variation of reaction temperature and initial water concentration was studied. It was shown that the addition of Ni and Co oxides improves the activity of Pd-catalysts, and the Pt oxides addition leads to the increase of activity and stability. The precursor influence on the catalytic properties of Pd/Al_2O_3 catalysts was also studied. The active component activity and stability depend on its phase composition and ox-red lability. XPS technique was used to indicate that the PdO ox-red lability strongly depends on the concentration and type of promoter [7].

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Concentration Hysteresis in the Oxidation of Methane over Pt/γ-Al_2O_3

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Currently, the reaction of methane deep oxidation is very intensively investigated. This is due to the fact that natural gas, whose main component is methane (98%), is widely used as domestic and industrial fuel, as well as motor fuel for automobiles. Another important application field of the methane deep oxidation is the development of catalytic heat sources (catalytic combustion).

It is known that the activity of platinum catalysts in the methane oxidation at low temperature depends on CH_4:O_2 ratio. Some authors suppose that the reaction has zero order in oxygen under fuel-lean conditions, whereas it has the order about unity under fuel-reach conditions. Others observed the zero-order reaction in oxygen in both cases. These data seem contradictory only at first glance; because platinum has high redox lability and can easily change the chemical state depending on the reaction composition. In our work [1], it was shown that there is concentration hysteresis in the low-temperature oxidation of methane over supported nano-sized particles of platinum. It was found that there are two stable stationary states of the catalytic system with low and high catalytic activity, which are realized at the same external conditions depending on the direction of change of CH_4:O_2 ratio. Discovered way for increase in activity allows improving the catalyst performance significantly without variation of the reaction temperature, contact time and the composition of the catalyst. For instance, the increase in methane conversion from 11 to 80 % can be achieved only by change in the composition of initial reaction mixture. Study of concentration hysteresis may form a new basis for the control of the Pt catalyst activity.

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OY-III-7

Bimetallic Catalysts of Selective Benzene Hydrogenation for Environmental Gasoline Production

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The incomplete combustion of the gasoline containing benzene can form the strongest carcinogen benzapyrene in exhaust gases. According to European standards, the content of benzene should not exceed 1% in exhaust gases. One of the methods is to remove the benzene by catalytic hydrogenation to cyclohexane. Selective hydrogenation catalysts of benzene in the presence of other aromatic compounds may solve this problem. The active and selective rhodium catalysts of hydrogenation supported on various carriers have been created [1-3].

The activities of mono and bimetallic catalysts based on rhodium, palladium and gold were presented in this work. Various carbon and aluminum-silicates were used as carriers. The catalysts were prepared by incipient wetness impregnation and colloidal methods. Hydrogenation was carried out in following conditions: the temperature between 20-80ºC, hydrogen pressure between 20-100 atm in the autoclave. The autoclave supplied with a turbine mixer in an isobar-isothermal mode, with measurement of volume of the absorbed hydrogen. The reaction mixture simulates the system gasoline – benzene approximated to the real gasoline which corresponds to Euro standards. The reactor allows testing and analyzing samples during the reaction.

The catalysts were characterized by the TEM, ICP, BET and XPS methods. The uniform distribution of bimetallic particles was determined using TEM with size in the range 1-5 nanometers. The loss of active metal in comparison with the calculated one were observed.

The bimetallic rhodium and gold catalysts showed their (i) high activity and (ii) the ability of selective hydrogenation of benzene in the presence of other aromatic compounds, such as toluene, xylene and cumene. Ethanol, octane and water were used as solvents. The highest activity was showed with water, because of polar medium. Reaction rate in ethanol was two times lower than in water. The decrease of polarity in the medium had impact on the reaction rate. In non-polar medium octane, low reaction rate of hydrogenation was observed. Complete conversion of benzene was observed in all cases. It makes possible to utilize the catalysts for removal of trace amounts of benzene in gasoline.

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OY-IV-1

Modeling of Associated Petroleum Gas Steam Reforming Process

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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 in Russia. Several of the existing APG utilization approaches are focused on generation of electric power (in gas engines, gas turbines). In order to increase methane content and, consequently, methane number of the gas mixture, APG heavy hydrocarbon components can be converted into methane-hydrogen mixture by a process similar to a pre-reforming step of hydrogen production from natural gas and refinery gases in petrochemical processes. In contrast to the known petrochemical process conditions (pre-reforming is performed at 400-450°C with high ratio of H_2O/C), this process is performed at temperatures below 350 °C with low H_2O content in the reaction gas mixture in order to prevent steam reforming of methane and obtain the highest methane concentration. In this work, laboratory studies of the reaction of steam reforming of hydrocarbons into methane-hydrogen mixture were performed using APG-simulating methane-propane mixtures. Ni- and Ru-containing systems were studied as catalysts. Detailed kinetic experiments were performed and the most appropriate reaction scheme was proposed. In the presence of water at low temperatures, the reaction of propane steam reforming proceeds predominantly; the main reaction products are hydrogen and carbon dioxide. As hydrogen appears in the reaction mixture, the exothermic reaction of hydrocarbon hydrocracking to produce methane occurs simultaneously. In the presence of water, the reverse water gas shift reaction does not proceed at temperatures below 350°C; all catalysts demonstrate low CO outlet concentrations.

Acknowledgements

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Solvent-Free Allylic Oxidation of Alkenes with O_2 Mediated by Fe- and Cr-MIL-101

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The mesoporous chromium and iron terephthalates, Cr- and Fe-MIL-101 have a rigid zeotype crystal structure, consisting of quasi-spherical cages of two modes (29 and 34 Å) accessible through windows of *ca* 12 and 16 Å [1, 2]. Both materials possess large surface areas and mesopore volumes (typically, 3200-3900 m^2/g and 1.4-2.1 cm^3/g, respectively) as well as have good solvolytic and thermal stabilities (up to 300 and 180^oC, respectively). Numerous coordinatively unsaturated transition metal sites can be easily created by a thermal activation in vacuum. All these allow considering Cr- and Fe-MIL-101 as prospective catalytic materials. Herein we report on the recent achievements in the catalytic applications of Fe- and Cr-MIL-101 in the liquid-phase selective oxidation of alkenes.

Both Fe and Cr-MIL-101 were found to catalyse allylic oxidation of alkenes with molecular oxygen in the absence of additional organic solvent [3]. The nature of the active metal had a strong impact on the product distribution. In both cyclohexene and α-pinene oxidation with O_2, Cr-MIL-101 allowed achieving higher selectivities towards enol/enone products than Fe-MIL-101. Cyclohexene or α-pinene oxidation over Cr-MIL-101 gave 94% cyclohexenol/-one total selectivity at 16% cyclohexene conversion or 70% verbenol/-one selectivity at 26% α-pinene conversion, while in the presence of Fe-MIL-101 only 73% selectivity to cyclohexenol/-one or 33% to verbenol (only traces of verbenone were found) at 8-12% substrate conversions were reached. Fe-MIL-101 demonstrated quite different product distributions depending on the reaction temperature due to the different oxidation mechanisms.

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OY-IV-3

Biomass Derived Lignan Hydroxymatairesinol Selective Oxidation over Au Catalysts

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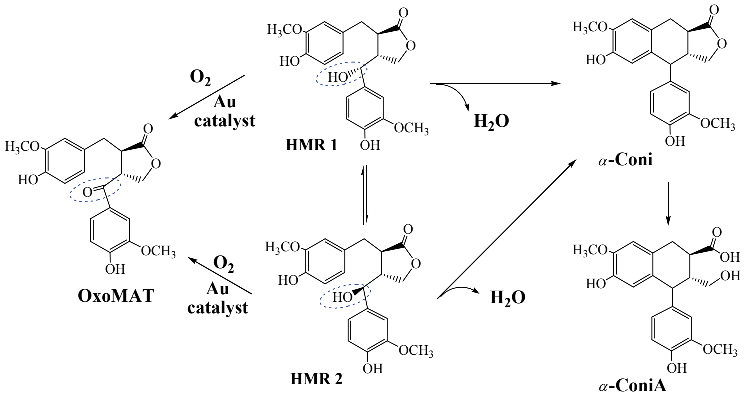
The high catalytic activity and selectivity of gold catalysts in the oxidation reactions resulted in the increasing number of studies on the application of these catalysts in the synthesis of fine chemicals. The selective oxidation of wood biomass derived lignan hydroxymatairesinol (HMR) to another lignan oxomatairesinol (oxoMAT) over gold catalysts was recently discovered [1]. The former one is a valuable compound for textile, cosmetic and pharmaceutical industry. The effect of reaction conditions, catalyst support and active phase on the activity and selectivity was studied. Several groups of gold catalysts were prepared and characterized by XPS, TEM, XRD, FTIR. The most active catalyst was found to be Au/Al_2O_3 displaying 100 % selectivity to oxoMAT. Catalyst deactivation and regeneration were investigated. The reaction scheme is presented below. Quantum chemical calculations were performed and the mechanism of the reaction in aerobic and anaerobic conditions was revealed.



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Direct Catalytic Treatment of Biomass Substrates Towards Hydrocarbon Fuel Components

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Current paper presents the results concerning development of nanosized heterometallic catalysts and scientific bases of biomass substrate conversion into fuel components over developed catalysts. The peculiarities and regularities of the next processes were studied that resulted in estimation of the most probable reactions pathways:

- Bioalcohols direct conversion into hydrocarbon components of gasoline;
- Cross-coupling reactions of bioalcohols mixtures modeling fermentation mixtures resulting in alkanes-olefins fraction formation of gasoline as well as mixtures of ethanol with either glycerol or acetone as biotechnology co-products and product of cumene method of phenol producing, respectively;
- One-step and high selective hydrogenation of different composition rape oils leading to alkane formation of either gasoline or diesel fractions;
- Cellulose hydrogenative liquefaction accompanied with its exhaustive deoxygenation towards hydrocarbon fraction formation with boiling point higher than 220°C.

Using XRD, XPS, EXAFS, SEM-EDX methods, the genesis of the most active and stable nanosized catalytic systems were studied and the mechanism of catalytically active cluster formation was determined.

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OY-IV-5

Could Calcination Temperature Stand for CaO Catalyst Real Activation Act in Transesterification of Sunflower Oil?

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In heterogeneous catalytic approach in biodiesel production, CaO is very popular due to its relatively high catalytic activity. Moreover, a right activation act may improve efficiency and rentability of commercial CaO. Commercial CaO and different catalysts prepared by using calcination temperatures in the range 500-1000°C have been studied comparatively in biodiesel synthesis process. Appropriate methods were used in order to characterize catalysts. Catalytic efficiency was tested in transesterification of sunflower oil under typical reaction conditions: temperature 65°C, pressure 1 atm, oil-to-methanol molar ratio = 6:1, and using 1% of CaO for 5h. Textural features show no substantial differences especially in case of CaO calcined at 500 and 900°C. Namely, results show that CaO treated at higher temperature possesses a relatively high surface area (4.3 m^2/g) and total pore volume (0.02 cm^3/g), as well as dominant meso-pores of 60 nm in size. XRD analysis proved that all calcined CaO catalysts consisted of pure oxide unlike uncalcined commercial CaO with unknown thermal history. Temperatures above 700°C do not affect grain size or even undesirable sintering. As thermal analysis exhibits, the higher the calcinations temperature, the lower the remnant of water (surface or constitutional one), particularly compared to commercial CaO thermally untreated. The authors suggest the presence of weak base sites on the surface of low-temperature activated CaO catalysts, while a surface of well dehydrated CaO catalysts (calcined at 900 and 1000°C) consist of strong basic sites. SEM images reveal nano-scale spongy-like morphology of CaO catalyst treated at higher temperatures. CaO calcined at higher temperatures (900 and 1000°C) applied in catalysis of the transesterification of sunflower oil for biodisel, presented excellent catalytic efficiency with the yield of 90.9%. Such activated CaO could be very attractive as a heterogeneous base catalyst of well-defined morphology, low cost and easy-to-prepare material, with a potential application in other catalytic fields on the industrial level.

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Influence of Different Parameters on Yield of Biodiesel Produced over CaO Catalyst

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Technology of biodiesel production by transesterification reaction based on homogeneous catalysis has been used almost one century. However, numerous advantages of heterogeneous catalysis (such as: ecological and economical approach, investement - type costs) over homogeneous are generally established. The majority of modern investigations on biodiesel production are oriented toward the discovery of suitable new solid catalysts.

The effect of a number of parameters on the yield of biodiesel produced by transesterification of sunflower oil using CaO as a catalyst was assessed. Influences of calcination temperature, reaction temperature, reaction time, pressure, methanol to oil molar ratio and stirring speed were taken into account. Reaction was performed in a batch reactor of type Parr 4520 under an inert atmosphere. Biodiesel yield was determined by standardized method (SRPS EN 14103) based on gas chromatography.

The results showed that the increase in reaction temperature shortens the reaction time to achieve maximum yield for any given temperature. However, a higher temperature does not secure a higher yield, since the maximum yield of 90.89% has been achieved at 80°C. In respect of stirring intensity, the highest yield was 89.92% accomplished after 5.5 hours at the stirring rate of 350 rpm. Regarding the reaction pressure, the highest fatty acid methyl esters (FAME) yield was achieved using 15 bars, but there is no consensus in final observation on impact of pressure. Calcination temperature of 900°C used in catalyst preparation was estimated as optimal followed by a higher activity of CaO. On the contrary, 500°C as calcination temperature resulted in completely inactive CaO based catalyst. A clear mechanism of catalytic act has not still been resolved taking into account a solubility of CaO in methanol. Therefore, the complete catalytic act can be supposed as a combination of heterogeneous followed by homogeneous catalytic approach.

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OY-IV-7

Novel Catalysts for Bio-Fuels Production from Biomass Fast Pyrolysis Oils

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In the recent decades, processes of biomass conversion into hydrocarbon fuels have been attracting much attention due to decreasing of crude-oil reserves. Now the technology level of biomass processing into engine fuels is lower than oil-refinery industry, which is the main reason for higher prime cost of bio-fuels production. The role of catalytic technologies of biomass processing into hydrocarbon fuels should be emphasized.

The product of flash pyrolysis of grinded wood, named bio-oil, is a perspective feedstock for the petrol production [1]. But these bio-oils contain considerable amount of oxygen, leading to poor heating value, corrosiveness, thermal instability and immiscibility with hydrocarbon fuels. Catalytic hydrotreatment or hydrodeoxygenation (HDO) is the most direct and effective way of bio-oils upgrading by oxygen elimination. The HDO catalysts were mainly concentrated on conventional sulphided CoMo or NiMo and noble metal catalysts. Noble metal catalysts exhibit high catalytic activity in the HDO reactions, but the high cost is their most significant drawback. Sulfided catalyst are easily deactivated via the oxidation of the active catalyst phase during the HDO. The addition of sulfiding agent (H_2S or CS_2) could maintain the catalytic activity, but it would lead to sulfur contamination of the upgraded bio-oil. Numerous investigations allowed formulation of essential requirements for HDO catalysts to meet. They should have low cost, non-sulfided nature, high activity in the HDO process, high stability in corrosive aqueous medium (against leaching), high thermal stability and ability for multiple regeneration by coke burning.

In the present work, we propose a new type of non-sulfided Ni-based catalysts for bio-oil HDO. The catalysts were produced by sol-gel technique and tested in HDO of guaiacol being a model of bio-oil [2]. Guaicol HDO has been carried out in an autoclave at 320 °C and hydrogen pressure of 17 MPa. Owing to high Ni content and high surface area, the catalysts possessed great HDO activity. However, these catalytic systems still require an improvement because of low thermal stability and tendency to dissolve in acidic medium. The catalyst improvement is the subject of the ongoing research.

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OY-V-1

Kinetic Study of *p*-Nitrophenol Photodegradation with Modified TiO_2 Xerogels

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Advanced oxidative processes represent new technologies for waste water treatment, because new compounds in effluents are not readily degraded by the conventional treatments. Oxidative processes can completely destroy organic pollutants (alkanes, pesticides, etc.) or microorganisms (bacteria, viruses, fungi, etc.). TiO_2 is widely studied in photocatalytic oxidation processes for environmental applications but it is activated with UV light only [1]. In this study, TiO_2 xerogels were sensitized in one step by the *in situ* introduction of nickel (II) tetra(*4*-carboxyphenyl)porphyrin (TCPPNi) into the TiO_2 matrix during sol-gel synthesis in order to extend TiO_2 activation to the visible light region of the solar spectrum. Crystalline photoactive phase TiO_2-anatase was obtained without high thermal treatments and was characterized by X-ray diffraction. The photoactivity of xerogels was evaluated for *p*-nitrophenol degradation in aqueous medium at 20 °C. Results showed that porphyrin doped TiO_2 degrades more than 40% of the *p*-nitrophenol whereas non doped TiO_2 xerogel degrades only 10% of the compound. Moreover, porphyrin was found to improve the photoactivity of TiO_2 xerogels in a similar way to UV-A pretreatment. A kinetic study on *p*-nitrophenol degradation was then performed with variations both in initial *p*-nitrophenol concentration and in temperature. Results were adjusted on a physico-chemical model based on a sequence of elementary steps. They showed that one type of active site corresponding to the hole of electron-hole pairs is created at the TiO_2 surface by light and that the rate determining step is the reaction between the adsorbed *p*-nitrophenol molecule and the adsorbed $OH^\bullet$ radical. The apparent activation energy was found to be equal to 12 kJ mol^{-1} [2].

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OY-V-2

Ultrasonically Designed Metal / Polypyrrole Composite Catalysts for Fuel Cells

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The electrocatalytic properties of mesoporous metal / polypyrrole composite materials could be used for conversion of chemical energy of fuel into electricity by electrochemical reactions. Here we report on design and properties of mesoporous metal / polypyrrole catalyst prepared by using ultrasound. As a starting material for the preparation of catalytic systems – aluminum / cobalt and aluminum / cobalt / iron alloys were chosen. All systems under investigation were sonochemically activated with the use of intensive acoustic cavitation at mesoscopic level. The catalyst design was completed by sonochemical or electrochemical deposition of conductive polymer such as polypyrrole. Ultrasound technique is a key tool for catalyst preparation. Mesoscopical catalyst activation results in formation of porous metals with high surface area, direct grafting of a polymer. Thus, we can achieve stable, selective, and reusable mesoporous composite materials for further electrocatalytic applications. Morphology of the prepared samples was studied with help of scanning electron microscopy (SEM) as well as X-ray scattering technique (XRD). The electrocatalytic activity of the as-prepared mesoporous systems was investigated by cyclic voltammetry (CV) and by electrochemical impedance spectroscopy (EIS) technique.

Microstructure Effects in Catalysis of Oxygen Reduction Reaction over Electrodeposited Platinum: Influence of Intergrain Boundaries

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Structural defects play important role in catalysis and electrocatalysis. Remarkably high activity of Pt-based catalysts with high concentration of defects, specifically, of nm-sized intergrain boundaries (IGB), has been previously reported for some electrooxidation processes [1-2]. Among preparation strategies providing high concentration of IGBs in the catalyst structure, electrodeposition technique is one of the most efficient [1]. Here, we apply electrodeposition for preparation of a set of model supported Pt catalysts with varied microstructure, and study their catalytic properties for the oxygen reduction reaction (ORR).

Glassy carbon (GC) electrodes were used as supports for potentiostatic (E_D = 0.05-0.40 V vs. reversible hydrogen electrode (RHE)) deposition of Pt from the 0.01 M H_2PtCl_6 + 0.01 M HCl solution at 25 ^oC. Kinetics of the ORR was studied using rotating disk electrode method.

SEM studies revealed that Pt/GC deposits comprise coarse (40-300 nm) globules composed of small (<20 nm) crystallites, and that E_D determines the transition from loose 'dendrite'-like (0.05-0.10 V) to compact (hemi)spherical (>0.2 V) structure. Specific surface area (S_{Pt}) of platinum was in the range of 4-12 m^2 g^{-1} (Pt), the highest value being attained at E_D = 0.1 V.

The surface-weighted ORR activity of the Pt/GC deposits acquired at $E_D \geq 0.2$ V decreases with the increase of S_{Pt}, following the Pt particle size effect for the ORR. Contrariwise, the activity of the 'dendrite' deposit (E_D = 0.1 V) with the highest S_{Pt} outnumbers the activity of all catalysts studied here and that of the Pt catalysts with close S_{Pt} reported in literature. Note that under employed deposition conditions, the highest concentration of IGBs is attained at E_D ~ 0.1 V [1]. The observed tendencies suggest that the ORR activity of Pt catalysts can be effectively tuned by varying their microstructure and defectiveness. Finally, we tested Pt/C catalysts prepared by electrodepositing Pt on the conventional Vulcan support at E_D = 0.1 V.

The work was financed by Russian Federation President Grants for the Leading Scientific Schools (NSh 524.2012.3) and for Young Ph.D. (MK-380.2011.3).

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OY-V-4

Cu-Cr_2O_3-Al_2O_3 Catalysts for Water Gas Shift Reaction and Methanol Synthesis

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Determination of the influence of catalysts composition on their physicochemical properties as well as catalytic activity in WGS (Water Gas Shift) and MS (Methanol Synthesis) reactions was the main goal of this work.

Catalysts were prepared by co-precipitation method from appropriate nitrates of Cu, Zn, Al. All samples were dried at 100°C and finally calcined at 400°C. Prepared catalysts were characterized by BET, TPR, TPO and XRD techniques. Catalytic activity was tested in WGS and MS reactions. Depending on calcination temperature and catalysts composition the specific surface area of all catalysts was in the range 40-200 m^2/g. Increasing of copper or chromium content leads to the decrease of catalyst specific surface. The influence of catalysts composition on their activity in methanol synthesis and WGS reaction is given in figure 1. One can notice that catalytic efficiency strongly depends on catalyst composition. Methanol productivity decreases with the growth of copper and chromium content. Opposite catalyst behavior was observed in WGS reaction. Highest activity reveal catalysts contained large amount of copper and chromium. One can notice that CO conversion decreases significantly with the decrease of copper content.

Acknowledgements
Partial financial support from NCN grant no: NN209 068040 is gratefully acknowledged

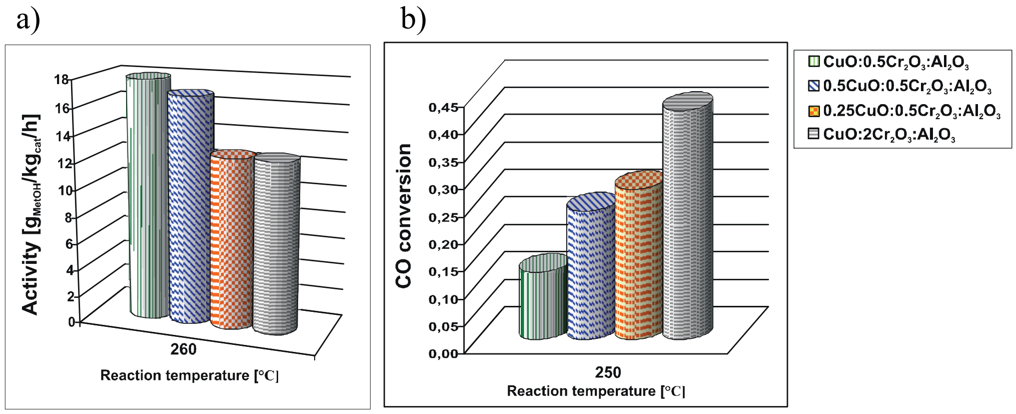

Figure 1. The effect of catalyst composition on their performance in methanol synthesis ($H_2/CO=2$, p=30bar) a) and water gas shift ($H_2O/CO=2.5$, p=1 bar) b) reactions.

POSTER PRESENTATIONS

Section I. Catalysis: from first principles
PP-I-1 ÷ PP-I-14

Section II. Mechanisms of homogeneous catalysis
PP-II-1 ÷ PP-II-20

Section III. Mechanisms of heterogeneous catalysis
PP-III-1 ÷ PP-III-123

Section IV. Catalytic processing of renewables
PP-IV-1 ÷ PP-IV-24

Section V. Electrocatalysis, photocatalysis, biocatalysis
PP-V-1 ÷ PP-V-15

Discrimination between Reaction Mechanisms for the Synthesis of Methyl 5-Acetyl-2-Pyrrolecarboxylate

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Pyrrolecarboxylic acids are of great interest as starting compounds for porphyrin and drug production. Thus, 2-pyrrolecarboxylic acid derivatives exhibit antiviral properties, in particular, they are active against classical fowl plague virus, and sodium salts of 2-aryl-5-pyrrolecarboxylic acids possess anticonvulsant activity.

Construction and analysis of the kinetic model is one of steps for identifying the mechanism of a complex chemical reaction. In the work [1], based upon the analysis of experimental data, two possible mechanisms for the reaction of 2-acetylpyrrole with CCl_4 and methanol under the action of iron-containing catalysts to afford methyl 5-acetyl-2-pyrrolecarboxylate (MAPC) have been proposed.

To discriminate the fitness of both models the following tests have been made:

– possible kinetic models have been designed and analyzed;

– mathematical descriptions in the form of nonlinear systems of ordinary differential equations (ODE) have been designed for the concentrations of substances involved in the reaction, namely, 2-acetylpyrrole, carbon tetrachloride and methanol;

– numerical values of kinetic parameters describing the experimental data were found by solving the inverse problems.

As a result of computer simulation [2], the most probable scheme of chemical transformations and the corresponding kinetic equations were defined; conclusions regarding physico-chemical parameters were made. In particular, the proposed scheme explains the possible reasons for the absence of intermediate products in the reaction mixture.

Inverse problems of chemical kinetics require a significant amount of computation. The use of multi-core systems in the physical-chemical calculations is a very important and actual task today.

Based on Fe-catalyzed reaction of 2-acetylpyrrole with carbon tetrachloride and methanol, a method for constructing kinetic models using parallel processing on multicore systems has been developed and tested.

The use of parallelism in solving inverse kinetic problems on the two core system, allow to achieve speedup of 35–40%, and of 50–55%, while using the four core system. The numerical values of kinetic parameters adequately describe the experimental data.

This work was financially supported by Ministry of Education and Science (State Contract No. 02.740.11.0631) and Russian Foundation for Basic Research (Grant No. 12-03-00183).

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Mechanism of H_2O_2 Synthesis from H_2 and O_2 on Gold and Gold-Palladium Nanoclusters: DFT Approach

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Supported bimetallic gold-palladium nanoparticles exhibit higher activity and selectivity in direct synthesis of H_2O_2 than the catalysts containing only gold or palladium nanoclusters. To understand the nature of such synergetic effect and to improve efficiency of a catalyst it is important to investigate the mechanism of the reaction. For this purpose modern quantum-chemical methods are frequently used.

Bare Au_2, Au_8, Au_{20}, Au_{32}, Pd_8 and mixed Au_4Pd_4, Au_7Pd, $Au_{19}Pd$ and $Au_{31}Pd$ have been chosen as active nanoparticles to investigate the mechanism of H_2O_2 synthesis. Au_8 and Au_7Pd have planar structure, Au_{20} and $Au_{19}Pd$ clusters are of tetrahedral structure, Au_{32} and $Au_{31}Pd$ possess cage-like structure. Calculations have been performed in the framework of DFT/PBE approach with relativistic all electron basis set.

Au_8 and Au_4Pd_4 clusters are potentially active in the direct synthesis of H_2O_2 as molecular adsorption of oxygen on these clusters takes place that is necessary in selective formation of H_2O_2. In case of Pd_8 dissociative adsorption of oxygen is more energetically favorable. Hydrogen adsorbs on Au_8 cluster in dissociative form. Hydrogen atom migration on gold cluster passes through several steps and deals with low energy barriers, except the last stage of H atom migration to form H_2O_2 (81 kJ/mol). Energy barrier of the last stage decreases in case of Au_4Pd_4 and Au_7Pd.

The modeling of the last stage of H atom migration has been performed on top, edge and facet of Au_{20} and $Au_{19}Pd$ tetrahedral clusters. This process passes on Au_{20} top atom with highest energy barrier (109 kJ/mol) and on Au_{20} edge atom with lowest energy barrier (3 kJ/mol). $Au_{19}Pd$ cluster is more active in this reaction as highest energy barrier of H atom migration on $Au_{19}Pd$ top atom two times lower than in case of Au_{20}. Kinetics of this reaction is determined by structural features more significant for Au_{20} than for $Au_{19}Pd$.

High catalytic activity of AuPd clusters is caused by charge redistribution in bimetallic systems.

This work has been financially supported by the grant of Russian Federation President MK-158.2010.3 and MK-107.2011.3. and the grant of government support of leading scientific group of Russian Federation НШ-6512.2010.3. Calculations have been performed using "Lomonosov" and "Chebyshev" supercomputer of M.V. Lomonosov Moscow State University.

PP-I-3

Mechanism Investigation of the NHC-Catalyzed Benzoin Condensation of Aldehydes

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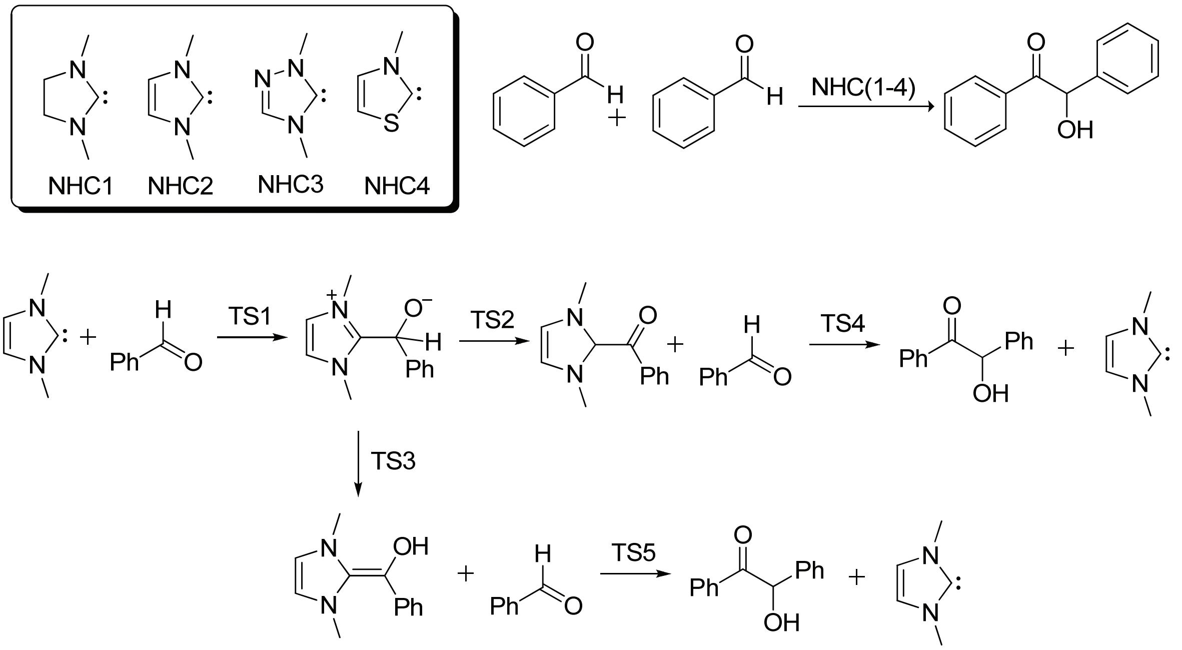
A computational study with the B3LYP and PBE density functional theory was carried out to study the reactions mechanism for the benzoin condensation for aldehydes catalyzed by N-heterocyclic carbenes. We used benzaldehyde and NHC(1-4) carbenes as a simplified quantum-chemical model substrate and explored the detailed mechanism to achieve a clearer understanding of the catalytic processes (*Scheme 1*).



Scheme 1. Mechanism for the benzoin condensation

The calculations presented in this work were carry out in the framework of density functional theory (DFT) using the B3LYP and PBEPBE functional as implemented in Gaussian 03 suite of programs. The full geometry optimization of all minima and transition states involved was performed at the chosen level of theory. Frequency calculations were carried out at the same level of theory to identify all of the stationary points as minima (zero imaginary frequencies) or first-order saddle points (one imaginary frequency) and free energies at 298.15 K to calculate, which include entropic contributions by taking into account the vibrational, rotational, and translational motions of the species under consideration.

Oxidation of Allyl Complexes of Pd(II) by Aqueous H_2O_2 Through Pd(IV) Intermediates: A DFT Investigation

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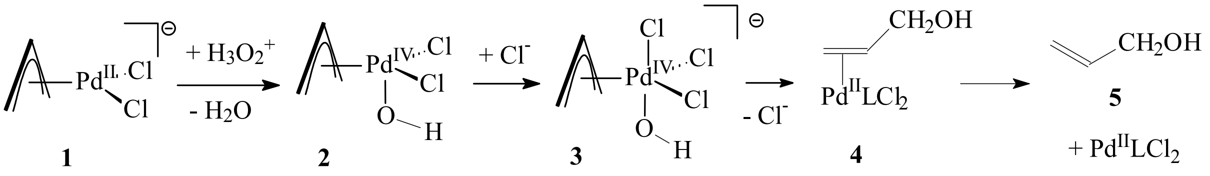
Hydrogen peroxide is an attractive co-oxidant for catalytic processes in view of its safety and low cost. Protonated H_2O_2 can be considered as hydrated ion OH^+ which is a strong electrophile capable to convert alkanes into alcohols [1]. While allylic complexes of Pd(II) are conventional electrophilic reagents [2], they can be selectively oxidized by aqueous acidic solutions of H_2O_2 into allyl alcohols [3]. Till now, mechanism of the reaction was unclear. DFT-study (PCM-B3LYP) of the reaction pathways supported hypothesis of Pd(IV) intermediacy. For series of terminally substituted anions **1** (R = H, Me, Ph, C_2H, CHO, CF_3) equilibrium geometries of intermediates **2-4** were found and most of transition states were localized.



Given mechanism is just representative. Several concurrent paths exist, in part *anti* addition of $H_3O_2^+$ resulting in isomeric **3**, which undergoes C-Cl reductive elimination yielding Cl-derivative. Depending on the substituent R in allyl ligand, either addition of $H_3O_2^+$ to **1** or reductive elimination in octahedral anion **3** can be the rate limiting step. As a whole, presented scheme is in accordance with earlier obtained [3] rate equation for **1** containing terminal CH_2OH-substituent: $r=k^{obs}\cdot[\eta^3][H_2O_2][H^+][Cl^-]$. The findings are useful for developing new processes based on Pd(II)/Pd(IV) scheme, in particular for catalytic synthesis of primary alcohols.

This work was financially supported by RFBR (#10-03-01035-a).

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PP-I-5

Mathematical Modeling of Reactivity of Olefinic and Acetylenic Compounds in Catalytic Reaction of Cycloalumination

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Among the many methods for the synthesis of organoaluminum compounds the greatest distribution was found of reactions of hydro-, carbo-and cycloalumination. Cycloalumination is relatively new and perspective direction, which requires a detailed study of the boundaries of the reaction application and its mechanism [1]. Now it is a little known about behavior in this reaction of functionally substituted olefins and acetylenes, and also no comparative data on the reactivity of different classes of olefinic and acetylenic compounds. The kinetics of the reaction and the influence of the nature of the unsaturated compounds on the mechanism of transformation were not studied. Thus, the problem is new and actual.

In this work the kinetic models of complex reactions of olefins and acetylenes cycloalumination by $AlEt_3$ in the presence of Cp_2ZrCl_2 catalyst in to aluminacyclopentane has been constructed [2]. On the basis of computer experiment, two stages were added in the scheme of chemical reactions, reversibility of the first stage was established (catalyst conversion), the key complex of the reaction was identified.

On the basis of the developed kinetic models:

a) mathematical conditions of origin and development of the induction period of the reaction of olefins cycloalumination were formulated; high parametrical sensitivity of the induction period to the temperature of carrying out of the reaction and the quantity of the catalyst was shown.

b) the numerical analysis of the reactivity of olefins and acetylenes was carried out for the cycloalumination reaction; the obtained dependence of the rate of unsaturated compound insertion in studied reaction from time completely coincide with the experiment.

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Computer Construction of Kinetic Model of Detailed Olefin Hydroalumination Mechanism

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Investigation of the hydroalumination reaction of olefins with organoaluminum compounds (OACs) such as diisobutylaluminum hydride $HAlBu^i_2$ (DIBAH), diisobutylaluminum chloride $ClAlBu^i_2$ (DIBAC), and triisobutylaluminum $AlBu^i_3$ (TIBA) has great significance in both synthetic chemistry and fundamental science. Several mechanisms of olefin hydroalumination have been proposed and include mechanism of the overall reaction and mechanisms for the selected separate reactions between each OAC and olefin in the form of final equations [1], the first and second specification of the selected reactions [2, 3] and the detailed general reaction mechanism with elementary stages.

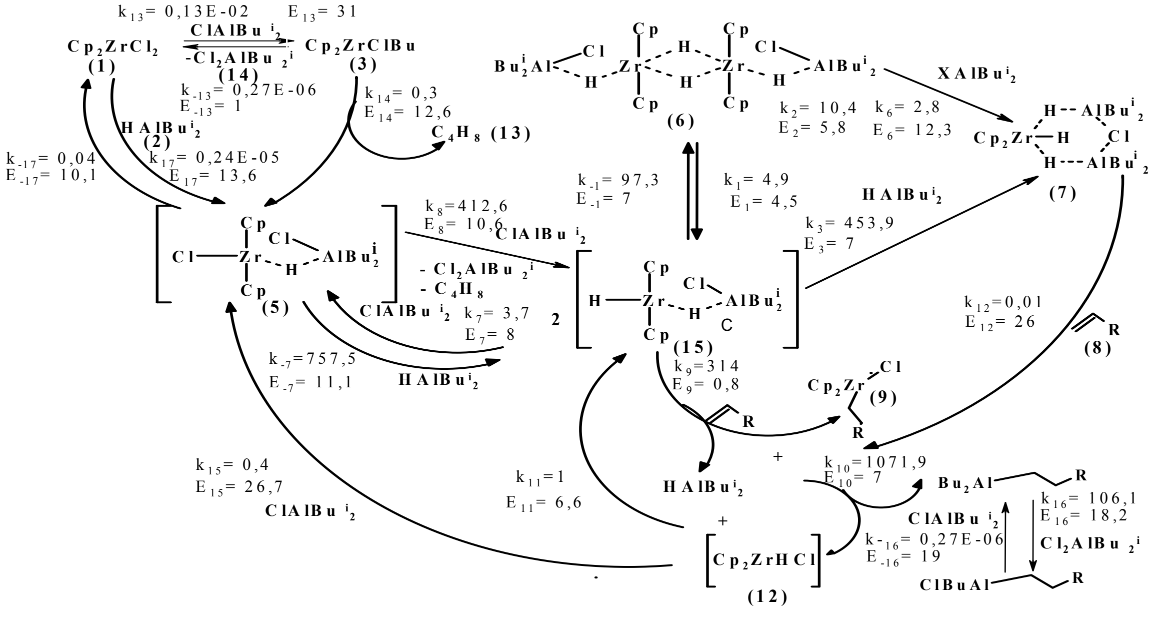

Figure 1. Generalized kinetic model of the catalytic olefin hydroalumination reaction.

It follows from Figure 1, that the dimerization reaction of complex **(15)** (E = 7,02 kcal/mole) and the interaction between **(15)** and a DIBAH molecule (E = 7 kcal/mole) are almost equally probable. But in hydroalumination of olefins with DIBAC diisobutylaluminum hydride is not initial substance, it is formed during the reaction in small quantities. Therefore, dimerization of **(15)** is more probable resulting in the formation of complex **(6)**. Taking into account the activation barriers for the reactions of complex **(12)** with DIBAH (E = 6,6 kcal/mole) and DIBAC (E = 26,7 kcal/mole), one can conclude that the reaction between Cp_2ZrHCl and $HAlBu_2^i$ is more probable providing formation of monomer **(15)**. As seen from the activation parameters for the reactions above initially there occurs the transformation **(12) → (15) → (7).** However, complex **(7)** has a lower activity since the activation barrier for its reaction with olefins is much higher (E = 26 kcal/mole) relative to **(12)** (E = 6,6 kcal/mol) and **(15)** (E = 7 kcal/mol).

Thus, a detailed research of mechanism of the olefin hydroalumination reaction allowed explaining a reaction course on the basis of the energy barriers. The quantitative assessment of the induction period found during laboratory experiments and its dependence upon initial amount of a catalyst and the type of olefin have been made.

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On the Role of Energy Distribution Functions of the Ad-Atoms in Recombinative Adsorption at Catalytic Surfaces

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We present a brief review on the modeling of the vibrational distribution functions of the adspecies in diatom formation at catalytic surfaces. The kinetic approach, which deals with a reactive mobile adlayer of adatoms under steady state conditions, is based on the use of master equations which describe the main processes occurring during the adsorption-recombination events [1,2]. They are, the accommodation of the adsorbed species via energy dissipation in the adsorption potential well and the formation of the diatom. In particular, we focus our attention on the impact of the distribution function on reaction rate and, in turn, on the interplay between reaction rate and energy disposal to the solid and to the adlayer. The kinetic model makes it possible to determine the conditions under which non-equilibrium energy distribution functions characterize the vibrational state of the adlayer. In fact, it is shown that "hyper-thermal" energy distribution functions entails a multi-level "hot-atom" reaction mechanism. Furthermore, the transition from thermal to hyper-thermal reaction rate has been studied as a function of rate coefficients, and the vibrational temperature of the "hot-atoms" estimated.

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PP-I-8

Allylbenzene Double-Bond Migration in Gold-Containing Catalytic Systems: DFT Study

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Supported metal particles on different bulk materials are effective catalytic systems, where the combination metal-support is crucial. In present time nanosized gold particles deposited on varied supports reveal high catalytic activity in numerous reactions, among which is allylbenzene double-migration. It has been shown that the activity of catalytic system in allylbenzene isomerization significantly depends on additional metal inclusion and support. In order to clarify the phenomena observed we have performed quantum-chemical simulation.

The purpose of our work is to study the influence of morphology and charge, as well as Au substitution on Ni, on catalytic ability of gold particles in allylbenzene double-bond migration. In cluster approach the models of active sites are Au_n^q (n=1, 4, 20, 21; q= -1,0,+1) and Au_3Ni. The calculations have been carried out using DFT/PBE in scalar relativistic approach with all-electron basis sets as implemented in Priroda 08 program. In order to study support influence regular C-support (the model is graphite(001)) and basic MgO(100) are considered. The calculations are performed within DFT/PBE framework with plane-wave basis set and ultrasoft pseudopotentials in periodic boundary conditions using CASTEP 5.5. The supercomputers SKIF MSU «Chebyshev» and «Lomonosov» are used.

The activation of allylbenzene double-bond through π-complex formation is observed at low-coordinated gold atoms (corner and edge atoms of a cluster). Three possible mechanisms of allylbenzene double-bond migration have been found out. The most optimal path of allylbenzene isomerization is at charged atoms of gold clusters via metal-allylic mechanism, where gold-hydride complex is an intermediate.

It is possible to control active sites formation by two modes: (i) additional metal inclusion, and (ii) support variation. We have studied the influence of additional metal (Ni) on the mechanism and an activation energy of the rate-determining step in allylbenzene isomerization. The modification of gold particle morphology and charge, as well as gold migration processes are studied on the surfaces of MgO(100) and graphite(001).

This work was financially supported by the Council on Grants at the President of the Russian Federation (Grant 107.2011.3).

Quantum Chemical Study of C-H Bond Activation in Methane and Methanol by Au(I) Complexes with Quercetin under Mild Conditions

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Selective catalytic functionalization of methane to form useful organic compounds constitutes an important and challenging problem. Recently it was found that gold containing enzyme from aurophilic bacteria *Micrococcus Luteus* can catalyze the oxidation of methane to methanol by air' oxygen at room temperature and atmospheric pressure and biomimetic models based on Au complexes with bioflavonoids (rutin or quercetin) were developed [1]. To understand the main features of the mechanism of methane hydroxylation in biomimetic systems and possible reason for the selectivity of this reaction quantum chemical modeling was applied. All calculations have been performed by means of PRIRODA program using the nonempirical PBE functional and the extended basis set for SBK pseudopotential. It has been done using the facilities of Joint Supercomputer Center of the Russian Academy of Sciences.

We were found that binuclear Au(I) aqua complex with quercetin $[Au_2Qc_2(H_2O)_2]$ is an active center in the biomimetic system. Formation of methane complex $[Au_2Qc_2(H_2O)(CH_4)](H_2O)$ is favorable for subsequent reaction of heterolytic C-H bond cleavage. It proceeds by means of proton transfer on the oxygen atom of quercetin ligand via water molecule and require the activation energy 0.4 kcal/mol. The formation of methane complex is the limiting stage with the activation energy 16.9 kcal/mol.

The interaction of the $[Au_2Qc_2(H_2O)_2]$ complex with the product CH_3OH, gives substitution H_2O ligand on CH_3OH ligand. The isomer structure of complex with activated C-H bond of CH_3OH like in methane complex has the energy on 19.3 kcal/mol higher than complex with coordinated OH group of CH_3OH. The energy barrier of the transformation of stable isomer into reactive isomer is rather high 27.4 kcal/mol. Thus, methanol oxidation rate is much smaller than that of methane oxidation, in accordance with experimental data.

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PP-I-10

Ethylene to Benzene Catalytic Transformation Mechanism Performed at Nanocluster of Platinum Pt_4 Based on the Results of Quantum-Chemical Computations

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Researches performed by our group [1-2] let us to explore the most energy-efficient directions of conversion reactions of hydrocarbons on the clusters of platinum. The figure 1 presents results of study of PES for the mechanism of transformation for three ethylene molecules to benzene performed on the tetrahedral cluster $^1Pt_4$. This process is integrally energy-efficient. Desorption of benzene's molecule is the limiting stage (enthalpy of activation is equal to 59 kcal/mole). The alternative mechanisms studied have the higher enthalpies of activation, so they don't have the competitive advantages.

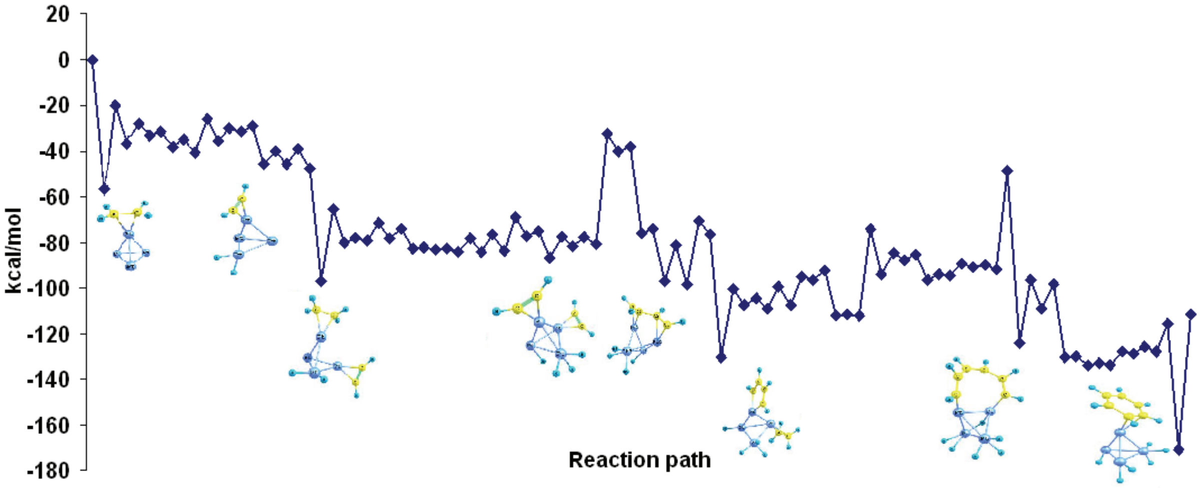

Figure 1. The chart of enthalpy for formation of C_6H_6 from C_2H_4 performed at the cluster $^1Pt_4$. The sum of enthalpies for isolated reactants of ethylene and neutral cluster $^1Pt_4$ is accepted as zero value. Computations were performed using GGA DFT PBE method in the Gaussian functions basis L11 ("Priroda" program[3]).

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Catalytic Transformations During Thermal Decomposition of Some Aliphatic Nitro Compounds

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Present report represents results of theoretical study regarding secondary steps of nitromethane (NM), nitroethylene (NE) and methylnitramine (MNA) thermal decomposition. It was found that catalytic and autocatalytic reactions are of great importance in these processes. It is well known that homolytic C-NO_2 bond cleavage is the predominant primary reaction pathway for NM thermal decomposition. Nevertheless, there is still uncertainty while interpreting entire decomposition process due to the lack of reliable data concerning secondary reaction steps. We have revealed the important role of reactions proceeding through formation of aci-form of NM. Effect of catalytic and autocatalytic reactions involving aci-form of NM in the course of NM decomposition have been studied.

It was determined that the primary act of NE thermal decomposition is the isomerization to 4H-1,2-oxazete-2-oxide involving following decomposition via multistage diradical mechanism. We have studied decomposition of bimolecular complex of nitroethane (NEthane) proceeding through multistage autocatalytic mechanism. The basic stages of process have significantly lower activation barriers compare to monomolecular decomposition. Studied mechanism can explain the possibility of increasing of reaction rates for decomposition in liquid phase.

The new mechanisms were studied also for MNA. Gas-phase decomposition involves aci-form formation. Further transformations of aci-form was investigated including catalytic and autocatalytic reaction pathways. Formation of two aci-forms of MNA was concluded to be the most energy-efficient channel during the interaction of MNA and its aci-form. This process may be assumed as the most favorable mechanism of thermal decomposition in liquid-phase.

PP-I-12

Thermodynamic Studying of Catalyst Processes and Systems – Possibilities and Efficiency

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Developed methodology of thermodynamic modeling and calculation allows to simulate all stages of different materials manufacturing and operation for catalytic processes, to take into account thus both chemical and phase transitions, etc.

Thermodynamic modeling and calculation for equilibrium phase-chemical composition $\{y_i^{(k)}\}$ of researched system, based on criterion of minimization of its corresponding characteristic function, lays in a basis of the method. As a result, the problem is reduced to the equations and inequalities system of the type:

$$\mu_i^{(k)} = \sum_{j=1}^{m} a_{ij}\mu_j, \qquad (i,k)\in I^0: \; y_i^{(k)} > 0 \tag{1}$$

$$\mu_i^{(k)} \geq \sum_{j=1}^{m} a_{ij}\mu_j, \qquad (i,k)\notin I^0: \; y_i^{(k)} = 0 \tag{2}$$

$$\sum_{k=1}^{r}\sum_{i=1}^{n} a_{ij} y_i^{(k)} = y_j^o \qquad j = 1..m \tag{3}$$

where r – number of possible phases; n – number of the different chemical forms of the system determined on source m components by means of stoichiometric matrix $\{a_{ij}\}$; I^0 – required set of the system phase-chemical forms, realized in equilibrium.

The proposed method of the iterative solution for (1) - (3) and the procedures, realizing it, have no restrictions neither on componentity, nor on a nature of researched systems. Required for modeling and calculations the standard and high-temperature thermodynamic characteristics of substances are received from the developed databases. These approach and developed methods are realized in a program-information complex ASTCALC.

Realization of the method has allowed to solve the put problems correctly and effectively for various classes of catalytic processes and systems (V_2O_5-K_2O-SiO_2-SO_2-O_2, ZnO-Al_2O_3-CuO, etc.) at 298–1500–2500 K is carried out. Received theoretically and by calculation way the results for all investigated multicomponent systems are not only well agreed with known experimental data, but also give qualitatively and quantitatively more abundant information on mechanisms of running processes for different compositions and nature.

Quantum-Chemical Investigation of Structural Effects of Ag_{20} in Propylene Epoxidation

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Currently used methods for the production of propylene oxides are energy-intensive and harmful to the environment. Silver containing catalysts have been used successfully in a "greener" epoxidation reaction of ethylene. However, the usage of silver catalysts in the reaction with propylene has been limited by low conversion and low selectivity towards propylene oxide and a detailed understanding of the mechanism is yet to be established.

The main aim of this study was to investigate the influence of the structure of the active center of the tetrahedral Ag_{20} cluster on the mechanism of the epoxidation reaction. Calculations was performed in the framework of DFT/PBE approach with relativistic all electron basis set.

Modeling of $Ag_{20}O$ complexes has revealed that oxygen atom is coordinated on the top and edge atoms of Ag_{20}. $Ag_{20}O$ with oxygen on the top of Ag_{20} is 26 kJ higher in energy than complex containing oxygen atom on the edge of a cluster. Oxygen atom leads to deformation of the initial Ag20 clusters.

Epoxidation reaction on both the top and edge of the cluster goes through the formation of a five-membered oxametallacycle consisting of two silver atoms and a –O-C-C- fragment and four-membered oxametallacycle including a single silver atom and –O-C- fragment correspondingly. At the end of catalytic cycle Ag_{20} cluster restores tetrahedral structure.

These results are essential for the improvement of the efficiency of the catalyst in the selective oxidation of propylene to propylene oxide.

Calculations have been performed using 'Lomonosov' and 'Chebyshev' supercomputer of Moscow State University.

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PP-I-14

Fractal Approach to Acid-Base Heterogeneous Catalysis

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The most important factors determining the catalytic properties of the substances are chemical nature of active sites and surface morphology. Recently, we have improved the fractal approach for quantitative description of an effect of the morphology of a catalyst on its catalytic performance [1]. Previously, the fractal approach has been applied only to the reduction-oxidation reactions, particularly, to catalytic oxidation of various substances [2]. However, it is difficult to correspond the obtained correlations to catalytic activity of the surface active sites. Contrary, for acid-base heterogeneous catalytic reactions activity of solids is determined by the acidity spectrum that can be determined experimentally [3]. As example to apply the fractal approach to acid-base catalysis, we performed a study of the synthesis of ethyl *tert*-butyl ether from ethanol and isobutene catalyzed by various solid acids:

$$C_2H_5OH + H_2C{=}C(CH_3)_2 \xrightarrow{H^+} C_2H_5\text{-}O\text{-}C(CH_3)_3$$

Our study reveals a relationship between the reaction rate (TOF) and the catalyst fractal dimension for different types of acidic catalysts, e.g. mixed oxides SiO_2-Al_2O_3-ZrO_2 and hydrogen ion-exchange resins [3-4]. Based on thermodynamic analysis of the reaction, kinetic studies, and studies of the mass transfer effects we analyzed the catalytic performance of these solids. Our results indicate that catalyst with a more ordered structure, which is characterized by lower fractal dimension, has the better catalytic performance associated with increasing the rate of the adsorption-desorption of reactants and products [4]. The performed analysis also allows one to speculate regarding a structure of the surface activated complex.

These results show that application of fractal approach to acid-base heterogeneous catalysis opens new avenues for correlations between surface morphology and its catalytic properties as well as gives new opportunities for technological design of optimal catalyst for "structure-sensitive" reactions.

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PP-II-1

New Bis(imino)pyridine Nickel Catalysts: Polymerization of Norbornene and Investigation of the Active Species

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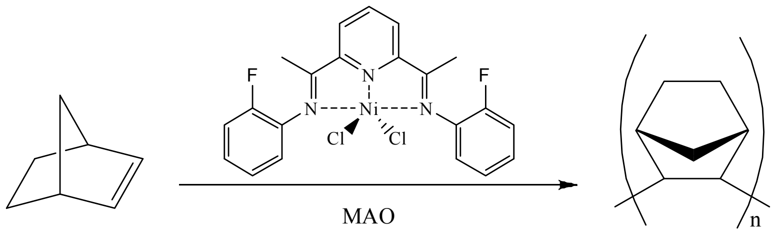
Bis(imino)pyridine complexes of iron(II) and cobalt(II) have captured attention in the last two decades due to their ability to polymerize ethylene into linear PE with high activities [1]. However, these complexes have been applied in polymerization of norbornene with only a limited success, while bis(imino)pyridine nickel(II) complexes with electron-donating substituents were shown to be highly active in vinyl polymerization of norbornene [2].

In the present work, a series of bis(imino)pyridine nickel(II) dichloride complexes containing electron-withdrawing substituents (F, Cl, Br, CF_3) in aryl moieties have been examined in norbornene polymerization, using methylaluminoxane (MAO) as co-catalyst. All complexes display high activities (up to $1.16*10^7$ g PNB*(mol Ni)$^{-1}$*h^{-1}) and yielded high-molecular-weight polynorbornene (M_w up to $4.5*10^6$). The catalytic activity has been found to correlate with the number and position of the electron-withdrawing substituents [3].

Formation of ion-pair intermediates of the type $[LNiMe]^+[MeMAO]^-$ or $[LNiMe]^+[B(C_6F_5)_4]^-$ (where L – bis(imino)pyridyl ligand) has been documented by NMR spectroscopy upon the interaction of nickel pre-catalysts $LNiCl_2$ with MAO or $AlMe_3/[CPh_3][B(C_6F_5)_4]$. The mechanism of polymerization is discussed.



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PP-II-2

Chemistry Carbcations: β-Methyl Shift – a New Rearrangement of the Carbcations Bridged Alicyclic Hydrocarbons

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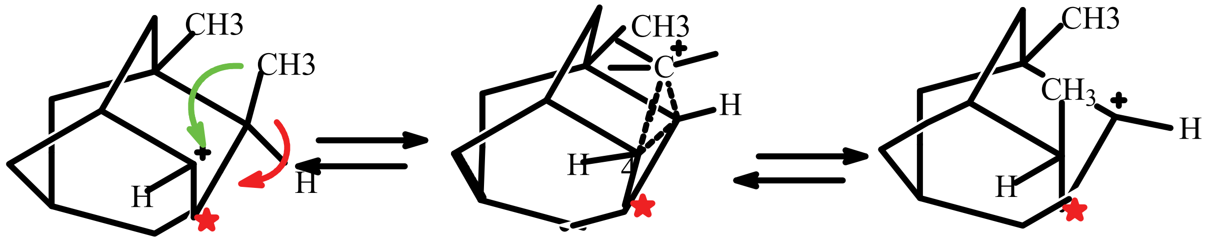
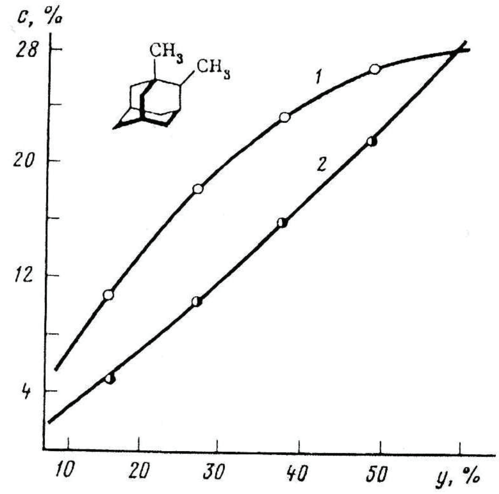
Results of researches on studying of the kinetics and isomerization mechanism of the alkyladamantanes in the presence of the catalysts of acid type are considered by author as detection of a new intramolecular rearrangement of the carbcations bridged alicyclic hydrocarbons – 2,4-moving of the methyl groups (β-methyl shift, BMS). The proof of realization of such rearrangement is direct and primary formation 1,4-dimethyladamantane (c.1, Fig.) from 1,2-dimethyladamatane, passing a formation stage of the thermodynamic much stable 1,3-dimethyladamantane (c.2, Fig.); direct formation 1,3,6-trimethyladamantane from 1,3,4-trimethyladamantane, excepting a formation stage 1,3.5-trimethyladamantane, and also other isomers which formation is impossible to explain by means of known 1,2-methyl shift (α-methyl shift). Rearrangement BMS is realized, mainly, when sterical or electronic difficulties arise for 1,2-movings of methyl groups. Realization of the BMS rearrangement at isomerous transformations of the higher alkyldiamondoids, such as methyldiamantanes, methyltriamantanes etc., also containing in petroleum and gase condensates is quite expected.



1,2-DMA-c

1,4-DMA-c



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PP-II-3

Isobutylalumoxanes as Effective Activators of Dimethylated Zirconocenes in Propylene Polymerization

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Here we present the results on synthesis of isobutylalumoxanes of different composition, their characterization by ^{1}H NMR, as well as their usage as activators of dimethylated isospecific zirconocenes *rac*-$Me_2Si(2\text{-}Me,4\text{-}PhInd)_2ZrMe_2$ (**1**) and *rac*-$Et(2\text{-}MeInd)_2ZrMe_2$ (**2**) in propylene polymerization.

Isobutylalumoxanes have been synthesized by hydrolysis of triisobutylaluminum (TIBA) with (i) $CuSO_4{\cdot}5H_2O$ at molar ratios of Al_{TIBA}/H_2O equal to 4, 2, 1.5, and 1; (ii) water suspension in toluene (2 mol/mol); (iii) diffusion of water vapour into toluene solution of TIBA (2 mol/mol). Method (i) is the most selective in synthesis of desirable alumoxane which mainly depends on the Al_{TIBA}/H_2O molar ratio. This method gives rise to associates of tetraisobutylalumoxane (TIBAO) with TIBA at $Al_{TIBA}/H_2O=4$ mol/mol (IBAO 1), TIBAO, most probably, as dimer at $Al_{TIBA}/H_2O=2$ mol/mol (IBAO 2), oligomeric (IBAO 3), and polymeric (IBAO 4) alumoxanes at further increased water proportion to TIBA. Methods (ii) and (iii) implemented at $Al_{TIBA}/H_2O=2$ mol/mol gave rise to predominantly oligomeric alumoxanes associated with residual TIBA (IBAO 5 (ii), IBAO 6 (ii), and IBAO 7 (iii)) instead of TIBAO. Associates of oligomeric alumoxanes with TIBA (IBAO 3, IBAO 5-7) demonstrate very high activating ability for zirconocenes **1**, **2** at low Al/Zr molar ratios (50-300) in propylene polymerization with activities 2-10 times higher than those with polymethylalumoxane (MAO) at Al/Zr=1000 under other similar conditions. Molecular weights of produced isotactic polypropylenes are also considerably higher, at M_w/M_n~2. Activating ability of IBAO 1 is about one-third of MAO. TIBAO showed no activating ability that does not meet to Galimberti *et* al. results [e.g. 1,2]. IBAO 4 also does not activate **1**, **2**.

So, simple, cheap, and effective way for activation of metallocene precatalysts instead of MAO will be presented.

The financial support from Ministry of Education and Science of RF (Contract N 02.740.11.0646) is acknowledged.

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A Role of Hydroxyl Group in Tunnelling Spectroscopy of Heteropoly Acid Catalysts

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Heteropoly compounds (HPCs) are wide class of nonorganic compounds molecules of which are “natural” nanoparticles. Lately known as effective catalysts these compounds are studied nowdays as new promising nanomaterials with wide possible field of application from nanocatalysis and nanoelectronics to nanobiology and nanomedicine. A great role allocated to HPC in science nowadays imposes the necessity of its development at actual “monomolecular” level. Nowadays this level is only approached by probe methods, first of all by tunneling one, nonvacuum (on air) and ultrahigh vacuum (UHV). In both cases hydroxyl complexes play major role in tunneling spectra and image formation. Such complexes always exist in STM nanocontacts containing HPC molecule which are always deposited on graphite or tip from water solutions. We have showed that in UHV and nonvacuum tunneling spectra the existence of OH-group appears as resonant maxima on I-V dependencies and, thus, negative differential resistance regions (where $dI/dV<0$). It is established that maxima are formed at voltages $|V_0| < \varepsilon_g$ (ε_g – energy band gap, $e = m = h = 1$), at which electron states localized at OH-group and at HPC are in resonance ($\varepsilon_{OH} = \varepsilon_{HPC}$). A model of electron tunneling transport at nanocontacts containing HPC molecule, which takes into account strong field influence (~10^7 V/cm) typical for STM experiments, was established. The model allows to explain experimental data obtained in both nonvacuum and UHV conditions. It was shown that location and form of resonant feature contains quantitative information on electron and vibration spectra of HPC and OH-group. The algorithm of electron level determination was proposed and approved using phosphorus molybdic acid (“typical” example of HPC with Keggin-type anion). Using this algorythm the energy level of OH-group was determined. The data obtained explains correlation between optical and tunneling spectra of heteropoly acid catalysts [1].

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PP-II-5

Mechanistic Scenarios for Homogeneous Catalytic Alkanes Oxidation

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Direct oxidation of alkanes C_1-C_4 to the basic petrochemical products is a promising area of natural and associated petroleum gas processing. It is related to the problem of the C–H bond of alkanes as well as dioxygen activation [1].

We used the following approaches to the design of catalytic systems [2,3]:

(i) Alkanes are activated by compounds of platinum group metals.

(ii) The reducing agent (CO, H_2) and a cocatalyst are introduced to activate dioxygen. The cocatalyst in the reduced form promotes the dioxygen transfer into the two-electron oxidants.

(iii) The compounds of platinum metals activate also the reducing agent and catalyze regeneration of the cocatalyst.

In accordance with the above-listed points, we developed the following catalytic systems: $RhCl_3$ / HI – I_2 – HOI / NaCl, $RhCl_3$ / Cu(I) – Cu(II) or Fe(II) – Fe(III) / NaCl, PdX_2L-L / Cu(I) – Cu(II) , (X = Cl, Br; L-L = α,α- bipy, o-phen) and also studied some aspects of the mechanisms of C_1-C_4 alkanes oxidation. Rhodium peroxocomplexes are mainly active intermediates.

We acknowledge financial support of this work by the Russian Foundation for Basic Research, (RFBR 09-03-00387 and 12-03-00458) and the Program of Fundamental Research of the Presidium of RAS No.3.

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Water-Gas Shift Reaction Catalyzed by Water Soluble Pd Complexes: Kinetics and Mechanism

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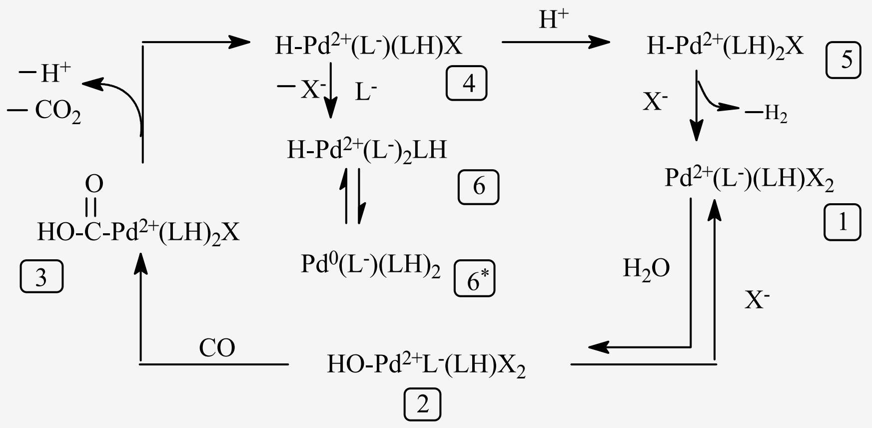
There are some advantages when carrying out water-gas shift reaction (WGSR) in liquid phase as compared with gas phase because equilibrium constant is rather high even at 100^{o}-200^{o}C [1]. Previously we developed an efficient water-soluble catalyst for WGSR based on Pd complexes with diphenyl-*m*-sulphophenyl phosphine (PPh_2PhS) [2].

In this paper we report the results of a study of the kinetics of WGSR catalyzed by $PdBr_2(PPh_2RhS)_2$ and consider probable mechanisms.

The following scheme is the best consistent with the kinetic data from a number of schemes considered:



L^-=Ph_2P-C_6H_4-SO_3^-(*m*) LH=Ph_2P-C_6H^4-SO_3H(*m*)

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PP-II-7

^{1}H NMR Study of Activation of Dimethylated 2-Substituted Bisindenyl Zirconocenes with Triisobutylaluminum and Isobutylalumoxanes in Polymerization of Hexene-1

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The most common and effective activator of metallocene and post-metallocene catalysts in homo- and copolymerization of olefins is polymethylalumoxane (MAO). However the most significant drawback of MAO is the high cost and necessity to use it at high molar excess to the precatalyst (Al_{MAO}/precatalyst=10^3-10^4 mol/mol). That's why the search of new effective and cheap activators or the ways of activation is the task of high priority. In our publications [1,2] we have shown that dimethylated 2-substituted bisindenyl zirconocenes are activated by triisobutylaluminum (TIBA) at low molar ratio Al_{TIBA}/ Zr ~ 10^2 mol/mol. The activity and stereospecificity of such systems in propylene polymerization is commensurable with MAO activated ones. The aim of the work was ^{1}H NMR study of metallocene activation by TIBA and isobutylalumoxanes, the products of TIBA hydrolysis.

Zirconocenes *rac*-Et (2-MeInd)$_2$ZrMe$_2$ (**1**) and *rac*-Me$_2$Si(2-Me,4-PhInd)$_2$ZrCl$_2$ (**2**) were chosen for ^{1}H NMR studies. Analysis of NMR spectra of catalytic systems **1** (**2**)/TIBA and **1** (**2**)/TIBA/hexene-1 showed that, in fact, an activator of dimethylated 2-substituted bisindenyl zirconocene were isobutylalumoxane impurities contained in a toluene solution of commercial TIBA. Experiments with TIBA free from impurities showed the formation of complexes **1** (**2**)·TIBA which were inactive in 1-hexene polymerization. Syntheses of different isobutylalumoxanes by hydrolysis of TIBA are presented. It was shown that isobutylalumoxanes (IBAO) are very effective activators of **1** (**2**) zirconocenes in 1-hexene polymerization at low molar ratios of Al/Zr (10^1-10^2).

Acknowledgement:

The work was supported by the Russian Foundation for Basic Research (project № 10-03-00926-a) and Ministry of Education and Science of RF. (project № 02.740.11.0646).

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The Mechanism of the Controlled Radical Polymerization of Acrylic Esters by Using of New Iniferters on the Basis of Thiocompounds

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In traditional radical polymerizations recombination and disproportionation reactions of radicals are carried out very quickly and, therefore the active centers practically aren't protected from the reactions of bimolecular termination. At enough higher monomer conversions, synthesized polymers are characterized with the broad molecular-weight distributions (M_w/M_n ~3, and sometimes even more than 5) that have significant negative influences on some their properties.

In a controlled/"living" radical polymerization the irreversible bimolecular chain termination is replaced by the reversible reaction of chain growing radicals with the fragments of the initiator and/or special additives - iniferters, introduced into the polymerizate in the "catalytic" amounts. A labile end group, capable in certain terms to disintegrate with the regeneration of initial or new active radical which continues growth of a polymeric chain, appears as a result of chain termination. The process of repeated termination and growth ("sleep" and "life") of the polymer chain provides a stepwise increase in the material chains during polymerization.

The purpose of this research is to investigate the mechanism of controlled/"living" radical polymerization reaction of alkyl-acrylate monomers (in particular, butyl-acrylate and 2-ethylhexyl-acrylate) in presence of different radical initiators (benzoyl peroxide, izo-propilbenzole hydroperoxide, di-cumyl-peroxide, etc) and new iniferters on the basis of organic O,O-di-alkylaryl-dithiophosphates, S-alkyl-aryl-thiophosphates, in particular.

In the chain of growing radical-regulators- iniferters, synthesized by us, the possibility of initiation of polymerization practically absents, which conduces to the synthesis with high yields (90-95%) oligomers and polymers of alkyl-akrylates with very narrow molecular-mass distributions. We set the optimum terms of synthesis of poly-alkyl-akrylates (in particular, poly-butyl-acrylate and poly-2-ethylhexyl-acrylate) with narrow molecular-mass distribution (within the limits of 1,05-1,5), which can be used as viscosity additive for the base motor oils. As the controlled radical polymerization and ordinary free radical polymerization occurs with the participation of radical particles, these processes are characterized by a number of common lines and features, and applicable for polymerization practically of the same range of monomers. At the same time there are some considerable distinctions between them and we'll be report about it in this presentation.

PP-II-9

UV-Visible Spectroscopic Study of Catalystic Systems $Ph_2CCpFluMMe_2$ (M = Zr, Hf) /TIBA/$[Ph_3C_3]^+[B(C_6F_5)_4]^-$

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UV-vis. spectroscopy is very informative tool for studying the activation processes of metallocene complexes [1-3]. It allows not only qualitative identification of the processes in the systems precatalyst/activator but also gives some quantitative information about them. The observed absorption spectral bands energetically reflect the process of ligand-to-metal charge transfer (LMCT) in the complex. LMCT is sensitive to the processes of complexation and cationization which take place under activation of metallocene precursor by traditional activators, such as polymethylalumoxane (MAO), perfluorophenylborates (PFPB) and boranes. The most widely spread PFPB using for activation of dimethylated metallocenes is $[Ph_3C]^+[B(C_6F_5)_4]^-$. However its application for spectroscopy studies is not useful because $[Ph_3C]^+$ absorbs light in visible part of spectrum. To avoid this we used $[Ph_3C_3]^+[B(C_6F_5)_4]^-$ which is transparent in the range 350-700 nm.

In the work the results of spectroscopic study of catalytic systems, containing dimethylated metallocene precursors $Ph_2CCpFluMMe_2$ (M=Zr,Hf) (**Mc**), $[Ph_3C_3]^+[B(C_6F_5)_4]^-$ (**B**) and triisobutylaluminium (TIBA): **Mc**/**B**, **Mc**/TIBA, **Mc**/TIBA/**B**, **Mc**/TIBA/**B**/hexene-1, are presented. The formation of unstable intermediates in **Mc**/**B** systems which decomposed during several seconds was found. It has been shown that addition of TIBA provides stabilization of the catalytic systems. Interaction of TIBA with **Mc** changes the shape of the spectral bands probably due to formation of a complex **Mc·**TIBA (M=Zr, λ=435 nm; Hf, λ=451 nm). Addition of **B** leads to reduction of **Mc·**TIBA bands and appearance of a new bands (M=Zr, λ=467 nm; Hf, λ=533 nm) which may be attributed to cationic species. Introduction of hexene-1 resulted in decrease of this band, and the formation of polyhexene inside of the cell. The absorption band of cationic complex is partially restored in 3 days after total consumption of hexene-1. The quantitative evaluations of LMCT energy of the processes are presented.

The work was supported by the Russian Foundation for Basic Research (project № 10-03-00926-a) and Ministry of Education and Science of RF. (project № 02.740.11.0646).

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Metal Depended Regioselectivity in Carbonylation of Substituted Halobenzenes

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Carbonylation of aryl halides is an example of transition metals catalyzed C-C bond formation. Pd and Co complexes are the main carbonylation catalysts. There is a general stage for these reactions: an activation of an aryl halide with a transition metal complex (OxAdd), which usually is a key step in the catalytic cycle and determines the reaction rate. This is the stage responsible for what will whether the catalyst activate one or another organic substrate.

We have examined the selectivity of substituted halobenzenes carbonylation catalyzed by Co- and Pd-complexes. It turned out that the influence of electronic factors in the substrate and the nature of the halogen on the reactivity is the same for both catalyst systems. At the same time, the steric factor manifests itself differently in these two processes. Substituents in the *ortho*-position to the reaction centre, as a rule, slow the carbonylation catalysed by Pd-complexes. In the case of cobalt catalyst the sign of the steric effect changes, and the carbonylation of substituted bromo- and chlorobenzenes is accelerated as the donor and acceptor substituents are in the *ortho*-position to the reaction centre.

This dependence of the *ortho*-effect sign from the metal nature can be explained within the concept of several possible ways to activate a halide. A key step of the cobalt-catalyzed carbonylation is radical anion non-chain activation of the aryl halide with an anion cobalt complex. In the case of the Pd-catalyzed carbonylation the activation of the aryl halide processes via a concerted mechanism (OxIns). A possibility of the selective synthesis *ortho*- or *para*-substituted benzoic acid by the Co- or the Pd-catalyzed reaction, respectively, is due to this difference.

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PP-II-11

Selectivity of the Nickel (0) Species in the Synthesis of the Polyphenylene-Based Block-Copolymers

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The catalytic system $NiBr_2(PPh_3)_2$ (5 mol%)/ Zn/ Ph-X are capable of providing both the controlled polymerization of styrene and methyl methacrylate [1] and the synthesis of biphenyls [2]. It was also reported that the nickel complexes with the monodentate phospine ligands catalyzed the synthesis of fluorescent polyphenylene-*b*-PMMA copolymers via the polycondensation of *p*-dibromobenzene and polymerization of MMA [3].

Two approaches to study the reactivity of Ni(0) species in the copolymerization of MMA with polyphenylene were applied. First approach was the one-pot nickel-catalyzed synthesis of polyphenylenes from *p*-dibromobenzene and block-copolymers of PMMA initiated by the formed oligophenylenes. The reaction of *p*-dibromobenzene and MMA in the presence of $NiBr_2(PPh_3)_2$ /zinc dust results in polymers with yields of 38 – 97% in 5 hours (M_n~3500). The reaction with the separately synthesized $Ni(PPh_3)_4$ complex was the second one. This catalyst was prepared from $NiBr_2(PPh_3)_2$ by reduction with zinc dust in THF, followed by decantation of its solution from zinc and the addition to the p-dibromobenzene solution of MMA in THF. This reaction affords polymers with the yield of 35% in 5 hours.

$$\mathrm{NiBr_2 + nPPh_3 + Zn \xrightarrow[25^{0}C,\ 15\ min]{THF} [Ni(PPh_3)_n]\ +\ ZnBr_2 \xrightarrow[25^{0}C,\ 20\ min]{BrC_6H_4Br} [BrC_6H_4NiBr(PPh_3)_2] + (n\text{-}2)PPh_3}$$

$$\mathrm{MMA\ +\ BrC_6H_4Br \xrightarrow[65^{0}C,\ 5\ h]{[BrC_6H_4NiBr(PPh_3)_2]} \text{-}(C_6H_4)_n\text{-}(CH_2C(CH_3)COOCH_3)_m\text{-} + PMMA}$$

Addition of the bipy ligand to MMA on the second stage reduces the polymer yield but causes the growth of its molecular weight.Analysis of MALDI-TOF spectra of the polymers prepared with bipy clearly indicates the presence of the three types of macromolecules with various end groups compared to that obtained only with Ph_3P. These facts confirm the difference in mechanisms in both cases.

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Preparation of Ionic Liquids on Base Methoxylpropylamine and Study Their Properties with VO(acac)$_2$ by ESR-Spectroscopy

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In the last 15 years, biphasic catalysis, based on using ionic liquids, has drawn essential attention in scientific community as an alternative medium for reactions in homogeneous catalysis. In respect to electrochemical application, ionic liquids seem to be very attractive for electro sedimentation of metals. A wide range of potentials wherein they are stable, allows one to carry out sedimentation of metals with standard electrode potential lower – 1V at room temperature, what is impossible from aqueous solutions. In this connection, searching for new molecular structures of the ionic liquids with high electro conductivity and low viscosity, with wide electrochemical window and thermal stability represents indubitable interest. One of perspective directions of researches consists in systematic synthesis of alkoxy-alkyl-amine ionic liquids which can be synthesised from accessible and cheap raw material. Surely, physical and chemical properties of this class compounds unknown in literature, while interest to catalytic application of ionic liquids is also growing. In particular, Chinese authors have first prepared acetate 3-methoxylpropylamine and used as catalyst for reactions Anry and Knevenagel [1].

In our work, electro conductivity of acetate methoxylpropylamine was found to be 4.0 мSм/cm. To assign signals in NMR spectra, along with acetate 3-methoxylpropylamine, we have synthesised trifluoroacetate 3-methoxylpropylamine. In NMR ^{13}C spectrum of 3-methoxypropylamine trifluoroacetate, among the strongest signals occurrence multiplet is revealed at 39,5 ppm. (solvent, DMSO), two quartets, apparently, concerning to trifluoroacetate to an ion at 117,2 ppm. (CF_3) and 159,5 ppm. (C=O) and four singlet at 27,3 ppm., 37,0 ppm., 58,0 ppm and 69,1 ppm, concerning accordingly to one methyl group and to three methylene groups.

ESR spectrum of VO(acac)$_2$ in 3-methoxylpropylamine acetate and trifluoroacetate as distinct from VO(acac)$_2$ in absence of solvent has revealed superfine structure.

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PP-II-13

The Role of Complex Aluminum Hydrides and Their Derivatives in the Formation and Operation of Hydrogenetion Catalysts of Group VIII Metals

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The study of Ziegler systems based on transition metals complexes in combination with the hydride and organic compounds of metals of I-III groups in the catalytic hydrogenation had been carried out from the second half of XX century. Despite such a long period of these systems study and their industrial applications, in particular, in the process of hydrogenation of polymers, some aspects of the formation and the nature of the catalytically active species require further fundamental research. First of all this concerns the establishment all of the functions of I-III groups metal compounds in the formation and functioning of Ziegler type catalyst. The report presents the results of studies of systems based on Ni (II), Co (II) and Pd (II) complexes, aluminum complex hydrides or their alkoxy hydride derivatives in hydrogenation catalysis. For these systems the kinetic characteristics (TOF and TON) are determined and the interaction of catalytic systems components is studied by spectral methods. On the example of nickel (II), cobalt (II) and palladium (II) acetylacetonates it is revealed that the $LiAlH_4$ role is not limited by reduction of the metal precursor to the nanoclusters that are 2-3 nm diameter. AlH_4-anions adsorbed on the surface act as stabilizers of nanoparticles. In addition, the AlH_4-anions and the products of catalytic decomposition of $LiAlH_4$ and alan, formed in the redox process, block active sites, thereby reduce or completely suppress the catalytic activity in hydrogenation. Activity of metal clusters in the decomposition of complex hydrides and alan can be arranged in the order: Ni >> Co> Pd. Inhibitory effect of coreagents on the catalytic activity decreases with the change of $LiAlH_4$ by $LiAlH_2$(*tert*-BuO)$_2$ and LiAlH(*tert*-BuO)$_3$. The processes of alkoxy hydrido derivatives side-conversion in the catalytic system is revealed using spectral methods and the most likely scheme of the disproportionation of LiAlH(*tert*-BuO)$_3$ and $LiAlH_2$(*tert*-BuO)$_2$ is considered.

Strategy for the synthesis of highly efficient and well-reproducible nanoscale catalysts is proposed, including the reduction of the metal precursor by $LiAlH_4$ ($LiAlH_n(OR)_{3-n}$) and the subsequent activation by proton donor substance. Alcohols possess the greatest promoting effect of the tested compounds.

Kinetic Schemes Evaluation for Homogeneous Ethane and Propane Dehydrogenation

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We studied mechanisms of homogeneous ethane and propane dehydrogenation under conditions of a wall - less reactor described in the articles [1-3]. The continuous CO_2 - laser was used as an energy source in this reactor. Since ethane and propane does not absorb radiation of the CO_2 laser, it was mixed with ethylene or propylene which are characterized by a strong absorption band at 10.6 μm. The product analysis was made using chromatographic technique.

Propylene was formed in amount of 1–1.5 vol % under any conditions of the ethane pyrolysis. Acetylene was detected at high conversions of ethane. No other product was detected.

The main products of the propane dehydrogenation in tube furnaces are methane, ethylene, hydrogen and propylene. Ethane, acetylene, butane, butene, divinyl are registered in smaller quantity. The products composition of propane dehydrogenation was founded to be similar to the one obtained in the pyrolysis furnaces.

Kinetic model was constructed for the proposed reaction scheme. Because of experiment conditions (high temperatures), the process is described by system of stiff ordinary differential equations, so AL-stable implicit Runge-Kutta methods were used for solving ODEs. To find the constants we used the approach of inverse problems of chemical kinetics. Using genetics algorithms, the constants were found, and confidence intervals of the constants too. Found schemes represent autocatalytic mechanism of the propane and ethane pyrolysis, which has an autocatalytic route with respect to ethylene.

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PP-II-15

NMR Spectroscopic Trapping of Nickel(II)-Alkyl Species in the Course of Polymerization of Ethylene with Neutral Ni(II) Complexes

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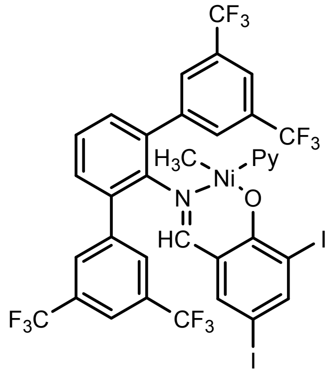

Figure 1. The structure of the complex $\mathbf{1^{Me}}$

The salicylaldiminato complex[1] of Ni(II) [(N,O)Ni(CH$_3$)(Py)] {$\mathbf{1^{Me}}$; [(N,O) = κ^2-*N,O*-(2,6-(3,5-(F$_3$C)$_2$C$_6$H$_3$)$_2$C$_6$H$_3$-*N*=CH-(3,5-I$_2$-2-*O*C$_6$H$_2$)}was used as well defined precursor that enables direct observation of various Ni-alkyl species formed in the course of ethylene polymerization (Figure 1). Nickel(II)-alkyl complexes [(N,O)Ni(alkyl)(Py)], where alkyl = ethyl, *n*-propyl, n-butyl and, probably, n-hexyl were found in the catalyst system $\mathbf{1^{Me}}$/C$_2$H$_4$ (50 °C, toluene–d^8, n(C$_2$H$_4$)/n($\mathbf{1^{Me}}$) = 30/1) at the initial stage of polymerization. At the end of polymerization, these diamagnetic complexes disappear, and two new paramagnetic complexes of nickel(II) (**2** and **3**, [**3**]:[**2**] < 1:3) arise. The quantitative measurements show, that in the course of polymerization, the major part of $\mathbf{1^{Me}}$ converts into **2**. Complex **2** exhibits broad paramagnetically shifted resonances of salicylaldiminato ligand. The chemical shifts of the resonances of **2** substantially increase and their widths decrease with time. Apparently, **2** is a mixture of complexes [(N,O)Ni(R)(Py)], where R is polymeryl ligand. At the beginning of polymerization, **2** contains a growing polymeryl ligand R, and is unobservable by NMR due to some dynamic processes broadening NMR signals. At the end of polymerization, these processes begin to decline, and [(N,O)Ni(R)(Py)] becomes observable by NMR. As polymerization proceeds, more and more nickel atoms become bonded to sterically crowded tertiary carbon atoms of branched polymeryl ligand R. This bonding increases paramagnetism of [(N,O)Ni(R)(Py)] and deactivates complex **2**. Formation of inactive paramagnetic complexes of Ni(II) is a still unexplored route of nickel polymerization catalysts deactivation. The positions and widths of the resonances of **3** do not essentially change in the course of polymerization and with changing temperature. Low paramagnetism of **3** evidences in favor of its dinuclear structure. Tentatively, **3** can be assigned to hydride-bridged nickel(II) complex [(N,O)Ni(μ-H)$_2$Ni(N,O)].

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Clean Synthesis of Adipic Acid Catalyzed by Keggin-Type Polyoxometalate

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The adipic acid is a valuable raw material, used in the production of nylon-6, 6, and food additives. Its industrial production, based on the oxidation of a mixture of cyclohexanol and cyclohexanone with nitric acid, leads to NO_x, pollutant gas, as by-products. An alternative synthetic pathway to this process for an environmentally more friendly is the use of Keggin-type polyoxometalates (POMs) as catalysts which offer a unique structural versatility that makes them possible to tune the composition in function of the requirements of the reaction [1,2]. In the present work, we report the catalytic performance of Keggin-type POMs of formula $M_xPMo_{12}O_{40}$ (M: H, Ni, Co, Fe) for the liquid-phase oxidation of cyclohexanol to adipic acid in the presence of aqueous hydrogen peroxide (30%).

The $M_xPMo_{12}O_{40}$ salts were prepared, characterized by BET method, IR and UV-Vis spectroscopies and XRD and tested in the liquid-phase oxidation of cyclohexanol by H_2O_2 (30%) at 90°C.

Among the POMs studied, $FePMo_{12}$ has no catalytic activity. For other POMs, the obtained catalytic results showed that both amounts and nature of counter–ion influence the adipic acid yields. With an amount of POM varying from 0.031 g to 0.250 g, the highest adipic acid yields, 19.3% for $CoPMo_{12}$, 16.4% for $NiPMo_{12}$ and 13.2% for $HPMo_{12}$ were obtained with a mass of 0.125, 0.062, and 0.125 g, respectively. The high catalytic activity observed in the presence of $CoPMo_{12}$ with respect to adipic acid could be attributed to the simultaneous presence of redox couples Co(III)/Co(II) and Mo(VI)/Mo(V). The mechanism of the liquid phase cyclohexanol oxidation can be similar to that of Mars-van Krevelen

This study showed the efficient POMs Keggin for the direct catalytic oxidation of cyclohexanol to adipic acid with hydrogen peroxide.

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PP-II-17

Nickel-Mediated Cross-Coupling of Aryl Halides with Aromatic Aldehydes

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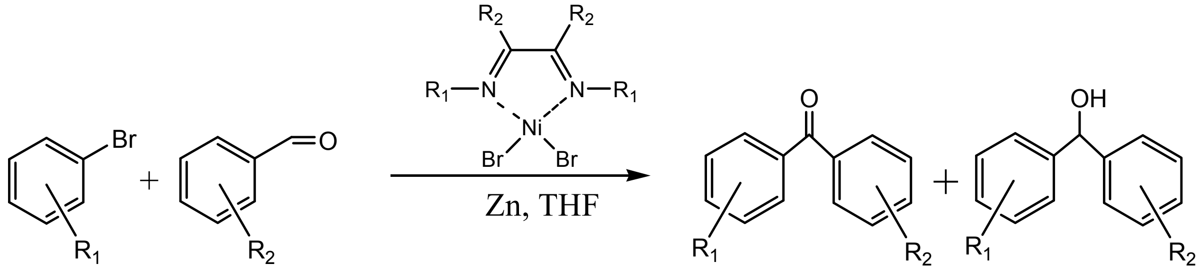
Synthesis of symmetrical biarylketones is an important topic of modern preparative chemistry, since many pharmaceuticals and agrochemicals include the functionalized benzophenone fragments. Nowadays there are few methods of synthesis of the functionalized benzophenones, though all of them possess some drawbacks. Recently, we have studied highly active nickel catalysts bearing diaminobutadiene ligands for homocoupling of aryl halides. Here, we discovered that these systems are efficient for synthesis of the substituted benzophenones and benzhydrols from aryl halides and aromatic aldehydes.

For instance, bromobenzene reacted with benzaldhyde in the presence of 10 mol.% of $NiBr_2(DME)$, 5 mol.% of diazabutadine ligand, and 1 eq. of zinc dust to form a mixture of benzophenone and benzhydrol in THF at 70°C. Under the best conditions, benzhydrol was obtained in as high as 95% yield. On the other hand, benzophenone was found to be a major product under similar conditions, but in the presence of LiCl additive. In this case, benzophenone was obtained in 68% yield.



The studied catalytic reaction goes readily for more commercially available aryl chlorides as well. In this case, benzhydrol can be obtained from chlorobenzene and benzaldehyde in as high as 90% yield. It should be noted that aryl chlorides gave both benzophenones and benzhydrols in better yields than similar aryl bromides.

This report also describes in details the results of our study of cross-coupling of aryl halides with aromatic aldehydes bearing different functional groups. In general case, aryl halides bearing electron-donaiting groups gave the respective diarylcarbinols in higher yields. However, benzhydrols bearing carbonyl, ester or nitryl group can be synthesized in this manner with yields not exceeding 80%.

Nickel-Mediated Cross-Coupling of Aryl Halides with Aromatic and Aliphatic Nitriles

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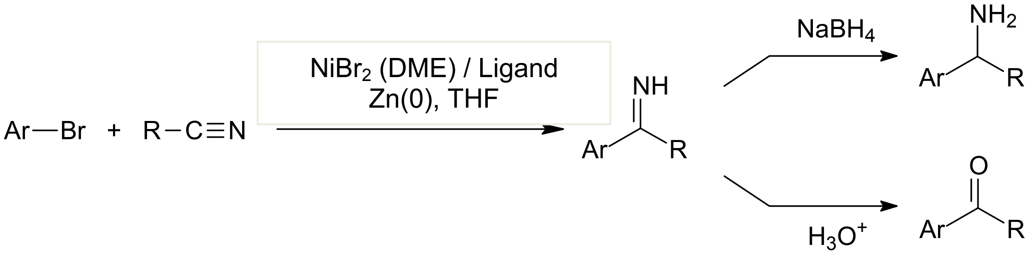
Organic imines are used as pharmaceutical intermediates to obtain pigments and colorants as well as organic photodiode materials. Additionally, imines are precursors of amines which are well-known biologically active compounds. Synthesis of imines including reactive functions via nucleophilic addition of Grignard reagents or organolithium compounds is impossible. An alternative approach, i.e. reaction between the respective ketone and ammonia in the presence of a catalyst at 130°C and pressure up to 200 bars, is technically difficult and cannot be used to obtain many important natural compounds and intermediates.

Nickel complexes bearing different diazabutadiene ligands were found to be active catalysts of coupling reaction between aromatic or aliphatic nitriles and aryl halides. This reaction gave the respective imines in mild conditions. It should be noted that this catalytic reaction was not described in the scientific literature so far, though it is a very useful and convenient protocol to synthesize imines bearing highly reactive substituents.



The studied reaction was found to give imines in high yield at 60-100°C in THF or 1,4-dioxane. Aryl bromides gave higher yields of the desired products than similar aryl chlorides and iodides. For instance, chloro- and iodobenzenes reacted with benzonitryl to give diphenylmethylimine with ca. two times lower yields than bromobenzene. Synthetic capabilities of this method were studied in detail particularly for the synthesis of various substituted imines. It should be noted that the obtained imines can be readily reduced by $NaBH_4$ in methanol to give the respective amines or, alternatively, hydrolyzed to form the respective ketones. Both hydrogenation and hydrolysis reactions gave the target products in almost quantitative yields.

PP-II-19

Modeling of Tetraisobutylalumoxane Structures and its Complexes with Triisobutylaluminum

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Despite the long history of studying the experimental data about structural characteristics of tetraisobutylalumoxane (TIBAO) are still rather ambiguous. Uncertainty occurs because TIBAO is often obtained as a mixture with oligomeric alumoxanes during hydrolysis. It is also known that TIBAO is formed mainly as a dimer [1]. One should keep in mind that TIBA-TIBAO associates may also be formed in the course of synthesis.

Here we report for the first time computed TIBAO structures (monomer and dimer) as well as its associates with TIBA which can be formed in the process of TIBAO synthesis.

Geometry optimization and electronic structure analysis were performed using DFT method implemented in Gaussian. The structures and energy characteristics were rendered using new hybrid long-range corrected functional, which also includes empirical correction for dispersion interactions (ωB97X-D). 6-31+G(d) basis set was chosen for H, C and O atoms, along with LANL2DZ set for aluminum valence electrons and ECP10MWB potential.

The monomeric TIBAO is found to be a linear molecule (<Al-O-Al=180°) with dihedral angle [^{i}Bu]C-Al-C[^{i}Bu] of 106°. NBO charge distribution supports strong polarization of Al-O-Al fragment: +2.06 (Al) and -1.55 (O). The structure is close to that calculated for monomeric form of tetramethylalumoxane [2]. TIBAO dimer structure includes two 3- and 4-coordinated Al atoms. In this configuration ^{i}Bu groups bound to equivalent Al atoms are in perpendicular planes. The lengths of Al-O bonds are 1.741 Å (Al-3) and 1.883 Å (Al-4), while in the monomer they are equal to 1.716 Å. The structural parameters are similar to those of tetratertbutylalumoxane dimer obtained by X-ray analysis [3]. Computed dimerization energy is ~ -60 kcal/mole. Complexation energies of TIBAO with one, two, and three TIBA molecules are evaluated as -39.5, -15.7 and -63 kcal/mol, respectively.

The financial support from Ministry of Education and Science of RF (Contract N 02.740.11.0646) is acknowledged.

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A New Nitrogen-Containing Derivatives of Diterpenic Acids in Asymmetric Catalysis

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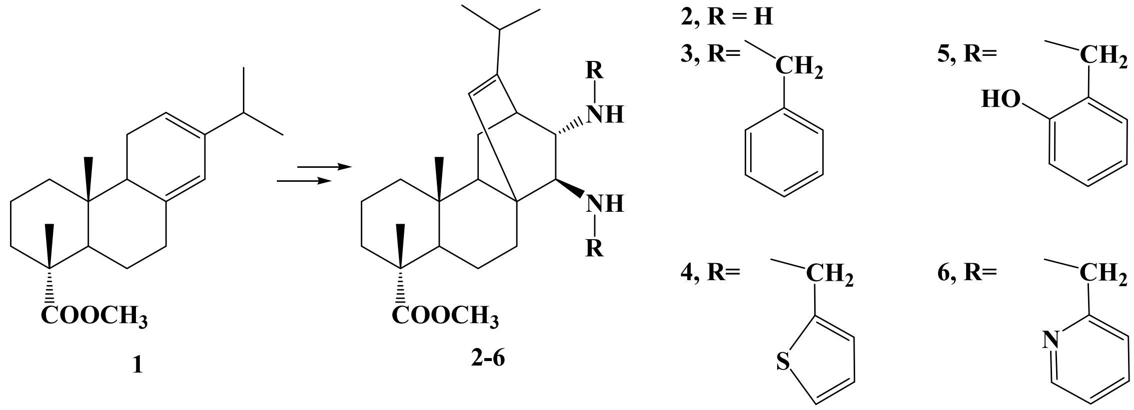
A prospective approach to the synthesis of optically pure compounds is a modification of natural compounds, including terpenes having chiral centers in its structure. Abietic and levopimaric acids are natural tricyclic diterpenes and main constituents of resin acids mixture of the *Pinus Silvestris* galipot. Besides, abietic acid is the main component of colophony.

In our earlier work we have developed the synthetic routes to optically pure amines, Schiff bases and ureas starting from dehydroabietic acid[1]. Further investigations in this area resulted in the development of the new chiral diamine (2) – a diastereomerically pure derivative of fumaropimaric acid. When heated with fumaric acid, methyl ester of levopimaric acid formed methylfumaropimarate, which was further transformed stereospecifically into the diamine **2** by Curtius reaction [2]. Further interaction of the resulting diamine **2** with various aldehydes led to the formation of imines, which were reduced with sodium borohydride to the corresponding diamines **3-6**.



The synthesized new chiral nitrogen containing compounds were used as organocatalysts and ligands for metallocomplex catalysts of asymmetric reactions of oxidation and carbon-carbon bond forming.

References:

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PP-III-1

Low-Level Hydrocracking of Mixture of Baku Vacuum Strippings with Light Gasoil of Coking

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The process of retarded coking which effectively refines petroleum residues is considered as one of the perspective processes of deepening petroleum refining.

At present the trend for further increasing capacities of the retarded coking plants is outlined. However, the gasoil fractions produced in the process, the yield of which makes 50-60 %, have a low stability and a tendency for resinification upon storage that is stipulated by an increased content of unsaturated and diene hydrocarbons in their composition. Nowadays they are mainly used as components of fuel oil which is economically inexpedient.

Large yields and significant resources of gasoil fractions of coking, an increase of demand in diesel fuel caused by enhancement of machine-stock dieseling necessitates their qualified use in oil refinery scheme.

Taking this into account, on the industrial GKD-205 catalyst there have been carried out researches of low-level hydrocracking of mixture of Baku vacuum strippings with light gasoil of coking at 85:15 ratio with the purpose of obtaining ecologically clean diesel fuel and low-sulphur feed-stock for catalytic cracking. The experiments were conducted at $T = 410\text{-}430\ ^{o}C$, $P = 6.0$ MPa, bulk speed of feed-stock delivery 1.0 h^{-1} at a flow-type model installation.

The analysis of the obtained results shows that an increase in the diesel fraction yield makes 30-35 %, total yield equaleing 50-55 %.

The produced diesel fuels with cetane number 49 points, aromatic hydrocarbons content 20 % and sulphur content 0.004 % wt. surpass the requirements of TU 38.1011348-99 for ecologically clean summer diesel fuels according to all indices.

The residue > 360 ^{o}C, isolated from the hydrogenation product, in comparison with the initial muxture has a lower coking capacity, density, sulphur content as well as aromatic hydrocarbons content. Therefore, it is an ideal feed-stock for catalytic cracking process.

Investigation of Mechanism of Oxidative Coupling of Methane to C_2-Hydrocarbons

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It has been studied oxidative coupling of methane (OCM) to C_2 – hydrocarbons in presence as catalyst natural clinoptilolite modified by cations Ca^{2+} and Li^{+}. It was found, that the comparatively high activity in this reaction shows (yield of ethylene -14%,acetylene – 26,4 % in conversion of methane – 70%) delaminated natural clinoptilolite with silicate module SiO_2/Al_2O_3=10,8, containg ions Ca^{2+}-7 weight % and Li^{+}-8 weight %.On this catalyst it has been studied kinetic laws of the reaction of OCM to ethylene and acetylene at atmospheric pressure in the quartz tube reactor with two beds of the same of equal volumes of the catalyst by means a sectional feed of oxygen.

Analysis of the products of the reaction in the outlet of I and II layer of catalyst show that in reactor take place the following reactions.

Oxidative conversion of methane to ethane

$2CH_4 + 0.5O_2 = C_2H_6 + H_2O$

Oxidative dehydrogenation of ethane to ethylene

$C_2H_6 + 0.5O_2 = C_2H_4 = H_2O$

Oxidation of ethane to carbon dioxide

$C_2H_6 + 3.5O_2 = 2CO_2 + 3H_2O$

Oxidation of ethane to carbon monoxide

$C_2H_6 + 2.5O_2 = 2CO + 3H_2O$

Oxidative conversion of ethylene to acetylene

$C_2H_4 + 0.5O_2 = C_2H_2 + H_2O$

On the basis of analysis of literature material and experimental data it has been suggested the mechanism of the reaction of oxidative coupling of methane to C_2H_6, C_2H_4, CO_2, CO and C_2H_2

It has been suggested the stage mechanism of the reaction of oxidative coupling of methane into ethylene and acetylene over natural clinoptilolite modified by cations Ca^{2+} and Li^{+}, developed the kinetic model of the reactions and calculated kinetic parameters of this model.

PP-III-3

The Mechanism and the Optimal Choice of Reactor Type for Heterogeneous-Catalytic Oxidation of Methanol to Methane Acid

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One of the main factors determining the completeness of the calculation of chemical-technological process is the selection of the optimal reactor. To study the process of gas-phase oxidation of methanol on the modified zeolite catalyst it was based on the kinetic model developed for the stationary field of activity of the catalyst and the theoretical results of the optimization. At the same time the possibility of implementing this process in a particular type of reactor was evaluated by comparing the volume of the reaction zone, required to achieve a given degree of conversion in different reactors.

The oxidation of methanol to formic acid was studied in single-stage continuous reactor of ideal mixing and ideal displacement reactor. The results of comparative studies of the process for both reactors are shown in Figure. They were obtained under identical conditions: at the temperature of the reaction zone T = 115^{0}S, partial pressures P_{O_2} = 0,26 atm, P_{CH_2O}=0,21 atm, molar ratio $CH_3OH:O_2:N_2$ – 1:1:2.

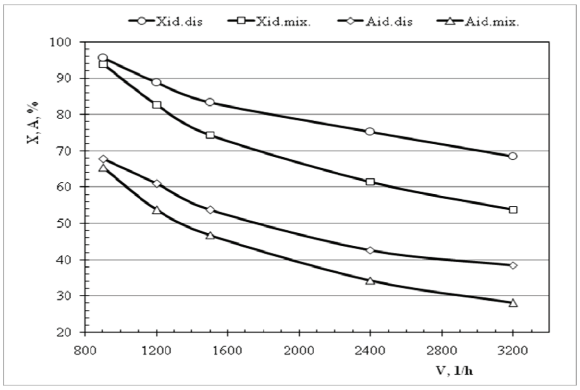

Fig 1. The dependence of the degree of conversion - A and selectivity – X of the process on the volume rate in the ideal mixing reactor (id.mix.) and in the ideal displacement reactor (id.dis.).

From Figure that the utilization rate of the reaction volume for all degrees of conversion in the reactor of ideal displacement greater than in the ideal mixing reactor. With increasing degree of conversion of 60 to 80% of the volume ratio of the investigated reactor increases from 1.22 to 1.38. Similar results were also obtained for other reaction conditions.

The Mechanism of the Reaction of Partial Oxidation of Isobutyl Alcohol over Modified Zeolite Catalyst CuPdCaA

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In the present paper, the results of the investigation of kinetic laws of the reaction of partial oxidation of isobutyl alcohol to isobutyric aldehyde and the results of the study of the mechanism of this reaction are reported.

The results of the investigation on selection of the high efficiency of modified zeolite catalysts for the reaction of partial oxidation of isobutyl alcohol to isobutyric aldehyde showed that the highest yield of aldehyde is obtained over CuPdCaA catalyst, containing 1.0 wt.% - Pd^{2+} and 3.0 wt.% Cu^{2+} and kinetics of this reaction has been studied over this catalyst for determination the mechanism of formation of isobutyric aldehyde. Kinetic experiments were carried out at temperatures 280-380°C, in wide range of change: space velocity and partial pressures of reagents.

On the basis of analysis of literature material and experimental data it has been suggested the probable stage mechanism of the reaction of partial oxidation of isobutyl alcohol over modified zeolite catalyst CuPdCaA. The isobutyric acid formed from interaction between dissosiatively adsorbed oxygen molecules and adsorbed alcohol molecules on the catalyst surface corresponding to the next mechanism (Z - an active site of zeolite):

$$O_2 + 2Z \xrightarrow{k_1} 2ZO$$

$$ZO + i-C_4H_9OH \xrightarrow{k_2} ZO(i-C_4H_9OH)$$

$$ZO(i-C_4H_9OH) \xrightarrow{k_3} i-C_3H_7CHO + H_2O + Z$$

According to this mechanism the kinetic equation for formation isobutyric aldehyde has been obtained:

$$r = k_1P_{O_2}\left\{\frac{\sqrt{1+4\left(\frac{k_1P_{O_2}}{2k_2P_{alc}}+\frac{k_1P_{O_2}}{2k_3}\right)}-1}{2\left(\frac{k_1P_{O_2}}{2k_2P_{alc}}+\frac{k_1P_{O_2}}{2k_3}\right)}\right\}^2,$$

where r – rate of reaction; P_{alc}, P_{O_2} – partial pressures of alcohol and O_2, k_i – kinetik constant of elementary reactions.

On the basis of experimental data the number values of the kinetic parameters has been defined.

PP-III-5

The Catalytic Oxidation of Hydrazine with Nitric Acid in the Presence of Ru and Bimetallic Pt-Ru Catalysts

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The stoichiometry, kinetics and the mechanism of heterogeneous catalytic hydrazine decomposition reaction in nitric acid solutions over 5% Ru/SiO_2 catalysts were studied. The reaction was shown to proceed via formation of gaseous nitrogen, hydrazoic acid and dinitrogen monoxide. Also it was found that the catalyst surface in solutions of HNO_3 is oxidized.

Hydrazine decomposition results from two processes: the catalytic dissociation of hydrazine nitrate on the oxidized catalyst surface accompanying by ruthenium dioxide recovery to a metallic state and the oxidation of hydrazine with HNO_2 catalytically generated in the reaction of metallic Ru sites oxidation with nitric acid. The established mechanism of the catalytic hydrazine decomposition reaction in nitric acid solutions over Ru/SiO_2 catalysts involves the catalytic redox cycle on ruthenium surface atoms implying both the oxidation and the reduction steps to obey chemisorption’s regularities. For this reason it is sensible to consider the overall reaction to be governed by principles of chemisorption.

Bimetallic Ru-Pt catalysts with particles of different size, morphology and Ru/Pt ratio loaded on granulated silica gel were synthesized and examined in the reaction of hydrazine decomposition in HNO_3 solutions. A strong synergistic effect between two metals was observed for bimetallic catalysts in the reaction comparing to monometallic counterparts. While studying influence of the Pt/Ru ratio in the catalysts (from pure Ru to pure Pt at the same total mass loading of metals – 5%) on the reaction rate constants a volcanic curve was obtained having a maximum near 66% (at.) of Pt. The rate constants of the most active prepared bimetallic catalyst (60% Pt, 40% Ru, at. %) exceed these of monometallic Pt catalyst in 4,5 times. This is an apparent illustration of synergistic effect between two metals taking into account the fact that pure Ru catalyst is at least in 3 times less active than Pt one in the reaction of hydrazine decomposition in nitric acid solutions! The explanation of reported synergistic effect phenomenon is expected to be proposed after further investigations.

PP-III-6

Liquid-Phase Oxidation of Halogen-Olefins on the Catalyst Ag/SiO_2

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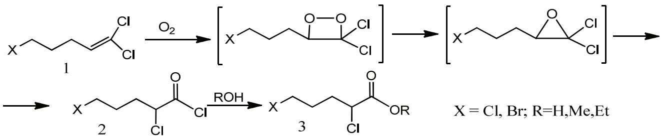
Liquid-phase oxidation (LPO) processes functional groups of organic molecules with air or oxygen, is one of the important areas of organic chemistry and are widely used in laboratory and industrial syntheses [1]. However, the reaction conditions (high temperature and pressure) initiate by-processes and the yield of the desired chlorides of α-halo carboxylic acids not exceed 50 %.
Obviously, the development of efficient catalytic systems and the use of special construction reactors to ensure maximum surface contact of the interacting phases, will increase the rate of oxidation. This will prevent long-term thermal effects on the reaction products and increase the selectivity of their formation. As a promising catalytic system we have chosen Ag/SiO_2 (100-200 μm, 5% Ag) and packed column bubbling reactor [2].

This report presents the process of catalytic LPO of 1,1,5-trichloro-1-pentene and 1,1-dichloro-5-bromo-1-pentene. The choice of these substrates due to the fact that the oxidation leads to the formation of acid chlorides to α, ω-dihalogenvaleric acid 2 (X = Cl, Br), which are widely used in the synthesis of many physiologically active compounds. The interaction can be represented by the following scheme:



The kinetic studies were based on determination of the velocity of substrate consumption and accumulation of reaction products (GLC analysis). The process is characterized by a pronounced induction period of 2.5-3 h. At the same time, after 1.5-2 h of interaction, there is complete homogenization of the metallic silver into the organic phase was observed. It is noteworthy that after the induction period the reaction rate increases dramatically, and after 8-10 hours there is a selective formation of desired products with a yield of 70-80%.

Thus the use of packed bubble reactor and the proposed catalytic system opens up new prospects for LPO process of halo-vinyl compounds in preparative and industrial syntheses, as well as in the utilization processes of halogenated waste.

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PP-III-7

Acid-Base Properties of Zn, Ga- Containing Zeolite Catalysts and their Activity in Associated Gas Conversion to Liquid Hydrocarbons

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Catalytic conversion of associated gas into aromatic hydrocarbons, which are important raw materials for the petrochemical industry, has been studied to utilize its as chemical resources more than 20 years [1,2]. In this report distribution of aromatics in the aromatization of propane and butane fraction over Zn,Ga/ZSM type zeolite are studied. The synthesised zeolite catalysts were characterised by X-ray powder diffraction and X-ray fluorescence analysers. Brönsted acidic-basic properties of Zn, Ga -contain HZSM zeolite have been investigated by IR-spectroscopy of adsorbed probe molecules (CO and $CDCl_3$). The strength of basic sites has been estimated on Proton Affinity (PA) scale. The thermodynamic characteristics of different type of surface OH – groups (PA^{OH} values) have been obtained by using of correlation between PA^{OH} and $\Delta\nu_{OH}^{CO}$. PA values for I types(1650-1520 kJ mol^{-1}), II types (1520-1420 kJ mol^{-1}) and III types of basic sites(1380-1360 kJ mol^{-1}) for ZSM based catalysts have been defined. Thermodynamic approaches to estimate Brönsted basic sites strength on PA from the corresponding PA^{OH} values, which are of great importance for the acid-base catalyzed reactions, have been proposed. The thermal analysis was carried out to determine the thermal stability of the HZSM-5 zeolite and to measure the loss of acidity as a function of temperature.

All catalysts are tested for their performance in associated gas conversion, where the products obtained are classified into three main groups namely, fuel gas- methane and ethane, LPG-propane and butane, and aromatics- benzene, toluene and xylenes.

By combining FT-IR study with catalytic evaluation, it is concluded that Zn,Ga/HZSM-5, which had more than 60% remaining number of Brönsted acid sites exhibited a good catalytic performance. The reaction mechanism for the production of aromatics proceeded via the formation of unsaturated hydrocarbon species are discussed.

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[1] N.Kumar and L.-E. //Catalyses Letters 38(1996)239-244.
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New Silica-Alumina Supports for Pt Ring Opening Catalysts

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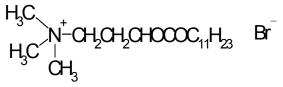
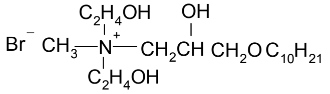
Morphology and texture of silica materials depends on the ratio of reactants, the type of surfactant used, the pH [1], time and temperature of hydrothermal treatment [2] and the chemical nature of the additional compounds entering the stage of the synthesis of materials received. In well ordered mesoporous silica, templating effect is based on electrostatic interactions (cationic, anionic surfactants) or hydrogen bonding (neutral surfactants) [3].

The aim of this study was to synthesized new silica and silica-alumina materials during hydrothermal synthesis. Templates (Table 1) were selected from the point of their biodegradability, economic aspects and availability. Platinum was supported on the obtained silica alumina materials and resulting Pt catalysts (1.5 wt.%) were tested in the transformation of tetralin and decalin (T=300-380 °C, p=5 MPa, H_2:CH=500 Nm^3/m^3; WHSV=2 h^{-1}) to analyze its performance in the hydrogenation (HYD), ring contraction (RC) and ring opening (RO) reactions. The activity of the catalysts obtained was compared with the activity of the Pt/AlSBA-15 catalyst. The content of RC and RO products at 380 °C over Pt/AlSBA-15 catalyst were 5.1 and 5.4 wt.% respectively (decalin conversion – 32 %).

Table 1. Surfactant used in support hydrothermal synthesis.

Template	Labeled	Used in
 $(H_3C)_2(CH_3)N^+-CH_2CH_2CHOOOC_{11}H_{23}\ Br^-$	DMPM-11	Laboratory scale
 $Br^-\ CH_3-N^+(C_2H_4OH)(C_2H_4OH)-CH_2CH(OH)\ CH_2O\,C_{10}H_{21}$	2OHNC-10	Laboratory scale
Ethoxylated alkylamines	ROCKAMIN SRK8	Industry scale
Di-(Nortallow Carboxyethyl) Hydroxyethyl Methylammonium Methosulfate	REWOQUAT WE18	Industry scale

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Research of Activity of the Pt-Ru Catalyst Supported on Metal Block Carriers in the Steam Oxygen Conversion of Methane

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It is known that the production of synthesis gas (a mixture of hydrogen and carbon monoxide) is the first stage of the production of fuels from natural gas. But on this stage it requires about two thirds of material costs in the industrial sector. Therefore, the development of new and improvement of available processes of the production of synthesis gas is an actual problem.

We have carried out a test of a block metal honeycomb carrier with Ø = 10 mm, h = 20 mm with supporting to block the active phase of 1.0% metals with Pt:Ru = 1:1 ratio in the SOC (steam oxygen conversion) of methane into synthesis gas. Thus, the metal block carrier with supported active phase 1,0% Pt-Ru/2%Ce/(θ+α)Al_2O_3 catalyst was investigated in the SOC reaction of methane to determine the effect of changing the $CH_4 : H_2O$ ratio and contact time on the performance of process at T = 1123 K. It was determined that the conversion of methane varied from 50.0% at $CH_4 : H_2O = 1 : 1$ ratio with a gradual increase to 58.1% at 1 : 4 ratio and a further decrease to the initial value of 50.0% at 1 : 5 ratio with high space velocity $1 \cdot 10^4$ h^{-1} with an increase in the system of water vapor. The selectivity by H_2 and CO at all ratios is equal to the maximum value of 100%. H_2/CO ratio varies from 5.4 - 9.3. Complete conversion of methane could not be reached in a given process conditions.

Further during the test of the same metal block carrier with a decrease in space velocity of process up to $1 \cdot 10^3$ h^{-1} with increase of water vapor in system methane conversion increases from 70.0% at $CH_4 : H_2O = 1 : 1$ ratio to 100% maximum value at 1 : 3 ratio and further decreasing to 83.1% at 1 : 5 ratio. The selectivity by H_2 and CO at all ratios is also equal to the maximum value of 100%. The relation H_2/CO increases from 5.1 to 13.3 with increasing amounts of water vapor in the reaction system.

Thus, it was shown that with decrease of space velocity all process indicators are improving, and at T = 1123 K, τ = 3,6 sec, V = $1 \cdot 10^3$ h^{-1} at CH_4: $H_2O = 1 : 3$ ratio complete conversion of methane with 100% selectivity by CO and H_2 is achieved.

Selectivity Control of Pairwise Hydrogen Addition over Catalytic Hydrogenation of C_4 Hydrocarbons on Supported Pt and Pd Catalysts

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In the last few years, parahydrogen-induced polarization (PHIP) became a tool for investigating hydrogenation reactions in heterogeneous catalysis [1,2]. Information extracted from the nuclear magnetic resonance (NMR) spectra of hydrogenation products allows to watch the position of hydrogen atoms which came to the substrate from the same hydrogen molecule. This distinctive feature of PHIP makes possible to explore reaction mechanisms of heterogeneous catalytic reactions. The fact that supported metal catalysts exhibit PHIP effects confirms that pairwise addition of H_2 to unsaturated compounds does contribute to the reaction in some extent even when the reaction occurs at the surface of a metal particle and the dissociation of H_2 on the metal surface with the subsequent addition of random hydrogen atoms to a substrate is expected to dominate.

In this work, the PHIP technique was applied to study the selectivity and the degree of pairwise H_2 addition in 1,3-butadiene, 1- and 2-butynes hydrogenation over supported Pt and Pd catalysts. Series of catalysts with different particle size distribution supported on Al_2O_3, SiO_2, ZrO_2, TiO_2 and carbon were examined. It was found that Pd and Pt catalysts behave differently in pairwise hydrogenation. If Pt catalysts were used in hydrogenation of 1,3-butadiene, all reaction products contained correlated hydrogen atoms, while the same reaction carried out on Pd catalysts led to the observation of polarization only for 1-butene. This selectivity disagreement towards pairwise hydrogen addition can be explained by different structure of active sites and not by the relaxation time differences of product molecules.

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PP-III-11

Heterogenization of Wacker Process over Palladium/Vanadium Catalysts

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Wacker oxidation is catalytic process for the selective oxidation of alkenes by dioxygen to aldehydes or ketones in aqueous hydrochloric acid solution of $PdCl_2$ and $CuCl_2$. The method was elaborated by Wacker-Chemie and Farbwerke Hoechst in 1959 for producing of acetaldehyde from ethylene [1]. By the end of the last century the acetaldehyde production of the world increased to about 2.9 million tons per year and about 85% of this amount came from Wacker plants [2]. The use of solution catalyst has several drawbacks, such as, high corrosivity of HCl in the presence of O_2, formation of undesired chlorinated by-products, low solubility of alkenes in the aqueous solution that strongly limits the reaction rate, difficult separation of the liquid products the solution catalyst, etc. In order to overcome these disadvantages intense research has been launched to develop solid Wacker catalyst for selective vapor phase oxidation. A recent report informs about commercial production of acetic acid by the direct oxidation of ethylene over heterogeneous Wacker-type catalysts [3]. The research to be presented focuses on new heterogeneous Wacker catalysts. The catalysts consist of Pd/V_2O_5 redox system, as active catalyst component, over oxide support, such as, Al_2O_3, TiO_2, SiO_2, layered double hydroxides and smectite clays. The catalysts were characterized by means of thermogravimetry, X-ray diffraction and scanning electron microscopy. Their catalytic activity was tested in vapor phase Wacker oxidation of ethylene by oxygen in presence of water at atmospheric pressure. A fixed-bed flow-through microreactor was used. The effects of catalyst composition and structure on the activity and acetaldehyde/acetic acid selectivity and yield was determined. From results at various space times and reactant partial pressures the kinetics of the reaction was established.

The effect of support and reaction conditions on the vapor phase Wacker oxidation activity is to be interpreted in conjunction with the possible reaction mechanisms.

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Spectral and Catalytic Study of Silica Modified Cr_2O_3/Al_2O_3 Dehydrogenation Catalyst

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Chromia-alumina microspherical catalysts have a great practical importance and are widely used in the C_3-C_5-alkane dehydrogenation process. The effect of the silica modification on the state of the active phase and catalytic performance of chromia-alumina catalyst was studied. The catalysts were prepared by incipient wetness impregnation of monophase boehmite support by aqueous solutions of the chromium and potassium compounds, and subsequent thermal activation. Catalytic properties were studied in the dehydrogenation of isobutane in a fluidized bed at 570ºC.

Catalyst activity and selectivity in the isobutane dehydrogenation process increased by 1.5 and 2 % respectively after modification by 2.5-4.5 wt.% of silica. At the same time an increase of the bands corresponding to the $Cr(III)_{oct}$-ion in the catalytically active Cr_2O_3-clusters on the EPR-, UV-Vis- and Raman-spectra were observed.

It was determined by UV-Vis-spectroscopy that upon modification by SiO_2 on the support surface Cr_2O_3-clusters with a lower energy of ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ electronic transitions in the $Cr(III)_{oct}$-ion formed. According to the heterolytic mechanism of alkane dehydrogenation process, it causes greater interaction between the $Cr(III)_{oct}$-ion and the adsorbed hydrocarbon molecule, the easier hydride-ion elimination and the C=C-bond formation.

The reason of catalyst selectivity increasing upon SiO_2 modification in addition to the formation of catalytically active Cr_2O_3-clusters is a decrease of surface acidity, which was investigated by TPD of ammonia.

PP-III-13

Isoquinoline Derivatives via Stepwise Regioselective sp2 and sp3 C−H Bond Functionalizations

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Considering the importance of cyclic amines and alkaloids in industry as dyes and as pharmaceutical and agrochemical drugs, straightforward and environmentally benign approaches for the preparation of these compounds still represents a challenging task for chemists. Among them, tetrahydroisoquinoline (THIQ) derivatives constitute an important class of compounds with numerous biological properties such as anti-HIV, antitumor, and antipsychotic activities. They are actually produced by multistep methods, and new direct synthetic routes to access THIQ derivatives are highly desired and at the center of active research activities. Main THIQ derivatives arise from the functionalization at position 1 via cross dehydrogenative coupling (CDC) or at position 3 with multistep syntheses.In contrast, functionalization at position 4 is scarce. In recent years, C−H bond functionalization involving activation of inert C−H bonds to allow direct C−C coupling has attracted considerable attention since this type of reaction minimizes the reaction steps and therefore the number of purification processes and the production of wastes and fullfills the criteria of sustainability.

In our laboratory, we have recently described, on the one hand, the first ruthenium-catalyzed C(β)−H functionalization of various cyclic amines and highlighted the formation of reactive enamine intermediates via hydrogen autotransfer processes and, on the other hand, the regioselective palladium-catalyzed C(5) functionalization of five-membered heterocycles.

Oscillatory Behaviour during Oxidation of C_2-C_3 Olefins over Nickel and Cobalt

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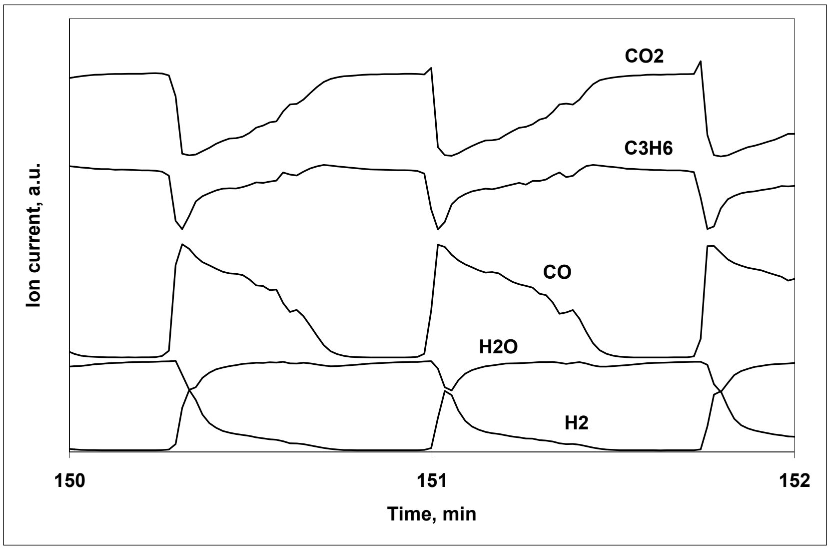
Although oscillatory behaviour during oxidation of C_1-C_3 paraffins over nickel and cobalt was intensively studied in recent years [1,2,3] there are no reports in literature on the oscillatory behaviour during oxidation of light olefins over these catalysts. The goal of the present study was to study the dynamic behaviour of ethylene and propylene oxidation over nickel and cobalt and to find out the oscillatory behaviour in these catalytic systems.

The dynamic behaviour of C_2H_4 and C_3H_6 oxidation over Ni and Co foils was studied using on-line mass-spectrometry and visual observations of the catalyst surface. Oscillations during oxidation of C_2-C_3 olefins over Ni and Co foils were detected at 650-700ºC. Colour variations indicated periodic oxidation and reduction of the catalysts similar to the oscillations during C_1-C_3 paraffins oxidation [3]. The typical example of the oscillatory behaviour, observed during C_3H_6 oxidation over the Co foil is shown below. It can be seen, that CO and H_2 oscillate in phase with similar waveforms, while CO_2 and H_2O produce out-of-phase oscillations with CO and H_2.



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PP-III-15

Supported Heteropoly Acids as Catalysts for Paraffin Isomerization

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Isomerization of n-paraffins over heterogeneous catalysts is one of the efficient ways for motor fuels upgrading, as well as for production of various organic compounds.

In the present work the results of n-hexane isomerization at temperature range 270 - 330 ^{o}C are established. Silica supported P-Mo, P-W, Si-Mo and Si-W type heteropolyacids (HPA) were applied as catalysts in this study. In particular, $H_3[PMo_{12}O_{40}]$ - HPA-1; $H_3[SiMo_{12}O_{40}]$- HPA-2; $H_4[PW_{12}O_{40}]$- HPA-3 and $H_4[SiW_{12}O_{40}]$- HPA-4 were synthesized.

Testing of catalytic activity was conducted over the samples with about 20% (wt.) of supported HPA. It was found that P-Mo and Si-Mo heteropolyacids (HPA-1 and HPA-2) did not show any substantial activity in n-hexane isomerization. However, P-W and Si-W heteropolyacids (HPA-3 and HPA-4) demonstrated somewhat higher activity than those of HPA-1 and HPA-2. For instance, yields of isomerization products (2-methylpentan and 3-methylpentane) over HPA-3 and HPA-4 were 0.8 and 2.4%, respectively.

Addition of Ni to silica supported HPA samples in amount 2% (wt.) drastically increased their activity with respect to isomerization products formation. Among them HPA-4 showed the best catalytic performance providing yield of isomerization products 25.5% at selectivity 82.5%.

Substantial increase of catalytic activity observed for Si-W HPA is due to higher acidity than that of other HPA samples [1]. Introduction of Ni enhanced the rate of dehydration stage of entire isomerization process [2] to form surface hydrogen atoms.

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Formation of Active Sites in NiZn/UDD Catalysts for the Selective Phenylacetylene Hydrogenation as Monitored by *in situ* EXAFS

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One of the most important problems in modern catalysis is the development of targeted approaches to the formation of active centers of a given composition and structure. The solution for this problem in addition to the expansion of tools for the directed synthesis is to provide detailed control of the structural characteristics of the catalyst directly in the process of its preparation and subsequent chemical modification. For this purpose methods of structural diagnostics in situ, including those based on X-ray synchrotron radiation are more and more often used worldwide.

In this work, the formation of active sites in NiZn bimetallic catalysts supported on ultradispersed diamond (UDD) is studied by temperature-programmed reduction with simultaneous monitoring of metal state changes by X-Ray absorption spectroscopy (EXAFS/XANES) in situ. These catalysts show high activity in the selective hydrogenation of carbon-carbon triple bonds to double bonds.

Catalyst precursors were prepared by impregnation from an aqueous solution of nickel and zinc nitrates (molar ratio 1:3), followed by drying and calcination in air (150°C, 2:00). For measurements a pressed pellet of a catalyst was placed in a gas stream 2% H_2 in He, and subjected to gradual heating. It was found that with the temperature increase two types of processes of changes in the state of nickel were activated. At T ~ 300°C the process of ordering of initially amorphous NiO begins with no change in the overall oxidation state of nickel atoms. At 400°C a slow chemical reduction of nickel sites to the metal state begins. The fraction of Ni (0) increases to ~ 25% within 4.5 hours and then ceases to change. This means that only specific types of Ni sites undergo reduction under these conditions. The chemical state of zinc remains essentially unchanged.

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PP-III-17

Sulfur-Promotion in Conjugated Isomerization of Safflower Oil over Bifunctional Structured Rh/SBA-15

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Catalytic hydrogenation of vegetable oils is an important process in the food industry to achieve techno-functional properties and oxidative stability. One drawback of this catalytic process is the isomerization side reaction of the naturally occurring *cis*-double bonds to *trans*-fatty acids (TFA) linked to coronary health diseases [1]. However, all *trans* fatty acids are not unhealthy, some conjugated linoleic acid (CLA) isomers are reported to have anticarcinogenic, -atherogenic, -diabetic and lean body mass-enhancing properties [2]. The sulfur effect on CLA isomer formation during the dual hydrogenation/directed isomerization of safflower oil over a bifunctional highly structured rhodium-based catalyst Rh/SBA-15 (1 wt. % Rh) was investigated either by direct addition of increased concentrations of 3-mercapto-1,2-propanediol to the reaction medium or by doping Rh/SBA-15 with the same sulfur-based (0.02 wt. %S + 1 wt. % Rh). The results obtained from partial hydrogenation and isomerization of safflower oil over these catalysts at high temperature (180°C), low hydrogen pressure (4 psi) and stirring rate (300 rpm) showed that it is technically possible to promote conjugated isomerization at the expense of *cis-trans* isomerization [3]. The CLA contents obtained with 0, 0.2, 1, 2, 5 and 10 ppm sulfur addition are 70, 100, 130, 110, 105 and 70 mg CLA/g oil respectively. These results suggest that there is an optimal ratio of sulfur to rhodium for CLA formation in safflower oil during the hydrogenation.

The sulfur promotion is explained mechanistically in particular with the rhodium sulfide (Rh-SH) formation more nucleophile than the hydride rhodium (Rh-H) and induces more easily the addition/elimination steps necessary for the double bond conjugation of linoleic acid.

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Preparation and Characterization of Nanosized Ni-Co/Al_2O_3 Catalysts Prepared by Polyol Method for Partial Oxidation of Methane

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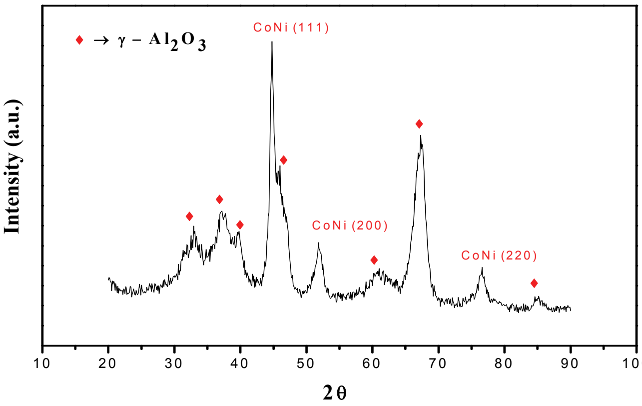
Extensive studies are being undertaken in academia as well as in industry to develop energy-efficient processes for production of hydrogen. Eventually catalytic partial oxidation process came out to be prominent as a good alternative Methane is referred to be the most significant source of hydrocarbon as it is the major component of natural gas and natural gas exists on earth profusely. Even though noble metals are relatively stable and active in catalytic partial oxidation process[1], high cost and limited access to those metals made Ni and Co based catalysts as best alternative in catalytic partial oxidation of methane . In order to improve these problems, in contradistinction to traditional catalyst preparing methods Ni-Co bimetallic catalysts were successfully prepared by polyol method on alumina support in the presence of protecting agent. CoNi alloy particles as a ferromagnetic metal-based materials were synthesized via polyol process [2] but the reduction of $Ni(Ac)_2$ and $Co(Ac)_2$ in ethylene glycol for the preparation of spherical bimetallic nickel-cobalt nanoparticles supported on γ-Al_2O_3 as a catalyst has not been studied. The weight ratio of [(PVP)]/metal] was fixed at 2. The crystal structure was determined by X-Ray diffractogram. The results indicate that the NiCo (fcc) phases are dominant. Also in terms of characterization studies of those catalysts TG-DTA, HRTEM, BET, TPD and AAS analysis will be performed. The activity, selectivity and stability tests of catalysts for partial oxidation of methane will be made on GC-Micro-reactor System existing in our laboratories.



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PP-III-19

Hydrotalcite-Like Catalytic Materials Obtained from Industrial Wastes for Oxidation of Sulfur Compounds

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This contribution concerns the preparation, characterization and the catalytic activity of hydrotalcite-like (HT) materials obtained from red mud (RM) industrial waste in the oxidation of sulfide ions from wastewaters with air. Several hydrotalcite-like compounds with the general formula $Mg_xAl_{0.75}Fe_{0.25(RM)}$ (where x = Mg/(Al+Fe) = 2-5) have been prepared by co-precipitation at constant pH = 10 using red mud as the main source for Fe cations. Taking into account the chemical composition of the red mud, the amounts of Al and Mg were adjusted in order to obtain the desired molar ratio Mg/(Al+Fe) using aqueous solutions of $Mg(NO_3)_2x6H_2O$ and $Al(NO_3)_3x9H_2O$. NaOH and Na_2CO_3 aqueous solutions were added in order to adjust the pH and favour the precipitation of the hydrotalcite-phase. For comparison purposes, hydrotalcite-like materials $Mg_xAl_{0.75}Fe_{0.25(HT)}$ with the same Mg/(Al+Fe) ratio were prepared according to the standard co-precipitation method at low supersaturation using aqueous solutions of Fe, Al and Mg nitrates, NaOH and Na_2CO_3 [1]. The solids have been characterized by XRD, DRIFTS, DR-UVVis-NIR, BET and their surface base sites were determined using a method consisting in the irreversible adsorption of organic acids with different pK_a [2]. The catalytic tests were performed during 2 h under continuous stirring at room temperature using different air flows in the range 1.8 – 5.4 L/h and sulfide concentrations in the wastewater varying from 50 to 200 mg/L. XRD results showed that $Mg_xAl_{0.75}Fe_{0.25(RM)}$ materials have a slightly modified HT-structure compared to the corresponding $Mg_xAl_{0.75}Fe_{0.25(HT)}$ materials. The catalytic tests results could be well correlated to the variation of the number of weak and medium strength base sites of the catalysts confirming the important role played by the basicity in the reaction mechanism.

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Ni-Based Catalysts for Reforming of Methane with CO_2

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Reforming of methane with CO_2 (dry methane reforming) for production of hydrogen or synthesis gas has attracted academic and industrial interest because offers additional advantages compared to other methane reforming processes. Ni-based catalysts have been found to exhibit high activity in dry methane reforming, but they deactivate very fast under reaction conditions due to the sintering of the active metal phase and carbon deposition. Different approaches have been attempted to avoid carbon formation, using different kinds of carriers [1] or addition of a small amount of noble metal [2].

Different oxides like δ,θ-Al_2O_3, $MgAl_2O_4$, SiO_2-Al_2O_3 and ZrO_2-Al_2O_3 were used as supports for Ni catalysts. The samples were characterized with different techniques: XRD, DRS, TPR, TPO and HRTEM. The effect of support composition on the structure and catalytic behaviour of Ni catalysts in dry methane reforming at 923 K was studied. It was shown that the activity of the catalysts increases in the following order: Ni/SiAl $<$ Ni $<$ Al $\cong$ Ni/ZrAl $<$ Ni/MgAl, which is in a good correlation with carbon resistance ability of catalysts. It was concluded that the best catalytic properties of Ni/MgAl catalyst is due to the smallest size of metal particles of 5.1 nm, caused by the strong interaction between Ni species and $MgAl_2O_4$ support.

Acknowledgment:

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Mechanism of Hydrogen Oxidation on Silver

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The present work concerns of the reaction mechanism of hydrogen oxidation by molecular oxygen on silver. This reaction is essential for catalytic science as a model catalytic redox reaction.

The rate of hydrogen oxidation by oxygen over silver was measured varying the composition of the reaction mixture at three temperatures of 473, 448 and 423 K and pressure of the reaction mixture $P_{H_2} + P_{O_2} = 1$ kPa. The study was carried out by flow differential method. The sample of metallic silver catalyst was prepared by hydrogen reduction of the silver oxide, which was precipitated from silver nitrate aqueous solution by potassium hydroxide. The measured reaction rate dependences on the composition of reaction mixture are shown at Fig. 1. Expectedly, the maximal rate is achieved at stoichiometric composition. With an excess of oxygen the reaction rate linearly depends on the composition of the reaction mixture and follows the kinetics of the step (III) with an activation energy of 43,5 kJ/mol. At the excess of hydrogen, the reaction rate sharply diminishes which indicates the complexity of the process and can't be explained by the previously proposed mechanism [1]. In this range, reaction rate is determined by the step (I) with an activation energy 82 kJ/mol. The apparent activation energy of reaction at stoichiometric composition of

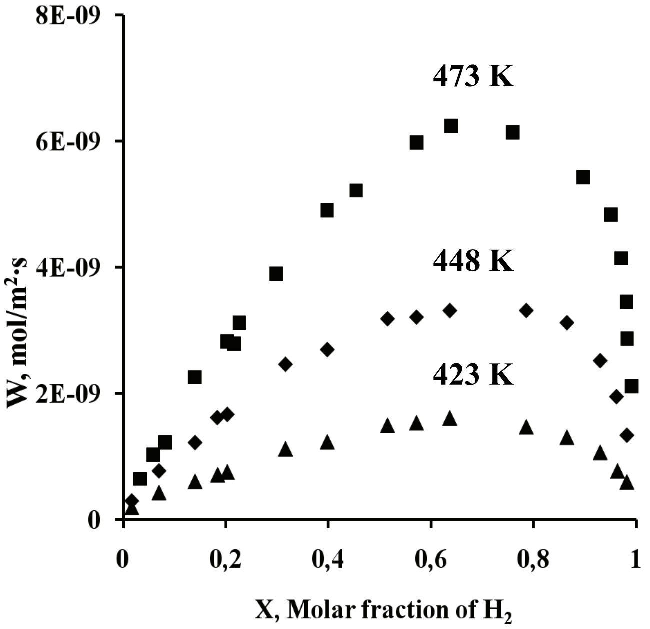

Figure 1. Effect of gas composition and temperature on the reaction rate

$$O_2 = 2O_{ads} \quad \text{(I)}$$

$$H_2 + 2O_{ads} = 2OH_{ads} \quad \text{(II)}$$

$$H_2 + OH_{ads} = H_2O + H_{ads} \quad \text{(III)}$$

$$2OH_{ads} = H_2O + O_{ads} \quad \text{(IV)}$$

the reaction mixture is 45 kJ/mol. Literature and experimental data, the calculation indicate a complex mechanism of the process, which includes at least four stages, including the hydrogenation (III) and disproportionation (IV) of the produced hydroxyl groups [2].

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PP-III-22

Mathematical Modelling of Benzene with Ethylene Catalytic Processing

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Raw materials for ethylbenzene synthesis are benzene and ethylene, which interact in presence of aluminium chloride complex, alkylaromatic hydrocarbons and hydrogen chloride forming the desired product. The main application area of ethylbenzene is the production of styrene as raw material for polystyrene obtaining production. Moreover, ethylbenzene is used in manufacturing of synthetic rubber, propylene oxide, cellulose acetate, as a component of automotive and aviation fuel.

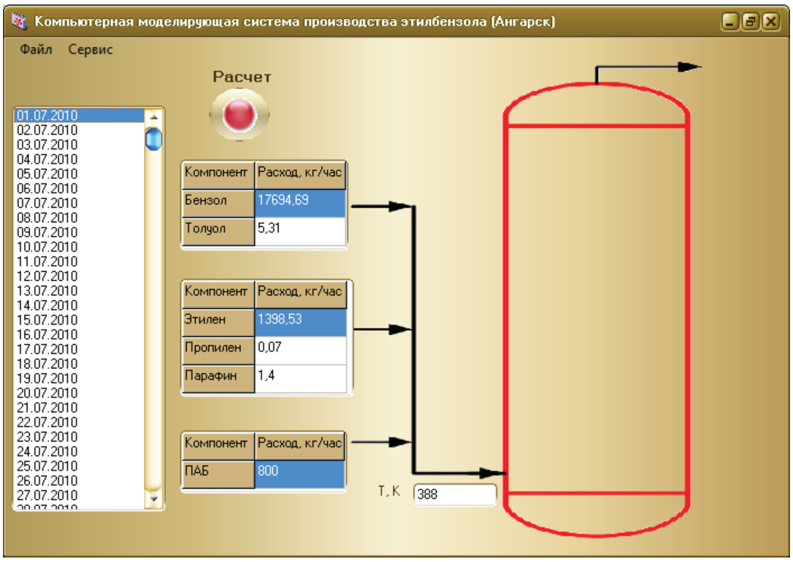
As is evident, use of ethylbenzene is widespread; therefore, task of its production efficiency improving is urgent.

One of the promising instruments of various parameters on yield and quality of the product influence investigation is method of mathematical modeling, which allows efficiency of existing production increasing without significant upgrades and associated costs.

Based on the mathematical description computer modeling system was created.

This program takes physic-chemical characteristics of process into account and allows choosing optimal technological parameters and predict work of the plant.

Active window of the program is shown in fig. 1.



Компонент	Расход, кг/час
Бензол	17694,69
Толуол	5,31

Компонент	Расход, кг/час
Этилен	1398,53
Пропилен	0,07
Парафин	1,4

Компонент	Расход, кг/час
ПАБ	800

T, K 388

Fig.1. Active window of the program

Developed on the basis of physical-chemical laws program will not only allow choosing of plant optimal conditions, but also to predict its work.

Structure and Catalytic Activity of Ag-Containing Zirconium Phosphates

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Acetaldehyde is used as an intermediate for production of ethyl acetate, butyl aldehyde, pyridine, etc. It can be synthesized by selective oxidation of ethanol or ethylene, hydration of acetylene and ethanol dehydrogenation. Taking into account the increasing interest to the processing of biomass-derived feedstock, particularly, bioethanol, the development of efficient catalytic systems for the alcohol transformation into useful derivatives is an important stage of "green" chemical technology development.

In the present work a comparative investigation of the structure features and catalytic performance of Ag-containing zirconium phosphate (AZP) and zirconium phosphate-silicate (AZSP) with NZP-type structure in the low-temperature transformations of ethanol has been carried out. The catalysts were characterized using HRTEM, XRD, FTIR, TPR, etc. Ethanol transformations were studied in the anaerobic and oxidative dehydrogenation conditions.

It was shown that silver zirconium phosphate-silicate as prepared contained anisotropic Ag particles, $Ag_n^{\delta+}$ clusters and ions. Silver particles on AZP sample were formed only after reduction treatment in H_2-containing flow. The sizes of Ag particles in the AZP-H_2 catalyst were from 2 nm to 1 μm with the predominant sizes of 5-10 nm according to HRTEM data. Distribution of Ag particles on the surface of the AZSP catalyst was more uniform and average size of particles was 5-7 nm. Ag particles were partially encapsulated by SiO_2. Maximum yields of acetaldehyde (74-76 %) for both catalysts were observed under the oxidative dehydrogenation conditions. The profiles of ethanol conversion and acetaldehyde yields for the AZPS catalyst contain low temperature peak at 433-453 K in both the anaerobic and oxidative dehydrogenation conditions. According to TPO/TPR data silver species, which were able to oxidized/reduced reversely, were formed on the catalyst surface in a temperature range of 433-453 K. The mechanism of active surface formation has been proposed.

PP-III-24

The Study of Adsorption of Benzene by IR Spectroscopy

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One of the main factors determining the scientific and technical progress in the petrochemical industry is the creation a high-performance methods of catalytic transformations of hydrocarbons. But the solution of this important problem is impossible without a detailed and comprehensive study of the mechanisms of catalytic processes.

In this paper studied the adsorption of benzene on 20%V_2O_5-5%MoO_3-2%P_2O_5/TiO_2 catalyst at the optimum reaction temperature was studied by IR spectroscopy method. The absorption bands at 3050, 3130, 3180 cm^{-1} were observed during the adsorption of benzene at 643K in the IR spectra. This group of bands belongs to the valence vibrations of C-H bonds, and a.b. at

1500 cm^{-1} - to the vibration of ν (CC) bond. Intense absorption in the spectra of benzene, located in the region below 900 cm^{-1} belongs to deformation vibrations of the C-H of aromatic ring (680 cm^{-1}). A.b. at 1390 cm^{-1} observed in the spectrum of adsorbed benzene, according to [1, 2], shows the formation of π-complex for the adsorbed benzene.

Thus, the adsorption of benzene from 20%V_2O_5-5%MoO_3-2%P_2O_5/TiO_2 catalyst occurs with the deformation of the molecule and the loss of aromatic character of the benzene molecule due to localization of double bonds (1500-ν (C = C) with forming of π-complex. Thus, the adsorption of benzene on the 20% V_2O_5-5% MoO_3-2% P_2O_5/TiO_2 catalyst occurs with the deformation of the molecule of benzene and the loss of aromatic character by localizing double bonds (1500-ν (C = C) with the formation of π-complex. Disturbance of the a.b. 680 cm^{-1} shows that benzene is adsorbed flatly on the surface of the catalyst and reacts with the acid centers [3].

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Carbon Nanotube Synthesis by CCVD Process: Kinetic Study on a Ni-Mo/MgO Catalyst

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A kinetic study was performed to determine the kinetic rate expression of methane decomposition into carbon nanotubes by catalytic chemical vapor deposition over a Ni-Mo/MgO catalyst using methane as the carbon source. A mass spectrometer was used to determine experimental reaction rates for methane partial pressures ranging from 0.1 to 0.9 atm balanced by hydrogen or hydrogen-helium and for three temperatures: 925°C, 975°C and 1000°C. Three kinetic models based on different mechanisms were fitted onto experimental data. They differ by the presence of one or two types of active sites and by the nature of active sites involved in the rate-determining step. In this study, hydrogen seemed to influence the catalytic activity rather than the kinetics of carbon nanotube growth. A statistical study is performed in order to discriminate between the different models and to validate the good agreement between the chosen model and the experimental data. As the models correspond to different mechanisms, the discrimination allows a better understanding of the elementary steps involved in carbon nanotube production. The best model involves the dissociative methane adsorption followed by the decomposition of the adsorbed methyl group, which is the rate-determining centre. The activation energy of methane adsorption was found to be equal to 79×10^3 kJ kmol^{-1}, while the activation energy of adsorbed methyl dehydrogenation was found to be equal to 221×10^3 kJ kmol^{-1} [1].

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PP-III-26

Study of the Liquid-Phase Isobutane Alkylation with Butenes over Aluminum Chloride Complexes Synthesized *in situ* from Activated Aluminum and *tert*-C_4H_9Cl

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The liquid-phase reaction between isobutane and butenes at 303 K and 2.5-3.0 MPa has been investigated using a model system [1]: aluminum activated by liquid Ga-In eutectic (Al*) and *tert*-butyl chloride (TBC). Molar ratio TBC:Al* was variable 0.35-4.0. It has been demonstrated by ATR/FTIR spectroscopy that the catalytically active aluminum chloride complexes forming *in situ* in the hydrocarbon medium vary in composition and structure. Alkylation as such takes place at equimolar proportions of the components (TBC:Al*=1:1). According ATR/FTIR data, the most abundant aluminum complexes resulting under these conditions are the $Al_2Cl_7^-$ and $AlCl_4^-$ ions and probably, the molecular complex $AlCl_3$ x *sec*-C_4H_9Cl. In a fourfold excess of TBC over Al* at butenes mass feed rate of 2.5 h^{-1}, isobutane undergoes a reaction of the self-alkylation. In this case, the most abundant complexes are $AlCl_4^-$, $Al_3Cl_{10}^-$ and the molecular species $AlCl_3$ x *tert*-C_4H_9Cl. The $Al_2Cl_7^-$ ion is not detected.

Thus, we propose that the observed direction of isobutane with butenes is due to the presence of the active form of the HCl x [$Al_2Cl_7^-$] complex. The scheme of possible catalytic cycle of this reaction is examined.

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Oxygen Isotope Exchange and Pressure Relaxation of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

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Barium—strontium cobaltites doped with iron are promising cathode materials for advanced electrochemical devices. Detailed understanding of the processes occurring on the boundary between oxygen in the gas phase and the oxide is necessary to improve the performance of devices in which these materials are used. In this work the oxygen exchange kinetics of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ has been investigated.

The oxide samples were analyzed by the following methods: *i*) the phase composition was determined by X-ray powder diffraction on a Rigaku diffractometer using CuKα-radiation at room temperature in air; *ii*) the elemental composition was checked by X-ray fluorescence spectrometry on a XRF-1800 spectrometer; *iii*) the microstructure of the samples was studied by SEM on a JSM 5900LV with INCA Energy spectrometer. Prior to the SEM investigations, the samples were grinded and polished on a Struers machine after epoxy impregnation in vacuum.

The kinetics of the interaction between gaseous oxygen and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ has been studied by *i*) pressure relaxation ($T = 450$—$750°C$, $Po_2 = 10^{-3}$—$10^{-1.5}$ atm) and *ii*) ^{16}O-^{18}O isotopic exchange with gas phase analysis ($T = 550$—$800°C$, $Po_2 = 10^{-3}$—$10^{-1.5}$ atm). The rates of equilibration, interphase exchange, and of the three exchange types [1], and the oxygen diffusion coefficient have all been evaluated from the experimental data. The first and third exchange types are found to prevail in oxygen exchange on $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$. The dependences of the rates of equilibration, interphase exchange and overall exchange on oxygen partial pressure have a power-law form. The order of the equilibration rate dependence is close to ½, which corresponds to the order for the overall exchange rate. For the interphase exchange rate and the third exchange type rate the orders are close to unity. The interphase exchange rates are found to be in good agreement with previous values measured by the pulsed isotope exchange method [2]. In this work, the mechanism of oxygen exchange is discussed for two cases: pressure relaxation and isotope exchange with gas phase analysis.

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PP-III-28

Influence of Support Treatment with Inorganic Solutions on Properties of Glass and Basalt Fiber Catalysts

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Catalytic properties of glass and basalt fiber catalysts containing transition metal oxides for CO and CH_4 oxidation reactions have been studied. Earlier investigations revealed [1] that preparation of catalysts by impregnation with nitrate solution resulted in formation of nickel oxide particles 11 nm in size on the fiber surface. In order to obtain a uniform catalytic layer with highly dispersed nickel oxide on the glass and basalt fiber surface, increase a specific surface area, we studied the influence of the fibers treatment with 20 % HCl solution (I way), 0.1 N solution of nitric acid with subsequent impregnation with Na_2SiO_3 (II way) and temperature of impregnation solution on dispersion of active sites and its interaction with fiber surface and metal content, specific surface area, acidity and catalytic activity of obtained catalysts.

Investigation of catalysts using TEM and SEM methods showed the preparation method according to the first way resulted in formation of nickel oxide particles 2.5 nm in size on the fiber surface. The treatment according to second way results in uniform distribution of nickel oxide particle with a size 1 nm on fiber surface. Impregnation by the third way at 130ºC results in uniform distribution of thin nickel oxide film on glass fiber surface. Reduction peaks of hydrogen (TPR) indicated that all ways of catalysts preparation lead to formation of strongly interacted with basalt and glass fiber surface catalytic layer as the desorption of hydrogen occurs at 350ºC. Basalt fiber catalysts treated with hydrochloric acid showed lower ignition temperature and temperature of full conversion determined by thermo-programmed oxidation of CO and CH_4 than untreated catalysts. The specific surface area of basalt fiber catalysts after the treatment increased from 1.68 to 2.89 $m^2 \cdot g^{-1}$. However the specific surface area, ignition and full conversion temperatures of CO and CH_4 unchanged after the treatment.

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PP-III-29

Supercritical Fluid – CO_2 Regeneration of the Nickel-on-Kieselguhr Catalyst

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The nickel-on-kieselguhr supported catalyst is employed for purifying isoprene from acetylene compounds, more specifically butyl acetylene and isopropyl acetylene. During the process catalytic reactivity reduction is occurred, because the deposition of coke at the catalyst surface.

The composition of decontaminant was determined by IR-spectroscopy. Essentially there are products of reaction: isoprene's oligomers, isoamylenes cis- and trans-, isopropyl group compounds and loose oxidation products.

In the first series of experiments, the regeneration of the catalyst was implemented using pure SC CO_2 at temperatures of 343 K and 423 K and pressures of 10, 20, and 30 MPa.

In subsequent experiments regeneration of catalyst was accomplished using modified (methanol 3%-mass fraction of carbon dioxide) supercritical carbon dioxide at the temperature $T = 343$ K and pressure $P = 15, 20$ MPa.

The conducted analysis of regenerated catalyst samples revealed recovery of catalytic activity up to 92 %. That confirmed a possibility of SCF CO_2 extraction implementation for catalyst regeneration.

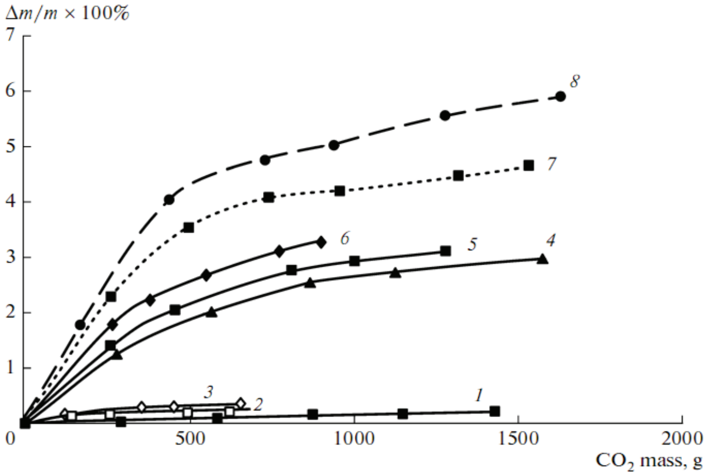

Fig. 1. Change in the mass of the catalyst in the course of its regeneration versus the amount of extractant used: (1–6) SC CO_2 and (7, 8) SC CO_2 +3 wt % methanol; (1–3, 7, 8) 343 K and (4–6) 423 K; (1, 4) 10 MPa, (2, 5, 8) 20 MPa, (3, 6) 30 MPa, and (7) 15 MPa.

PP-III-30

Interaction of Single Metal Nanoparticles with Molecular Hydrogen and Oxygen

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The catalytic properties of metal nanoparticles can significantly differ from the properties of mono- and polycrystals of the same substance. Using scanning tunneling microscopy and spectroscopy (STM/STS) we investigated the structure, conductivity type and adsorption properties of gold, nickel and platinum nanoparticles deposited on the surface of pyrolytic graphite by the laser electrodispersion method [1]. It was found that lateral nanoparticles' diameters are in the range of 2-20 nm with a height of 1- 5 nm. The gold nanoparticles had minimum variation in geometric dimensions (near 2-3 nm in diameter). Refurbished by STS measurements the electronic structure of nanoparticles led to the conclusion that the most homogeneous gold nanoparticles had not containing impurities, while the nanoparticles of nickel and platinum were covered by various modifications of the oxides. Interaction of hydrogen and oxygen with metal nanoparticles was studied, and a number of parameters of such interactions was identified. In particular, it was established that hydrogen adsorbed on gold nanoparticles even at room temperature. The interaction of hydrogen adsorbed on the nanoparticles and oxygen led to the formation of water molecules detected by their electron-vibrational excitation spectra measured by STM [2]. For the first time the recovery of a single platinum nanooxide in hydrogen was directly investigated. The activation energy of the process (E = 24 kcal / mol) and the averaged sticking coefficient (s = 0.25) were obtained on the assumption of a linear relationship between the number of surface oxygen atoms and the size of the bandgap oxide.

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Variation of Surface and Texture Nanodiamond Properties to Create Effective Hydrodechlorination Catalyst

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Since the most part of industrially important reactions are catalytic, directed synthesis of catalysts with desired properties is of great importance. In present time for many reactions the structure of active site is known but the problem of its synthesis still exists. The development of new catalysts and revelation of general approaches to catalysts design are discussed in the present work. All studied approaches are based on chemical or electronic interaction of metal nanoparticles with support or second metal and directed on formation of M(0)/M(δ+) pair to achieve desired catalytic properties. Nanodiamond (ND) could be successfully used in catalysts design due to unique properties.

Several types of NDs with different set of surface functional groups and porous structure were investigated. Metal (Ni or Pd, 0.5-5 wt.%) was supported by wet impregnation or equilibrium electrostatic adsorption. Combined FTIR-ATR and dzeta-potential measurements for pristine ND and ND supported metals revealed that metal precursor coordination is strongly defined by the nature of surface functional groups. Carboxylic O-containing groups of negatively charged ND participate in coordination with M^{2+} that results in large metallic particles. Positive surface charge is provided by cyclic anhydride –C(O)–O–C(O)– and N-containing groups which favour formation of M(δ+) and small M(0) particles.

Therefore, catalytic properties are strongly affected by the type of nanodiamond used as support. Pd or Ni supported on mesoporous ND with positive surface charge was found to be the most active in gas and multiphase hydrodechlorination of chlorinated benzenes. Pd-containing catalyst was successfully used for hydrodechlorination of chlorobenzene, 1,3,5-trichlorobenzene; p-chloroacetophenone; 2,4,8-trichlorodibenzofurane as dioxin model and hexachlorobenzene (commercial pesticide).

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PP-III-32

Promoting Mechanism by Fe in Preferential Oxidation of CO on Pt/CeO_2 and Pt/ Metal Oxides

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The addition of Fe enhanced the activity of preferential oxidation of CO (PROX-CO) on Pt/CeO_2 and Pt/metal oxide. The mechanism followed for Pt/CeO_2 is the Water Gas Shift at the interface of Pt and CeO_2 [1,2]. In present study, additive effect of Fe weakened the interaction between CO and Pt [3]. Similarly, adsorption between oxygen and Fe is also weak [4]. The mechanism facilities rapid conversion of CO to CO_2. The hydrogen which is comparatively strongly bonded with Pt does not participate in reaction and hence lowers the probability of methane formation. The simultaneous operation of W-G-S reaction at the interface of Pt and CeO_2 and the promotion mechanism is proved by using characterization tools such as FTIR and XPS. Promoting mechanism of Fe cleanup the CO to an acceptable concentration for application of PEMFC and the catalysts performed over the course of 10 -24 h stability test.

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A Theoretical and Experimental Study of Nickel-Alumina Eggshell Catalyst Preparation Process for Reforming Reactions

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Catalytic reforming is a well-established industrial process for converting hydrocarbons into hydrogen or synthesis gas and has been extensively studied in recent decades. Among active catalysts for reforming reactions, it has been reported that noble metals present high activity, however their limited availability and high cost promote the use of nickel catalysts due to the fact that this metal offers its redox properties and its lower cost, which makes it easily accessible. To improve the catalytic performance and minimize coking of the nickel catalyst, several conditions can be modified, such as characteristics of the support, metal content, *preparation method* and the introduction of promoters into the catalyst formulation [1]. Egg-shell catalysts are useful in processes where the reaction has a very high rate and the intraparticle diffusion becomes the limiting step. For a positive order reaction (e.g. reforming reactions), in the absence of selectivity or poisoning considerations, an "egg shell" catalyst seems to be optimum [2]. In this study, Ni supported on alumina catalysts with core/shell structures, were prepared in different metal loadings (7 and 15wt % Ni) by a combination of the *edf* method [3] with the wet impregnation technique. The physicochemical properties of the final catalysts were determined by XRD, ICP-AES, TEM and SEM. Moreover, a theoretical model of the catalyst preparation process for nickel catalysts supported on cylindrical γ–alumina extrudates, based on the *Lee and Aris* model, was developed. The model was validated against the experimental data concerning the radial deposition profiles of Ni on γ-alumina cylindrical extrudates prepared by the *edf-wet* method proposed by the authors. It can be concluded that there is a satisfactory theoretical prediction of nickel species concentration profile for given experimental conditions, while the parameters predicted by the model were discussed along with those derived from previous work according to the literature.

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PP-III-34

Studies of the Thermal Decomposition of Methanol Adsorbed by Zeolite Based Catalyst Using TG/DSC and GC/MS Analysis

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Today catalytic conversion of methanol to hydrocarbons (MTH) is very attractive process and zeolite based systems are extensively used as catalysts for this process [1-4]. The present paper aims are TG/DSC and GC/MS study of thermal decomposition features of methanol adsorbed by ZSM-5 based catalyst. The used catalyst (2-6 wt.%)Co-(2-6wt.%Ln)/ZSM-5 is prepared by impergnation technique and characterised by the Horiba Scientific XGT-7000 X-ray fluorescence (XRF) microscope. The zeolites thermal behavior is studied by thermogravimetric (TG) and differential scanning calorimetry (DSC) methods at temperature interval of 20-500°C with heating rate of 20^oC/min in the corundum crucible using Simultaneous TG-DTA/DSC Apparatus “STA 449 F3 Jupiter”. Gaseous products are analyzed by on-line gas chromatography-mass spectroscopy (Thermo Scientific ISQ Single Quadrupole GC-MS) using a capillary column (15m x 0.25mm) and DynaMax XR detection system in the 30-500 u mass range.

The TG/DSC-GC/MS analysis results suppose thermal stability of catalyst up to 500°C and obtaining gasoline range hydrocarbons (hexane, benzene, toluene, xylene) from the methanol adsorbed over ZSM-5 based catalyst. Ethane, propane, butane and pentane are also detected. The conversion of methanol to aromatic hydrocarbons increases as the Ln loading increases. The formation of Ln-Co structures as active sites necessary for formation of aromatic hydrocarbons and mechanism of the reaction are discussed.

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Reactivity of Ni and Co Hydrotalcite Type Catalysts in Dry Reforming Reaction of Methane

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Dry reforming of methane is more endothermic and produces a more adequate CO/H_2 ratio for the synthesis of the valuable oxygenated chemicals than steam methane reforming, which is the conventional route to transform natural gas into synthesis gas. In recent years, a renewed interest in the CO_2 reforming reaction has arisen from an environmental point of view since this reaction is a CH_4 and CO_2 greenhouse gases consuming process.

In this work we propose to examine the catalytic performances in this reaction of five hydrotalcite type components, quoted Co-AlHT, Co-Mg-AlHT, Ni-AlHT, Ni-Mg-AlHT and Ni-Co-Mg-AlHT. These solids were synthesized by coprecipitation method [1] and characterized by chemical analysis, BET, XRD, FT-IR, thermogravimetric analysis (ATG/ATD) and TPR. The study of the reaction was conducted in a differential dynamic system, it was done in a quartz fixed bed reactor at atmospheric pressure, the scale of reaction temperatures varied from 400 to 800°C and the CH_4/CO_2 ratio is equal to 1. Before each catalytic test, the sample was activated under hydrogen flow (DH_2= 1.2L/h) at 600°C for 12 hours. All materials are active from the first minutes of contact with the reactional mixture. The nickel based catalysts reach stationary state very fast (after 30 minutes), in comparison to the cobalt based catalysts (100 minutes). The effect of reaction temperature showed that the catalysts presented better catalytic performances at 650°C. At each examined temperature, the binary catalysts are less active than their ternary homologous. At high temperature, the addition of magnesium improves notably the CH_4 and CO_2 conversions of all systems, especially that of the NiMgAl-HT catalyst for which these values reach respectively 87.08% and 70.7%. The influence of this addition on the productivity of CO and H_2 is also noticeable. The best performances of the Ni-Mg-AlHT can be partly related to its texture and structure and to the fact that it is less acid than the cobalt compounds. The influence of the magnesium was justified by its dispersion effect [2], [3].

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PP-III-36

Hydrogen Assisted Growth of Nitrogen-Doped Carbon Nanotubes over Au/Al_2O_3 Catalyst

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As it is known, metallic gold particles of few nanometers in size when deposited onto oxide supports may exhibit a high catalytic activity to numerous reactions including low-temperature CO oxidation, selective reduction of NO_x by propene, selective oxidation, hydrogenation and skeletal rearrangements of hydrocarbons. Multi-walled carbon nanotubes are prepared by C_2H_2 decomposition at 650-850°C over Au nanoparticles deposited onto the surface of the "classical" oxide supports (Al_2O_3, TiO_2, SiO_2-Al_2O_3) [1]. Recently, we have reported a first example of growing N-doped carbon nanotubes (N-CNTs) by chemical vapor decomposition of a N,C-precursor over a supported Au/Al_2O_3 catalyst [2]. Compartmentalized CNTs containing up to 5 at.% N (as determined by XPS) were produced via decomposition of pyridine (Py) vapor at 800°C and 1 bar of the reaction gas mixture (feed stream composition: 5 vol.% Py + 10-20 vol.% H_2 in Ar) over the Au/δ-Al_2O_3 catalyst with a mean diameter of Au particles around 3.0 nm. In this report, the mechanism of N-CNTs formation over the Au nanoparticles is considered on the basis of the experimental data obtained. It is suggested that the heterocyclic ring of Py is destroyed over small Au particles *via* catalytic hydrodenitrification reaction with successive dissolution/diffusion of carbon and nitrogen atoms inside the metal particles that is required for the growth of tubular carbon structures. SEM and TEM results show that the nanotubes grow further mainly *via* the "base-growth" mechanism. This is in agreement with the observations of strong attachment of Au nanoparticles to the alumina support caused by the possibility of epitaxial interaction between Au crystallites and the Al_2O_3 surface [3]. The N-CNTs obtained are characterized by a very broad size distribution with the minimal outer diameter of 6-10 nm that is exceeded the dimensions of metal active sites, probably, due to self-assembling of individual N-CNTs.

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Influence of the Electronic Properties of Palladium Particles Deposited on Alumina on the Reaction Mechanism of Hydrogenation of Vinylacetylene

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The influence of the structural and electronic characteristics of nonpromoted Pd catalysts on their adsorption and catalytic properties is studied. It is shown that the conversion of vinylacetylene depends on the dispersion of palladium for both types of catalysts synthesized from acetate and acetylacetonate complexes. It is established that the selectivity of vinylacetylene conversion into 1,3-butadiene on palladium acetate and acetylacetonate catalysts depends on the state of the 3d-orbitals of surface Pd atoms. The palladium acetate catalysts are characterized by a higher electron density on the 3d-orbital in comparison with the acetylacetonate samples, thus producing higher selectivities of vinylacetylene conversion into 1,3-butadiene.

It is shown that the largest number of converted acetylene and diene hydrocarbons hydrogenated to 1-butene. At the same time for the samples synthesized using as the starting compound of palladium acetylacetonate complex, there is a high selectivity (up to 40.9%) conversion of acetylenic hydrocarbons and 1,3-butadiene in 2-butenes, compared with samples based on palladium acetate, which is probably due to the presence of palladium particles on the surface atoms with lower electron density in the 3d-orbitals valence, stabilizing πδ-allyl intermediates, and catalytic hydrogenation reaction of a 1,4-addition with the formation of 2-butene. The ratio of tr- and cis-butene increases with 6,3-8,3 to 10,3-12,4 up. Increase the concentration of tr-C_4H_8 due to higher thermodynamic stability of the tr-isomer of 1,3-butadiene and the absence of intramolecular transformation of cis- and tr-π-allyl intermediates.

PP-III-38

Graphene as a Matrix for Catalytically Active Nanoparticles

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In view of ongoing progress in catalysis, the application of novel nanosized materials becomes increasingly important. Nowadays, plenty of heterogeneous catalytic processes applied in industry are based on utilization of nanoparticles of catalytically active materials fixed on the various porous structures. Application of graphene and related compounds as catalysts for facilitating synthetic reactions is a relatively new area of research with outstanding potential. The unique properties of well-defined 2D nanomaterials, such as graphene and graphene oxide are suitable for facilitating of a wide range of reactions and may offer new routes in the design of novel catalytic systems. For example, platinum and palladium nanoparticles immobilized on the surface of graphene oxide were used in the electrooxidation of methanol and the hydrogenation of alkynes [1], and palladium nanoparticles on the surface of graphene oxide have shown high efficiency in cross-coupling reaction of phenylboronic acid with aryl bromides and iodides [2]. However, in most of experiments, expensive precursors had to be used or synthetic procedure requires long time.

In this paper, nanoparticles of noble metals (Au, Pd, Rh, etc.) on the surface of graphene and graphene oxide have been obtained. As a precursor for the synthesis of nanoparticles, salts of the suitable metals have been used. The resulting nanocomposites were characterized by methods of physicochemical analysis and then tested as catalysts for organic reactions (cross-coupling reaction, formylation, etc.). High degree of conversion of organic reactions with noble metal nanoparticles on the surface of graphene oxide and graphene used as catalysts has been demonstrated in these studies.

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Nature of Low Bond Oxygen Form in $La_{1-x}Sr_xFeO_3$ Perovskites

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Perovskite-like oxides $ABO_{3\pm y}$ (A = La; B = Mn, Co, Fe) due to their unique physical and chemical properties and stability in reaction mediums are very promising for application in many high temperature processes with oxygen participation as catalysts, catalyst membranes, cathodes and anodes in SOFC, and so on [1,2]. It is well known that catalytic properties of perovskites depend on nature of 3d cations, their coordination and charge state, which depend on preparation route and substitution degrees in A and B sublattices, that in final influence the number of oxygen forms, their mobility and reactivity. For example, substitution of lanthanum for strontium in $LaFeO_3$ leads to formation of low bond oxygen form (its quantity increases in proportion to substitution degree) that removes during H_2- TPR experiments at 400-600 ^oC. Usually based on electroneutrality principle and using H_2-TPR data the quantity of iron cations in oxidation state +4 (due to substitution) may be calculated [3].

The main goal of the paper is investigation of charge and coordination states of iron and oxygen ions in $La_{1-x}Sr_xFeO_{3-y}$ ($0 \le x < 1.0$) perovskites with Mossbauer and XPS.

According to H_2-TPR perovskites with $x < 0.8$ are fully oxidized and consequently should contain iron cations in +4 oxidation state in proportion to x. According Mossbauer data there are iron cations in +3.5 oxidation state probably due to fast electron exchange between Fe^{+3} and Fe^{+4} ions. Hence there is a possibility for oxygen ions to take a part in the electron exchange as well that may lead to change their charge as well. All iron ions at room temperature are in octahedral coordination, only for $x \ge 0.8$ there are iron ions in penta coordination state. No iron ions in tetra coordination state were revealed.

According XPS data only Fe^{+3} ions were revealed probably due to low sensitivity of XPS for iron ions. The detected peak with E=531,4 eV may be due to low bond oxygen form with lower electron density on oxygen ions as compared with usual O^{-2} oxygen form. Peak's intensity decreases with temperature and after Ar treatment; there is a correlation between x and peak intensity also. Hence very probably that $Fe^{+3.5}$ and O^- ions are formed in substituted perovskites, and high reactivity of low bond oxygen form is due to formation of O^-.

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PP-III-40

Regularities of Formation of Hydrocarbon Cracking Catalysts for Modification of Natural Zeolite by Acids of Various Nature

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The report examines the scientific basis of the creation of hydrocarbon cracking catalysts in the synthesis of long chain α-olefins. It is known that the cracking of hydrocarbons runs on acidic centers, therefore ideal catalysts for this process are solid acids. Zeolites as solid acids are the main catalysts for hydrocarbon cracking processes.

We established that stepwise modification of natural zeolite by mineral, organic and heteropolyacids leads to an increase in its catalytic activity. The regularities of formation of cracking catalysts modified by acids were identified by modern physical methods (XPS, SEM, TEM, BET). It is shown that as a result of active interaction of the surface with modifier new structures are formed, which leads to a significant increase in specific surface area and catalytic activity. Thus, when stepwise modification by mineral acid at first and then by heteropolyacids, dispersibility of the particles of heteropolyacids on the surface of natural zeolite is high, and the layered structure of the zeolite are covered with agglomerates of heteropolyacid evenly distributed and firmly bounded to its surface. Detailed study of the surface of the zeolite by HQ TEM showed the formation of stable structures of clusters, which are partially embedded in the volume of the zeolite. The size of these clusters is 1-2 nm and they are available for the reactants. It is believed that when applied and as a result of calcination of the catalyst, transfer of the particles of heteropolyacids in highly dispersed state in which the heteropolyacid particles reach specific adsorption and catalytic properties are achieved.

Obviously, the formation of nanostructures and the presence of the large number of strong acid sites lead to increase in cracking activity of catalysts in the cracking of heavy hydrocarbons. [1,2]

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Resistance towards Sintering of Pt Nanoparticles Supported on γ-Al_2O_3

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Catalytic activity and selectivity are influenced by the size of Pt nanoparticles in hydrogenation of benzene, furan, pyrrole, crotonaldehyde and oxidation of methanol and formic acid [1, 2]. Catalysts for these processes are characterized by high temperature of pre-treatment conditions, but there is not much information available concerning the resistance towards sintering of such systems at higher temperature.

Colloidal solution of platinum nanoparticles was synthesized by reducing hexachloroplatinic acid in ethylene glycol solution at 120˚C in the presence of a stabilizer with further precipitation in aceton and redispergation in ethanol. Deposition of Pt nanoparticles on γ-Al_2O_3 was performed by mixing appropriate amounts of γ-Al_2O_3 and colloidal solution of nanoparticles under stirring with future drying in air. Sample of Pt/γ-Al_2O_3 was heat-treated at 100, 300, 400, 500, 700 and 900ºC under air and under H_2.

Fig.1 shows dependencies of diameter of supported Pt nanoparticles from heat-treatment temperature. Diameter of heat-treated under air supported nanoparticles increases with rising of processing temperature, whereas the diameter of heat-treated under H_2 supported Pt nanoparticles stays nearly the same.

Pt nanoparticles supported on γ-Al_2O_3 exhibit high thermal stability under reducing conditions up to 700ºC. Under air they start to sinter at 300ºC.

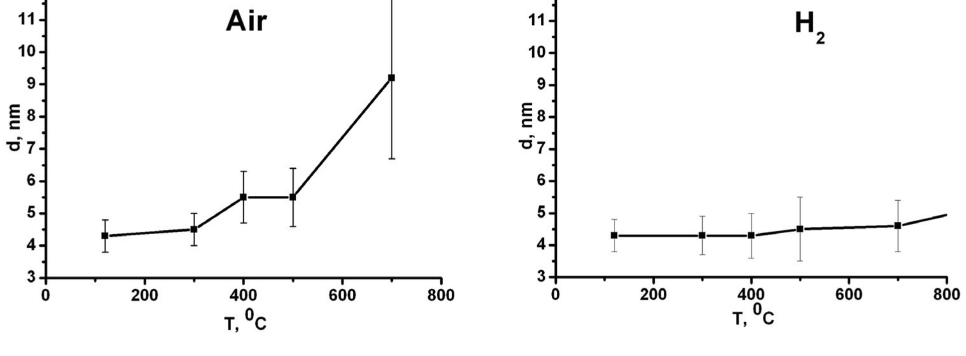

Fig.1. Dependencies of average diameter of supported nanoparticles from temperature of heat-treatment under air and under H_2.

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PP-III-42

Catalytic Behavior of Decomposed Molybdophosphoric Acid Supported on Alumina for Oxidative Dehydrogenation of Ethane to Ethylene

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Ethylene is one of the largest base chemicals for the chemical industry. Ethylene and other light alkenes are produced by steam cracking and dehydrogenation of light alkanes. These processes are typically carried out at high temperatures (usually >800 °C) and at higher pressures, and thus become energy intensive. Besides, there is a scope for significant side reactions and catalyst deactivation owing to carbon deposition. Oxidative dehydrogenation of ethane (ODHE) is one good option to produce ethylene as it operates at relatively lower temperatures. Many catalysts were applied for ODHE since last two decades [e.g. 1-4]. Among them, Mo based catalysts are gaining importance due to their selective nature. In this contribution, we describe the preparation, characterization and application of Mo based catalysts derived from molybdophosphoric acid (MPA) for ODHE.

Alumina supported molybdophosphoric acid catalysts were synthesized with varying MPA loading (5-25 wt%) using wet impregnation. The catalysts were calcined at 600 °C (6h, air) and characterized by different techniques. Catalytic tests were carried out in a fixed bed catalytic reactor in the range of 400-550 °C. The product analysis was made using an on-line GC (NUCON 5765) equipped with TCD.

Calcination of the catalysts at 600 °C for 6h in air caused destruction of Keggin structure of MPA. XRD supports this view and revealed no reflections belonging to Keggin structure, however some reflections corresponding to pure γ-Al2O3 can be seen. FT-IR analysis also confirmed this phenomenon. Despite such destruction, the decomposed MPA/Al_2O_3 catalysts displayed reasonably good activity in ODHE. At 550 °C, the selectivities of C_2H_4 and CO_2

varied in a range of 30-65 % each with varying parent MPA loading. On the other hand, the conversion of ethane is found to change from 16-24 %.

On the whole, it can be said that 20wt% MPA loading seems to be optimum due to its superior performance (X(ethane) = 24%, S(ethylene) = 65%).

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PP-III-43

XPS and STM Studies of Oxidation by NO_2 of Platinum Particles Supported on HOPG

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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. With the view of testing this supposition, the present work is devoted to the reaction of model catalysts with NO_2 studied by X-ray photoelectron spectroscopy (XPS) and Scanning Tunneling Microscopy (STM). The model catalysts were prepared by evaporation of platinum nanoparticles on the surface of high-oriented pyrolytic graphite (HOPG) in vacuum. Graphite was selected as the support, since it is an ideal object for STM studies and, in contrast to oxide supports, gives an opportunity to evaluate the state of oxygen in platinum particles using XPS O 1s spectra. All experiments were performed in XPS spectrometer SPECS (Germany) using monochromatic irradiation Al K_α and scanning tunneling microscope GPI-300.2. 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. Peculiarities of Pt particles formation on graphite and their role in graphite oxidation were also studied in this work. The reaction of a clean HOPG surface with NO_2 was additionally studied to compare with the behaviour of the model catalysts. The results of this work can be used for explanation of the size effect in the reactions of oxidation catalysis on supported metallic catalysts.

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Rationalisation of the Catalytic Role of Triazole-Linkers in Asymmetric Aldol Reactions in Water Catalysed by Polystyrene-Supported Hydroxyproline

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While investigating a newly developed polystyrene-supported hydroxyproline catalyst for the purpose of asymmetric cross-aldol reactions [1], water was found to be an optimal solvent for enantio- and diastereoselectivity, in contrast with polar organic solvents such as DMSO and DMF. In a following study where different strategies for linking hydroxyproline to the polystyrene resin were compared [2], it was furthermore discovered that the presence of a 1,2,3-triazole unit as a linking group was essential for high enantioselectivity, in addition to the use of water as solvent. The 1,2,3-triazole unit, introduced by the means of a copper-catalysed 1,3-dipolar cycloaddition between an alkyne and an azide for the purpose of catalyst immobilization, and initially considered as an innocent linking group was thus shown to actively take part in the catalysis and positively influence enantioselectivity.

This effect has been rationalised computationally by means of DFT methodology. The four possible diastereomeric transition states in model aldol reactions were calculated employing a combination of a continuous solvation model (PCM), and explicit water molecules. It was thus demonstrated that the formation of a bridge, consisting of three water molecules, between the triazole and the carboxylic group of the proline would lead to increased stabilization of the transition states leading to the favoured enantiomer, and thus result in increased enantioselectivity compared to the situation where either the triazole unit or water is absent.

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PP-III-45

Au-Ni Synergism in the Alumina Supported Catalysts in the Hydrodechlorination of Chlorobenzene

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After success of Haruta's early work many researchers focus their attention on catalysis by gold. Numerous of them deals with supported gold. Different active sites were proposed for the various catalytic systems but the nature of the active site is still unclear. For the investigation of catalysis by Au it's important to choose a structure-sensitive reaction because gold particles of narrow size region are active in catalysis. In the present work catalytic activity of γ-Al_2O_3 supported Au and Ni monometallic and Au-Ni bimetallic catalysts was investigated in the hydrodechlorination of chlorobenzene (HDC) at 50-350^{o}C in the gas-phase flow type fixed-bed system. Au particles with different size (3, 6, and 10 nm at up to 1%mass. loading) were deposited on γ-Al_2O_3 or 6%Ni/γ-Al_2O_3 (prepared by wet impregnation of support with Ni nitrate) from the colloidal dispersions. Catalysts were examined by HR TEM, XPS, and TPR. Ni sample with high spinel content was chosen for comparison to minimize deactivation under the influence of reaction medium, though it is hard to reduce.

Catalytic activity of 6%Ni/γ-Al_2O_3 was negligible in the low-temperature region; 100% chlolobenzene (CB) conversion was achieved only at 350°C. On Au/Al_2O_3 CB conversion achieved maximum of 42% at 250°C with no further increase till 350°C. CB conversion on Au-Ni catalysts proceeded at lower temperature and depended on the Au particle size. The best catalyst (Au particles of 6 nm) demonstrated 50% conversion already at 180°C, the other two (Au particles of 3 and 10 nm) at 220°C, and all three samples provided 100% conversion at 250°C. Therefore synergism of action of Ni and Au in CB hydrodechlorination takes place. This fact could be explained by the changes in the metal state and was confirmed by the negative (0,3 eV) shift of E_B of Au 4f in Au-Ni (10 nm Au) sample as compared to that in Au sample. After the Au deposition temperature of Ni reduction lowered according to TPR data.

This work was supported by RFBR (№ 10-03-00372, 11-03-00820) and Leading Scientific Schools grant НШ-2724.2012.3. Results were obtained with the help of SRCCU "Nanochemistry and Nanomaterials" of Lomonosov Moscow State University.

On Different Polarization Ability of Different Ion Exchanged Bivalent Cations in Different Zeolites

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It is generally belived that chemical activation at different molecules adsorbed by cation exchanged zeolites results from their polarization by cations. In the present study this was examined by IR spectra of molecular hydrogen, methane, ethane and propane adsorbed by bivalent cations in ZSM-5, mordenite and Y zeolites. The obtained results indicated that polarization of those molecules by the same cations in these zeolites is different. It is the strongest in ZSM-5 and the weakest in Y zeolite, while polarization of adsorbed molecules by bivalent ions in mordenite is intermediate.

In was suggested that this is connected with different state at exchanged bivalent cations in these zeolites [1]. In ZSM-5 where the negatively charged [AlO_4] tetrahedra are strongly distantly separated from each other only one half of them is neutralized by bivalent cations resulting in superacidic adsorption Lewis sites while the second part of negatively charged [AlO_4] tetrahedra is free. In Y zeolite each positively charged bivalent cation interacts with two neighboring negatively charged [AlO_4] tetrahedra that results in a better neutralization of their positive charges. Mordenite represents an intermediate case with weaker compensation of positive charges of bivalent cations than in Y zeolite. Such superacidic Lewis sites dissociatively adsorb light alkanes. In [2] this conclusion was supported by quantum chemical calculations.

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PP-III-47

Doped Apatite-Type Lanthanum Silicates as Catalysts for Oxidative Coupling of Methane

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The oxidative coupling of methane (OCM) is an attractive method of the natural gas transformation to valuable semi-products of petrochemical synthesis, which in the measurable future can become competitive with the ethylene production via conventional methods [1, 2]. In spite of the fact that a lot of oxide systems have been studied as catalysts for OCM, the search of new promising materials continues [3-5]. Recently, Zhang has shown that an apatite-type lanthanum silicate $La_{9.33}(SiO_4)_6O_2$ demonstrates a high catalytic activity in OCM at rather low temperatures [5]. In the meantime the apatite-type lanthanum silicate doping may provide a possibility to regulate catalytic characteristics of these materials [6, 7].

In the present paper Al-doped apatite-type lanthanum silicates $La_{9.33+y/3+x}(SiO_4)_{6-y}(AlO_4)_yO_{2+3x/2}$, y = 0–1, x = 0,33 have been studied as catalysts for OCM. The substitution of Al for Si in the apatite structure has been shown to improve catalytic characteristics (C_2-hydrocarbons selectivity and C_2H_4/C_2H_6 molar retio) of lanthanum silicate. To specify the nature of such effect, the results of Raman spectroscopy, XPS as well as methane temperature programmed reaction and isotope-exchange experiments will be discussed.

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Nanosize Catalysis New Nanoscale Gas Molecular Structures

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Catalytic system used in a computer chromatography has been examined. The sorbent represents the nanostructure composite with hard polymer electrolyte. Nanostructure polymeric dendrimers were absorbed on the surface to form monolayer. Dendrimers promote selective bind of substratum, resulting in increase efficiency and selectivity of the anchored metal complex catalysts [1,2]. At the research concentration of toluene and pyridine as sorbed gases (c= 4,45 • 10^{-2} M/l, V=2 ml), the dimensional effect in properties of the catalyst active component in formation of ionic tees is observed in the chromatography column. The reaction is thermodynamically forbidden. Experiment demonstrates that the size of a particle is the thermodynamic variable specifying system conditions. The size of a particle operates a role of temperature [3]. Calculations show that the particle radius of sorbent initiating reactions at temperatures studied changes for toluene within r_s=0,025÷2,24Å, and for pyridine r_s=1,48÷3,03 Å. At some temperatures the spin catalysis can be observed, which stimulates a triplet-singlet conversion of radical pair. The hypothesis on the triplet nature of paramagnetism in conducting polymers [4, 5, 6] is supported. At volume change of toluene adsorbed (c=4,45 • 10^{-2}M/l, = 0,5 ml; ΔG<0), a quantum oscillation between two microscopic conditions of superconducting structure is observed . The $KN^{-}K$ structure is supposed, where K – carb-cation of toluene; N - nitride ion.

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PP-III-49

An Efficient Nenitzescu Indole Synthesis in the Presence of Lewis Acid Catalysts

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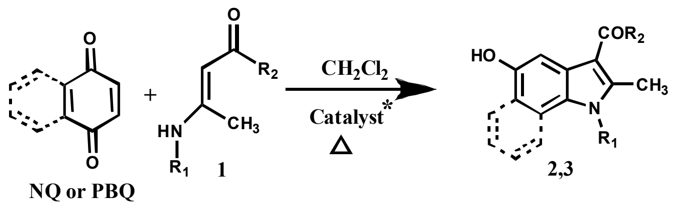

NQ –1,4- naphthoquinone PBQ – 1,4-benzoquinone
R_1 : Bn, Bu, allyl, Ph, C_6H_4-4-Cl, C_6H_4-4-COOMe, C_6H_4-3-COOMe, C_6H_4-4-CH_3, C_6H_4-3-CH_3, C_6H_4-2-CH_3, C_6H_4-4-OMe, C_6H_3-3,4-di-Cl, C_6H_3-3-NO_2-4-Me,
R_2 : OEt, Me, Ph
* Catalyst : ZnI_2, $ZnCl_2$, $InCl_3$ – 60-85% yield of **2**,**3;**
$Cu(OTf)_2$, CuCl, CuI, $Hg(OAc)_2$, CAN –17-32% yield of **2**,**3**
$AlCl_3$ –65% yield of **2**

Scheme 1

The Nenitzescu indole synthesis is a chemical reaction that produces the medicinally relevant highly functionalized 5-hydroxyindoles and 5-hydroxybenzo[g]indoles from substituted enaminoesters or enaminoketones **1** and 1,4-benzoquinone or 1,4-naphthoquinone under non-redox Lewis acids catalyzed very mild conditions**[1]**. However, the yields and selectivities are strongly dependent on the metal salt (Lewis acids) employed. Competing oxidative transformations of intermediates are typical for the classical redox conditions (in polar solvents without application of a catalyst). We studied which type of simple Lewis acids (from “oxophilic” to “azaphilic”) (Scheme 1) can be better than $ZnCI_2$ or ZnI_2 employed by us and others in non-redox modification of the Nenitzescu reaction **[1]**. The weak and hard oxophilic Lewis acids were shown to afford the indoles in low yields. The azaphilic CAN and Cu salts proved to be unsuitable as catalysts for the indole synthesis probably due to their oxidative properties. The best yields (60-85%) of indoles 2, 3 were gained when the process was conducted in the presence of catalysts with moderate Lewis acidity and oxophilicity, such as $ZnCI_2$, ZnI_2 or $InCl_3$ **[2].** Thus, the reaction pathway is dependent on the Lewis acid catalyst applied.

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Peculiarities of Partial Oxidation of Glycol over P-Modified Ag Catalysts

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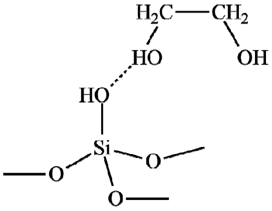
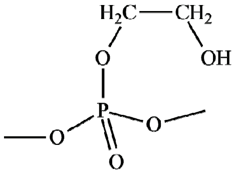
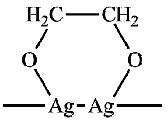
Partial oxidation of ethylene glycol using air allows obtaining a number of valuable chemicals, such as glyoxal, glycolaldehyde, glycolic and glyoxylic acid, etc. The most active catalysts for this process are silver systems. It is known that the effectiveness of Ag in the process of partial oxidation of ethylene glycol can be increased by addition of phosphorus-containing compounds into reaction mixture or directly into the catalyst composition. The addition of alkylphosphates, phosphoric acid, etc., increases the selectivity with respect to glyoxal by 10-15%, and also enhance the ethylene glycol conversion to up to 100%. In the present work using *in situ* IRS we have carried out the investigation of the catalysts for ethylene glycol oxidation representing silicagel-supported silver modified by phosphoric acid. It was stated that the following species are formed when glycol interacts with the surface of the investigated samples:



(I)



(II)



(III)

Ethylene glycol forms hydrogen-bonded complexes with SiOH groups (I) which are stable up to 125 °C. The POH groups form covalently bound complexes with ethylene glycol (II) which are stable up to 400 °C. Similar structures with silver are also formed (III), and selective oxidation of ethylene glycol into glyoxal proceeds only in case of two-site adsorption of the diol.

Formation of ethers of ethylene glycol and polyphosphate provides high selectivity of the process due to the opportunity of consecutive oxidation of diol into glyoxal via formation of glycolaldehyde. This allows varying the process conditions to produce both glyoxal and glycolaldehyde selectively.

Thus, it was shown that when ethylene glycol interacts with polyphosphate-promoted supported silver catalyst the process may proceed through formation of ether of ethylene glycol with polyphosphate. This provides high effectiveness of the samples in comparison with unpromoted systems.

The work was supported by the grant of the Russian Federation Ministry for education and science (state contract No. 13.G36.31.0001 from 07.09.2010).

PP-III-51

The Concept of Interlayer Dynamics and Poly-Functionality of TMS-Based Catalysts in HDS and Alcohol Synthesis

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On the basis of the fundamental concepts of catalysis by transition metal sulfides (TMS) a new dynamic model of the promoted Mo-sulfide catalysts functioning under HDS conditions has been developed. The model describes oscillations by sulfur and promoter atoms between the adjacent layers of the slab. The driving force of such processes is the heterolytic dissociation of the gas phase hydrogen and formation of hydride hydrogen linked to a promoter atom. This model correlates with radio isotopic data [1] and an earlier suggested "forcing out" mechanism [1,2] and gives some new interpretations of the important statements of the electron theory of promotion and the "rim-edge" model. The present model (Fig. 1) supposes that an AS is non-promoted single cluster located on terminal of the MoS_2 slab layer ("rim") and responsible for hydrogenation. A non-promoted site located on the edges is denoted as "empty site" (ES). Its catalytic properties are the same as of a "slow" site. A "rapid" AS consists of combination of the promoted and non-promoted single clusters placed on the terminals of the adjacent layers of the MoS_2 slab (Type II) or on the same layer (Type I). The result is that "rapid" sites transform into "slow"/"empty" ones and vice versa. The frequency of such migrations determines the activation degree of the catalyst [3,4].

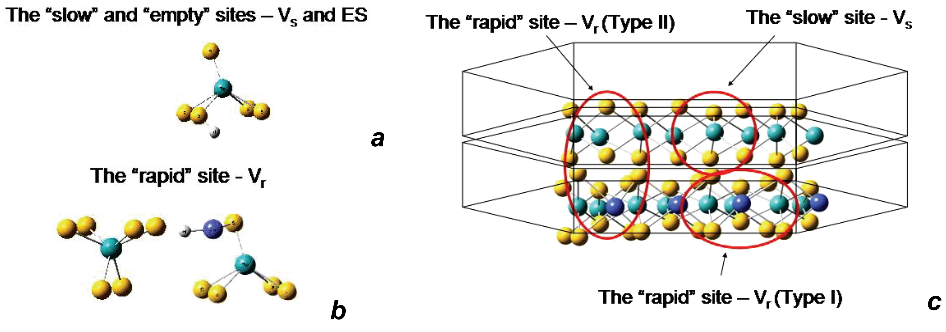

Fig. 1. (a) The "slow"/"empty" single site; (b) the "rapid" single site; (c) location of the sites of various types on the terminal surface of the $CoMoS_2$ slab. Color code: turquoise – Mo; blue – Co; yellow – S.

Basing on the suggested model we can advisedly vary composition and morphology of the active phase and nature of support aiming to control amount and distribution of the different (AS)s between rims and edges of the slabs in the newly designed catalysts for most effective hydro-treating of various types of crude [5]. This concept allowed us to assume that the reaction of alcohol formation from synthesis gas proceeds on the same two types of the (AS)s as it takes place for HDS. Attracting these models we proposed the schemes of the mechanisms of synthesis gas conversion on sulphide Co(Ni)-Mo catalyst modified by potassium and differ by various steps and sites involved into the catalytic transformations.

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PP-III-52

Synthesis of Catalysts for Diesel Fuel Hydrotreatment by Method of SHTS

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Catalytic processes of hydrotreating of diesel fuels are particularly important for the production of diesel fuels Euro-4, 5. Currently the most widely used alum-cobalt-molybdenum and alum-nickel-molybdenum catalyst that receives by impregnating technology which thin adjust texture as a catalyst, as well as the composition and structure of the active centers of desulphurization that does not always receive fuel Euro-4, Euro-5.

Optimal composition of catalyst tends to pick up a brute-force attack metal oxides catalyst ratio that determines the length of and the high cost of works on creation of new catalysts.

Use to calculate the optimal composition of catalyst principles "Theory of catalysis polyhedral" lets you quickly and with minimum expenses to determine the optimal composition of catalyst.

Laboratory of "Industrial kinetics and Catalysis» of Gubkin Russian State University of Oil and Gas together with the ISMAN RAS wounds received and tested at pilot plant new nanooxide yttrium-nickel-molybdenum catalysts hydrotreating by spreading high temperature synthesis (SHTS).

The SHTS is combustion of solids in condensed matter without or little gas space. Combustion takes place in a mixture of solid-reducing agent and oxidizer. This combustion generates highly defective structure. The particle precursors within contain intermetallic phase were covered with an oxide film.

X-ray structural analysis of the phase composition of precursors was examined, which revealed that SHTS-precursors had a developed structure but had poor texture.

For the development of texture samples of precursors specified chemical composition were monitored by the process of leaching of aluminum from the structure of acid or alkali. At standard conditions diesel fuel containing 9900 ppm of sulfur compounds were hydrotreated. The SHTS-nanocatalyst provides hydrotreated diesel fuel requirements Euro-4 and Euro-5.

The research was held within the framework of the federal targeted programme "Scientific and scientific-pedagogical personnel innovative Russia for 2009-2013," and "Research and development in priority directions of development of scientific and technological industry of Russia for 2007-2013 years."

Mechanism of Methanol Steam Reforming over Cu-Containing Catalyst in a High Excess of Water

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Purification of water waists from methanol and other oxygenates is of practical interest, especially, in hydrocarbons, ammonia and methanol production industries. Among existing technologies of water purification a catalytic conversion of methanol is more efficient, since does need high investment and exploitation expenses. In the present work a mechanism of methanol steam reforming established basing one the results obtained over Cu-containing catalyst tested in reaction mixture 5% methanol in water at temperature range 200-300oC and flow rate 1250/hr. It was found that catalyst before and after treatment in hydrogen demonstrated the same activity. Thus, suggested catalyst does not require any activation procedure in hydrogen. Study of the catalyst oxidation state showed that under reaction conditions copper oxide almost completely reduced to metallic form. Carbon dioxide and water were only desorption products by heating the catalyst in helium flow after switching off reaction mixture. Possible mechanism of methanol conversion in a high excess of water is discussed.

Aromatization of Methane over Fe-Mo/ZSM-Catalysts

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Non-oxidative conversion of methane into aromatic hydrocarbons over Mo/ZSM-5 catalysts has attracted a considerable attention in recent years as an efficient method for utilization of natural and associated gases. To increase the time of stable catalyst operation in methane dehydroaromatization, the catalysts are modified with various metals [1, 2]. In this work, we study the modifying effect of nanosized powder of iron on the catalytic properties of Mo/ZSM-5 during a methane dehydroaromatization reaction.

Catalysts were prepared by mechanically mixing the ZSM-5 zeolite of the molar ratio $SiO_2/Al_2O_3 = 40$ with the nanosized powders of Mo and Fe in a KM-1 vibratory ball mill for 4 h. Thereafter, the resulting mixtures were calcinated at 540 °C for 4 h. The Mo and Fe nanopowders were prepared by the method of electrical explosion of wires in an argon atmosphere. The concentration of Mo in the zeolite was 4.0 wt %, and those of Fe in the 4.0% Mo/ZSM-5 catalytic system were varied from 0.05 to 1.0 wt %. The non-oxidative conversion of methane (99.99% purity) was performed in a flow setup at 750 °C and atmospheric pressure, methane was supplied at a volume velocity of 1000 h^{-1}. The reaction products were determined by gas chromatography. The microstructure and composition of Fe-Mo/ZSM-5 catalysts are studied by high-resolution transmission electron microscopy and energy dispersive X-ray analysis.

It has been found out that the 4.0% Mo/ZSM-5 catalysts modified with nanosized Fe powders ensures much higher methane conversion, better selectivity of hydrocarbons and higher yields of benzene. The highest methane conversion was achieved by adding 0.05-0.1% of Fe nanopowder. As follows from TEM and EDX data, particles of different nature are formed in the Fe-Mo/ZSM-5 catalysts: molybdenum clusters (~1 nm in size) within zeolite channels, molybdenum carbide particles (5-20 nm) on the outer zeolite surface, and Fe-Mo alloy particles, whereon carbon filaments grow under reaction conditions. Such a deactivation of the catalytic system due to formation of carbon filaments, which block the pores in the zeolite structure.

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Diffusive Model of Isoamylene Dehydrogenation to Isoprene Using Ferric Potassium Catalysts

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Usually, dehydrogenation of isoamylenes to isoprene is carried out under industrial conditions in adiabatic fixed-bed catalytic reactors. For understanding physical-chemical nature of dehydrogenation process, determining conditions under which it can be industrially feasible, and further optimizing operation conditions of chemical reactor, its mathematical model should be simulated. The model described in papers [1, 2] does not provide information about particle size of catalytic bed. However, laboratory tests being carried out by using pelletized catalyst of varied particle size distribution show that the reaction rate is a function of pellet size. This makes us to assume that catalytic reaction occurs in the internal diffusive regime. In particularly, it follows herefrom that kinetic parameters resulted from routine tests by using 1-2 mm spherical catalyst pellets can not be used for simulating industrial reactors to be loaded with pellets 4 mm in diameter and 10-20 mm in length.

The mathematical model proposed for dehydrogenation of isoamylenes to isoprene on the КДОМ-type industrial self-regenerating ferric potassium catalyst has been simulated according to the particle size distribution of catalyst, the effective diffusion coefficient, rate constants and activation energies of direct and reverse reactions. This mathematical model allows adequate characterization of dehydrogenation process with varied reaction parameters (raw feedstock feed rate, dilution rate, inlet temperature).

This work was supported by the RF Ministry of Education and Science.

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PP-III-56

Transformation n-Hexane on the High-Silica Zeolite Modificated by Chrome and Bismuth

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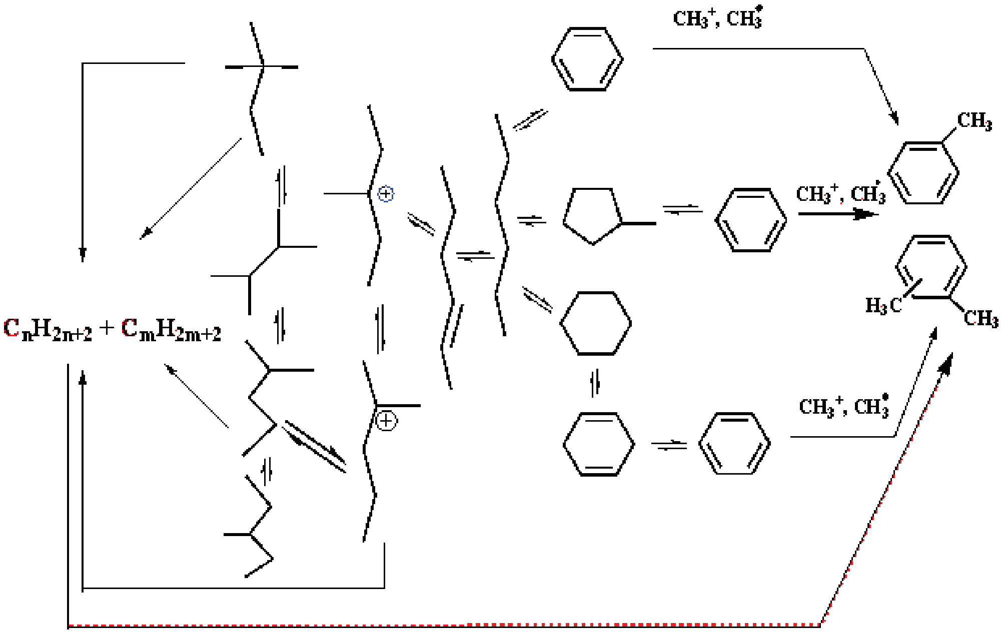
Transformation of n-hexane on the zeolite (M=80 mole/mole) modificated by oxides was researched by us in this article. Studying physicochemical characteristics high-silicon zeolite and cromotographic analysis of gaseous and liquied transmutation products is led to offer sheme of transformation hydrocarbons on the surface of high-silicon zeolite.



The creation of aromatic hydrocarbons resulted from the reaction of dehydrotation of n-alkanes and alkylation of benzol by the products of reaction of cracking. Benzol (0.8%) was produced by the dehydrogenation of n-hexane on the metallic site (chromium, bismuth) and following cyclization on the acid site with formation of the benzol. Changing in the mechanism of formation of aromatic hydrocarbons resulted from rise of temperature. Decreasing of content of structural OH-groups on the surface of bismuthromtseolitnoy system reduced the ability to protonation of ethylenes with formation of a carbonium ion. Further dehydrogenation of produced unsaturated hydrocarbon with following closing of hydrocarbon chain is led to formation cycloalkenes and cycloalkadienes which dehydrogenate in benzol. Raising of temperature led to increasing of transformation of n-hexane. We suppose that intensification of dehydrogenation, cyclodehydrogenation and cracing, reaction takes place as evidenced by the increase in the yield of propane (with 26.2 to 53.8 %) and aromatic hydrocarbons (with 26.2 to 53.8 %).

Mechanism of Propane Dehydrogenation in the Presence of Carbon Dioxide over Chromium and Gallium Oxides Catalysts

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Propene is one of the most important substances for chemical industry. The increasing demand of propene takes the development of new methods for its production. A perspective one is dehydrogenation of propane in CO_2 presence. Chromium and gallium oxides catalysts are to be promising ones for oxidative dehydrogenation of low paraffins because of their high dehydrogenation activity and selectivity. Designing new catalysts requires depth knowledge on the reaction mechanism. Data on the mechanism of low paraffin dehydrogenation in the CO_2 presence are few. This work is devoted to the study of propane dehydrogenation in CO_2 presence over chromium and gallium catalysts prepared by impregnation of silica from water solutions of chromium and gallium nitrates and direct hydrothermal synthesis embedding chromium and gallium species in the siliceous framework of MCM-41. Catalysts were investigated by DR-UV-Vis and IR-FTIR spectroscopy, XRD, TEM, BET, TPR. It was shown that the activity, selectivity and stability of chromium oxides catalysts were higher than these parameters for gallium ones. Mechanism of propane dehydrogenation was studied using kinetics (stationary and unstationary) and spectroscopic methods. It was shown that surface hydroxides took participation in propene formation over Cr-catalysts and hydrides – over Ga-ones. Propane and carbon dioxide participated in the reaction from the adsorbed states over investigated catalysts but they differed by the adsorption capacity of the reaction components and their surface covering. The role of CO_2 in this process was determined: CO_2 took an active participation in reverse water-gas shift reaction and in the oxidation of the catalyst surface over chromium oxides catalysts, the main role of CO_2 in propane dehydrogenation consisted in a decrease of coke deposition over gallium oxide catalysts.

Step-schemes of propene and cracking products formation were proposed.

PP-III-58

Kinetic Features of the Hydrogenation of 4-Nitroaniline in Aqueous 2-Propanol Solutions on Skeletal Nickel

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The processes of liquid-phase catalytic hydrogenation of unsaturated organic compounds are widely used in various fields of chemistry and chemical technology. One of the main problems of fine organic synthesis is the development of methods for selecting the optimal conditions for reactions involving substituted nitrobenzene.

The kinetics of the hydrogenation of 4-nitroaniline on skeletal nickel catalyst in aqueous 2-propanol solutions of azeotropic composition was studied. This system was also studied with the addition of acetic acid and sodium hydroxide.

We used a comprehensive approach that includes the study of liquid-phase hydrogenation reactions that is kinetic method and the analytical monitoring of the process by gas-liquid chromatography.

It was experimentally shown that in aqueous 2-propanol solutions of azeotropic composition, the hydrogenation reaction of 4-nitroaniline on skeletal nickel catalyst proceeds selectively to amine, without accumulation of intermediate products in the liquid phase. It was observed that the hydrogen that is related to the active centers of the catalyst surface takes part in the reduction of 4-nitroaniline.

It was proven that the addition of sodium hydroxide to aqueous 2-propanol solutions leads to the increase of the observed reaction rate, and the addition of acetic acid – to its decline. It was noted that in the presence of additives, the rate of the hydrogenation reaction was not proportional to the adsorption of the 4-nitroaniline.

The change of the reaction rate of the hydrogenation of 4-nitroaniline on skeletal nickel in aqueous 2-propanol solutions in the presence of additives is associated with the difference in the reactivity of the adsorbed hydrogen. It was established that in the reduction of 4-nitroaniline the β-atomic form of the adsorbed hydrogen is more active.

Catalytic CO Oxidation over Pt and Pd supported over WO_3

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A series of Pt/WO_3 and Pd/WO_3 catalysts was prepared by incipient wetness impregnation method and reduced by H_2-Ar at different temperatures being in the range 80–500 °C. The catalytic properties of H_2-reduced WO_3 with Pt and Pd metals for the oxidation of CO were studied in the gas mixtures with O_2 excess. It was shown that the catalysts reduced at 400 °C characterized by highest activity in the CO oxidation. XRD and TPR studies showed that the reduction process of Pt/WO_3 and Pd/WO_3 varied with the temperature, gas flow velocity and the composition of reduction mixture. The reduction of Pt/WO_3 and Pd/WO_3 involved the formation of H_xWO_3 which presence in the reacting gas mixtures can yield the active species for CO oxidation. It is shown by TPD-MS that the estimated energy of CO desorption (E_{des}) changes symbate with the catalytic activity and the lowest E_{des} values are found for the most active catalysts reduced at 400 °C. The CO conversion temperature dependence characterizes by abrupt transition from low active (LA) to high active (HA) states of the catalysts and by a counterclockwise temperature hysteresis. The CO oxidation over the catalysts is the first order with respect to CO and the zeroth order with respect to oxygen (HA). The reaction was found to be zeroth in CO and first-order in oxygen (LA). The clockwise by C(CO) and counter-clockwise by $C(O_2)$) hysteresis phenomena were observed for $r - f(C(\text{CO})$ and $r - f(\text{C}(O_2)$, respectively, at the intermediate range of temperatures. The dependences of $r - f(\text{C}(O_2))$ and $r - f(C(\text{CO}))$ observed at kinetic studies over the catalysts can be well explained by possible changing of CO oxidation reaction mechanism from heterogeneous Langmuir-Hinshelwood (LA) to the direct-impact Eley-Rideal and/or heterogeneous-homogeneous mechanisms (HA).

PP-III-60

Mechanism of NO-SCR with Methane over In,H- and Co,In,H-ZSM-5 Catalysts

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Mechanism of selective catalytic reduction of NO (NO-SCR) by methane was studied over zeolite In,H-, Co,H-, and Co,In,H-ZSM-5. The results of H_2-TPR and XPS experiments showed that the catalysts contain indium as $[InO]^+$/$[InOH]^{2+}$ cations, whereas cobalt was in the form of Co^{2+}/$[Co\text{-}OH]^+$ cations and/or Co-oxide clusters in amounts controlled by the applied preparation method. The NO-SCR by methane was shown to proceed in two coupled processes on distinctly different catalytic sites. One of the processes is the oxidation of NO to NO_2 by oxygen (NO-COX reaction) over Brønsted acid sites and/or cobalt-oxide species giving NO/NO_2 gas mixture. The other process is the N_2 formation (CH_4/NO-SCR reaction), which is the result of the reaction of methane and the NO/NO_2 mixture. Operando diffuse reflectance infrared Fourier transform spectroscopic (DRIFTS) results suggested that molecules of NO and NO_2 became activated together as NO^+/NO_3^- ion pair in reaction with $[InO]^+$/$[InOH]^{2+}$ or Co^{2+}/$[Co\text{-}OH]^+$ sites. The reaction of methane and NO_3^- generates an unidentified intermediate that rapidly reacts with the NO^+ to give N_2. The former methane activation on active NO_3^- surface species was confirmed to be the rate determining step. The In-bound nitrate has significantly higher reactivity towards methane than Co-bound nitrate, therefore the In-catalysts are more active in the NO-SCR reaction than the Co-catalysts. Co-oxide clusters, if present, showed significant promotional effect, which was related to their much higher NO-COX activity than that of the Brønsted acid sites. The accelerated NO-COX reaction speeds up the formation of NO^+/NO_3^- species and the rate of the methane activation, being the rate-determining step of the NO-SCR reaction. Thus, the connection between NO-COX and CH_4/NO-SCR reactions was clearly established. It was also shown that the NO-SCR reaction could proceed, if NO-COX and CH_4/NO-SCR catalysts were placed in the reactor to form consecutive separated beds. However, to avoid rate controlling NO_2 transport between the sites the close proximity of the different catalytic sites is favorable.

Binary Oxides of Transition Metals on Aluminum and Titanium in CO Oxidation

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The composites with binary oxides of transition metals on aluminum and titanium have been obtained using combination of plasma electrolytic oxidation (PEO) technique and impregnation in nitrate solutions following by air calcination. The general composite formula is $CuO+M_xO_y$/PEO-layer/Ti(Al), where M_xO_y is oxide of transition metal (Mn, Fe, Co, Ni). Solutions of $Zr(SO_4)_2$ and of $Zr(SO_4)_2+Ce_2(SO_4)_3$ as well as of Na_2SiO_3+NaOH have been used for PEO treatment of titanium and only the last have done for treatment of aluminum.

The composites have been investigated by XRD, XSA, SEM and XPS. Catalytic tests in oxidation of CO into CO_2 showed that both metal support and PEO layer effected catalytic activity of the composites. It has been demonstrated that all the composites containing binary transition metal oxides were active in the oxidation of CO into CO_2 at temperatures above 150-250°C. The attempts have been done to relate catalytic properties of the composites with their composition and surface morphology.

The comparative analysis of the resulting composites showed, that binary oxides of copper and cobalt deposited on silicate PEO coatings on titanium are more perspective catalytic systems for further research. Activation energy E_a was evaluated for the $CuO+Co_xO_y/SiO_2+TiO_2/Ti$ composite and the SiO_2+TiO_2/Ti sample from the dependences 1 and 2 (Fig.). In the case of Co-, Cu-containing coatings E_a=98.7 kJ/mol and for SiO_2+TiO_2/Ti composites E_a=42.5 kJ/mol in kinetic region.

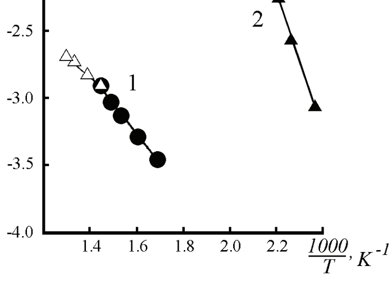

Fig. The dependences of the catalytic activity W (ml/g·c) in CO oxidation on an inverse temperature T for SiO_2+TiO_2/Ti (1) and $CuO+Co_3O_4/SiO_2+TiO_2/Ti$ (2) composites

Ethanol and CO Oxidation over $Ag/MeO_x/SiO_2$ Catalysts

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It is known that Au/TiO_2 or Au/FeO_x catalysts show high activity in low-temperature CO oxidation and oxidative dehydrogenation of ethanol to acetaldehyde [1]. However, their application is limited due to relatively low stability in the presence of water vapor and expensiveness. Ag-containing supported systems become alternative catalysts for the catalytic processes mentioned. Ag/SiO_2 catalysts can be used in low-temperature CO oxidation [2]. In the present work we investigated Ag-containing SiO_2 systems modified or not modified with CeO_2 and MnO_2 oxides in the low temperature oxidation of CO and selective ethanol oxidation to acetaldehyde.

It was shown that Ag/SiO_2 catalyst (5%wt.of Ag) had high activity in selective ethanol oxidation (95% selectivity towards acetaldehyde and 90 % conversion of ethanol at 220 ^oC). Temperature of 90 % CO conversion was 145 ^oC. Introduction of CeO_2 and MnO_x on the Ag/SiO_2 surface allowed increasing the activity in CO oxidation (temperature of 90 % CO conversion was 90 ^oC) and insignificantly effected on the activity of Ag-containing systems in selective ethanol oxidation. According to H_2 TPR data the reduction peaks of oxide modifiers for $Ag/CeO_2/SiO_2$ and $Ag/MnO_x/SiO_2$ shifted to low temperature and occurred during the reduction of silver from Ag_xO_y species at 0-150 ^oC. Therefore, close interaction between oxide modifiers and silver nanoparticles was achieved on the catalyst surface. Small silver particles (2-5 nm) stabilized on silica surface provide O_2 activation at room temperature (TPO and TPR results). TPR CO data indicated on the high activity of oxidized Ag/SiO_2 surface toward CO.

Ethanol conversion weakly depended on the modifier addition. Selectivity toward acetaldehyde reached 95-100 % (at 100 % ethanol conversion) in a wide temperature range for $Ag/CeO_2/SiO_2$. Only above 220-240 ^oC the reaction of the total alcohol oxidation took place, and yield of CO_x for CeO_2- and MnO_x-containing catalysts was higher than for Ag/SiO_2. This indicated the participation of CeO_2 and MnO_x in reaction of total oxidation. Thus, catalyst based on Ag/SiO_2 may be used for CO and ethanol low-temperature oxidation.

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PP-III-64

Ceria-Induced, Sb-Promoted, V_2O_5-TiO_2 Based Catalyst for NH_3-SCR of NO_x

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Efficient abatement of nitrogen oxides, under severe SO_2 poisoning condition, have already been reported using antimony promoted vanadia-titania catalyst [1]. The current study was carried out to further enhance its efficiency as well as to lower the reaction temperature. A series of experiments was done in order to assure the optimum percentage of ceria addition. The experiments showed that the system with addition of 10% cerium had the best catalytic activity among all. In order to know the effect of water and SO_2, the catalytic activity was measured both in their absence and presence alone and altogether. The physical properties of the systems under consideration were carried out using BET surface area and BJH adsorption, scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). The results were supported with X-ray diffraction (XRD), fourier-transformed infrared spectroscopy (FT-IR) and Temperature-programmed desorption (TPD) techniques.

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Physical-Chemical Properties of Phosphated Zirconia in the Reaction of *n*-Hexane Isomerization

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Zirconia based catalysts promoted with different concentrations of phosphates (4 or 10 wt. %) were prepared, calcined at different temperatures (600 and 700°C) and tested in the *n*–hexane isomerization reaction. The catalysts were characterized by BET, XRD, SEM methods, and total acidity was evaluated by using the Hammett indicators. The BET surface areas of the catalysts are in the range from 41 to 55 m^2/g with the exception for the catalyst 4-PhZrO_2–600 that S_{BET} exceeds 100 m^2/g. Such high specific surface area may be correlated with a bimodal pore size distribution. The general feature of the catalysts texture of phosphated zirconia-based samples with the same phosphates content is that the increase of calcination temperature leads to decrease of specific surface area and simultaneously an increase of the average pore diameter. XRD patterns show presence of a mixture of tetragonal (t-ZrO_2) and monoclinic (m-ZrO_2) zirconia crystal phases. In the higher presence of phosphate additives, the m-ZrO_2 peaks are partly suppressed in the XRD patterns, which are dominated by peaks originated from t-ZrO_2. Thus, the above results reveal that the presence of phosphate ions (10 wt.%) in $Zr(OH)_4$ stabilizes the tetragonal ZrO_2 structure at 600 and 700°C. The estimated total acidity values indicate that catalysts with higher incorporated phosphate content and calcined at lower temperatures show higher acidity. SEM micrographs indicate that the higher the calcination temperature used the bigger particles sizes are obtained, also the higher phosphate amount incorporated into zirconia matrix the smaller particle size achieved under the same thermal treatment applied. Relatively poor catalytic performance of zirconia-based catalysts promoted by phosphates, despite the favorable particular property, speaks in favor of the complexity of the active phase formation/transformation in the catalyst. In addition, there is the evident joint role of catalyst surface, textural, structural and morphological features in determination of the final catalytic performance.

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PP-III-66

Platinum-Nickel Catalyst for Hydrogenation of Edible Oils

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The oils and fats industry was among the first to use catalytic hydrogenation in order to transform liquid products in solid pastes to improve the odor and taste qualities. The most common metal catalyst for hydrogenation of fatty acids is nickel, due to its high activity and selectivity, among others. However, at present bimetallic catalysts study is successful, aiming to find alternative catalysts. On the other hand, research has shown that trans fatty acids have adverse health implications, therefore, more studies are needed to meet the new specifications for a greater concentration of cis isomer.

In this paper we study the adsorption of cis-oleic acid on a surface Pt-Ni-Ni (111) of a catalyst model. We designed the system and optimized by computer calculations using the method of superposition and electron delocalization, analyzed 4 potential sites of adsorption on the surface: mono-coordinated (1C), di-coordinated (2C), tri-coordinated with tetrahedral symmetry (3CT) and tri-coordinated with octahedral symmetry (3CO).

The results show generally a weak interaction between cis-oleic acid and the bimetallic surface. The adsorption energies of cis-oleic acid on the surface Pt-Ni-Ni (111) follow the following order 1C> 3CO> 3CT> 2C. At the minimum energy positions, the molecule is adsorbed through the C = C double bond at distances of 3.9 Å surface (1C), 4.2 Å (3CO), 4.0 Å (3CT) and 3.9 Å (2C), respectively. Comparison of the catalytic activity between the surfaces Ni-Pt-Ni (111) and Ni-Ni-Ni (111) showed that the stronger a molecule adsorbed the shorter distance from the surface became in the pure Ni catalyst. These results have special significance in the subsequent study of the chemical bonding and the electronic structure.

Study of Mechanism of Benzene Alkylation by Alkanes over Pt-Zeolite Catalysts

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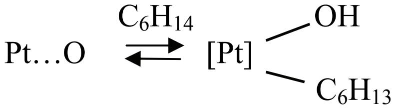
Mechanism of alkylation of benzene with hexane and heptane has been studied on synthetic zeolite ZSM-5 and Y modified by Pt. The catalysts are characterized by the methods of - BET, porosimetry, IR spectroscopy, electron microscopy, temperature-programmed desorption of ammonia. By IR spectroscopy the adsorption of benzene and hexane on the surface has been studied. On the base of results of these studies a likely mechanism of alkylation of benzene by alkanes with formation of alkylbenzenes with the yield of 40-50% has been suggested.

The main stages of this process are the activation of the alkane on the Pt centers (dehydrogenation with the formation of an alkene) and the alkylation of benzene by the classical mechanism of carbocations. Alkanes react with the oxidized form of platinum on the zeolite Bronsted center, forming an intermediate product:

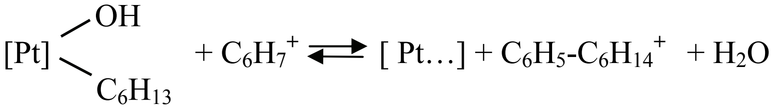


$$Pt...O \overset{C_6H_{14}}{\rightleftarrows} [Pt]\begin{smallmatrix} OH \\ C_6H_{13} \end{smallmatrix}$$

Benzene reacts with Bronsted acid centers (BAC) and the carbocation $C_6H_7^+$ is formed (BBC - Bronsted base center):

$$BAC + C_6H_6 \rightarrow C_6H_7^+ + [BBC]^-$$

Then strong and movable carbocation $C_6H_7^+$ protonated hydroxyl group:



$$[Pt]\begin{smallmatrix} OH \\ C_6H_{13} \end{smallmatrix} + C_6H_7^+ \rightleftarrows [\ Pt...] + C_6H_5\text{-}C_6H_{14}^+ + H_2O$$

Formed intermediate reacts with Bronsted center of the zeolite to form product – hexylbenzene:

$$2\ C_6H_5\text{-}C_6H_{14}^+ + [BBC]^- \longrightarrow 2\ C_6H_5\text{-}C_6H_{13} + H_2\uparrow$$

Reduced Pt (inactivated during the reaction) in the last stage of the reactions by interacting with water is oxidized and the activity of the metal center is regenerated again.

$$[Pt...] + H_2O \rightarrow Pt...O] + H_2$$

PP-III-68

Non-Steady-State Kinetics of D-Glucose to D-Sorbitol on Ru-Containing Heterogeneous Catalyst

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Ru-containing heterogeneous catalyst for the hydrogenation of D-glucose to D-sorbitol was synthesized with the help hyper-crosslinked polysteryne as a carrier of the active phase. The catalyst obtained had a developed specific surface of more than 1000 m²/g (BET analysis), it was characterized by monodisperse distribution of the active phase particles, the mean diameter of which was 1.4 nm (TEM analysis). Ruthenium-containing nanoparticles contained Ru(0) and Ru (IV) (XPS analysis) which allowed suggesting the existence of two types of active sites on the catalyst surface. The kinetic testing revealed that the catalyst is highly active. It allows carrying out the process of hydrogenation of D-glucose to D-sorbitol selectively (not less than 98 %).The study of the kinetics showed the presence of two consecutive stages of the hydrogenation process, the rates of which differ by several orders. Fast stage of the process is explained by non-steady-state processes connected with the catalyst pretreatment with hydrogen. Phisical-chemical, kinetic investigations and mathematic modeling allowed suggesting the mechanism of D-glucose to D-sorbitol hydrogenation on Ru-containing heterogeneous catalyst.

Investigation of the Mechanism of Deactivation of Pd/Sibunit Catalyst Hydrodechlorination of Polychlorinated Biphenyls

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Previously we have shown that nano-dispersed Pd supported on the graphite-like carbon Sibunit is a good catalyst for hydrodechlorination of polychlorinated biphenyls (PCBs). Repeated used test showed that the catalytic activity decreased after the first and second run, and stabilized in after the third. In this paper we investigate the mechanism of deactivation of the catalyst 5% Pd/Sibunit by XPS and TEM.

Table 1. The content of elements on the surface of the samples (equivalent atoms).

No.	Sample of catalyst	C	Pd	Na	Cl	O
1	Initial catalyst	55698	1228	305	120	6579
2	Catalyst after hydrodechlorination of PCBs with NaOH, washed with ethanol	35463	780	3486	3465	3402
3	Catalyst after hydrodechlorination of PCBs with NaOH, washed with ethanol and water	47215	862	26	117	5110
4	Catalyst after 3rd run hydrodechlorination of PCBs with NaOH, washed with ethanol and water	56307	601	545	159	5670
5	Catalyst after hydrodechlorination of PCBs without NaOH, washed with ethanol	62937	1154	9	1301	5760

Analysis of the catalyst surface by XPS showed that NaCl is crystallized on the surface of catalyst (No.2) (the reaction is carried out in ethanol, because PCB is insoluble in water). Washing with water releases the catalyst surface from the NaCl (No.3). Carrying out the reaction without NaOH leads to the adsorption of chlorine (No.5). The surface concentration of Pd in used catalysts decreases (samples Nos. 1, 2, 4 - 14, 9, 7%, respectively). In the absence of NaOH the leaching of Pd is less (No.5). Elemental analysis of samples (4.81% Pd in the initial catalyst and 4.02% after the 1st run) also shows leaching of Pd during the reaction, but the content Pd in the solution was <0.22%. Therefore, Pd is deposited, not only on the catalyst, but also on the reactor walls, stirrers, etc. This process is accompanied by increase of the Pd particle size in the catalyst (TEM). Analysis of the shape of the Pd3d and Cl2p peaks shows that Pd and Cl are present on the surface of the samples in several states.

Thus, the reduction concentration of Pd (mainly on the surface), the increasing the Pd particle size and the sorption of NaCl (in the presence of NaOH) and Cl-ions (in the absence of NaOH) on the catalyst surface are the main cause of reduced catalytic activity. The possibility of sorption of chlorinated products (as such or as compounds Pd) requires further study.

PP-III-70

Decomposition and Steam Reforming of Methanol over Pd, Cu - CNT Catalysts

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Introduction

Hydrogen and fuel cells are a great opportunity to reduce emissions of toxic compounds such as nitrogen oxides, carbon oxides, various hydrocarbons, and thus contribute to reducing environmental pollution and the possibly tackling global warming [1].

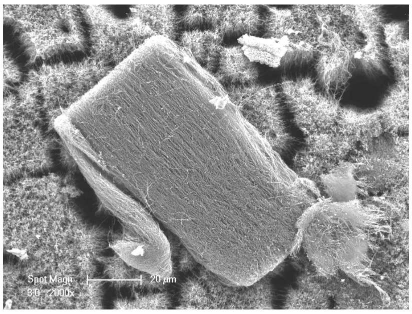
Hydrogen is also one of the most important raw materials used for synthesis of chemical products such as ammonia, hydrogen chloride, methanol, synthetic gasoline and it is also important as a propellant [2, 3]. Today the development of economically viable hydrogen generation technology that will allow realization of these important future applications is a matter of urgency.

Experimental

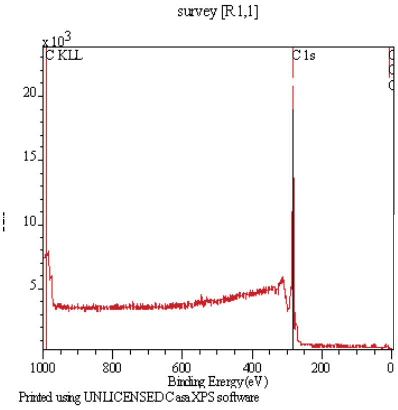
The monometallic palladium and copper catalysts supported on multi-walled carbon nanotubes were prepared by conventional impregnation methods. The multi-walled carbon nanotubes were prepared by CVD method based on catalytic decomposition of 5% ferrocene in toluene at two temperatures 850 and 925°C. The obtained support material was impregnated by appropriate aqueous solution of palladium chloride and copper (II) nitrate (V). Then the catalysts were dried and calcined 4h in air at 400°C. The physicochemical properties of catalysts were examined by BET, XRD, XPS and TPR methods. Chemisorption uptakes were measured using ASAP 2020C apparatus from Micromeritics (USA). The activity tests in methanol steam reforming (SRM) and methanol decomposition were carried out over palladium and copper catalysts in the temperature range 160 to 320°C in a flow quartz reactor under atmospheric pressure, molar ratio $H_2O/CH_3OH = 1$ and 2.

Results and discussion - The obtained high purity carbon nanotubes have an average thickness of ca. 60 nm and a length of 450 microns, as indicated by XPS and a scanning electron microscope (SEM) figures which are shown below.

The phase composition studies of copper and palladium catalysts after calcination process confimed the occurece of followng phases for approciate catalytic systems : C, CuO and PdO. The XRD patterns recorded for analogical catalysts after reduction and reaction showed the reflexes stem from metallic Cu and Pd formed during reduction of CuO and PdO phases for appropriate systems.



SEM image of multi-walled carbon nanotubes collected from the reactor



XPS spectrum of multi-walled carbon nanotubes collected from the reactor

Reduction studies of prepared catalytic systems confirmed the occurrence of oxide phases observed on diffractograms for copper and palladium catalysts. The activity tests in methanol decomposition showed that total conversion of methanol was obtained at 260°C for all systems, while in the case of SRM the same yield for all systems was obtained until 320°C. It is worth to note that 50% conversion of methanol was achieved for decomposition and SRM reactions at 220 °C and 280 °C, respectively. The increasing of metal content in both systems caused the activity improvement.

Conclusions

Multi-walled carbon nanotubes are useful material as a support for monometallic copper and palladium supported catalysts. Cu/CNT and Pd/CNT catalysts are promising systems for hydrogen production in methanol steam reforming reaction. Methanol conversion, selectivity to hydrogen and yield of hydrogen production depends on composition of reaction mixture.

Acknowledgements The financial support of this work by the Foundation of Polish Science supports (START Programme Stipends for young researchers) is gratefully acknowledged.

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PP-III-71

New Approaches for Study of the Formation Processes and Composition of Active Centers of Supported Titanium-Magnesium Catalysts for Olefin Polymerization

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The contemporary highly-active supported titanium-magnesium catalysts (TMC), which contain titanium chloride ($TiCl_4$, $TiCl_3$) on the "activated" magnesium chloride as a support, in combination with the organoaluminum co-catalyst (AlR_3), found the widest application in the production of polyolefins (polyethylene and polypropylene). Studies of these catalysts have a long history, nevertheless some questions, such as the mechanism of the formation of active sites (AS) by interaction of titanium chlorides with the support, structures of AS, correlation between the activity, the molecular-mass characteristics of polymers and the composition of these catalysts are still a subject of discussions. Formidable difficulties in a study of the active sites of these catalysts at the molecular level are connected with their heterogeneity and their low concentration (less than 10% of the content of titanium in the catalyst).

We established that the catalysts with the very low titanium content ($\leq$ 0.1wt.- %) have the extremely high activity (30 000 kg of PE/mol of Ti·h·bar $_{C2H4}$) in the polymerization of ethylene and co-polymerization of ethylene with α- olefins, compared with the activity of "single site" homogeneous metallocene and postmetallocene catalysts. According to the data of radiochemical studies [1], the increased activity of "low-percentage" TMC is connected with the high concentration of active sites (0.30-0.55 mole/mole Ti). Thus "low-percentage" TMC, in which the high share of the titanium is active in the polymerization, is convenient object for investigating of the processes of their formation, composition and structure of active sites.

The interaction of the $TiCl_4$ with $MgCl_2$, and activated of TMC with different content of titanium with the organoaluminum co-catalysts is studied using calorimetry, EPR, IR and chromate-mass-spectroscopy methods. The obtained results of physico-chemical studies in combination with the catalytic data about the activity and the molecular structure of polymers (molecular- mass characteristics of polyethylene and polypropylene, the sterioregularity of polypropylene) made it possible to formulate new ideas about composition and structure of active sites in the model "low-percentage" ($\leq$ 0.1 wt.-% of Ti) catalysts and usual TMC, (1.0-2.0 wt.-% of titanium). The mechanism of formation of these sites by interaction of TMC with the organoaluminum co-catalyst and places for localization of stereospecific and nonstereospecific AS on the different faces of activated $MgCl_2$ are discussed as well.

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Conversion of Methanol to Formaldehyde on Supported Copper-Zinc Catalysts in Synthesis-Gas Medium

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Production of formaldehyde by methanol dehydrogenation is considered to be more advanced process as compared to its partial oxidation as hydrogen evolved in the reaction returns into the stage of methanol synthesis, which reduces drastically raw material consumption.

In the paper presented, methanol dehydrogenation to formaldehyde was carried out on supported copper-zinc catalysts, with porous silica gel being used as a carrier. The surface of the latter has been modified with carbonate and silicate compounds of potassium, which enables the activity of the catalysts concerned to considerably increase. The effect of the reaction medium simulating the composition of synthesis-gas of methanol production has been studied by varying the composition of the initial gaseous mixture by altering carbon monoxide, carbon dioxide and hydrogen ratio, with the concentration of methanol remaining constant.

The raise of carbon monoxide partial pressure increases the efficiency of copper catalysts for dehydrogenation reaction. In this case, it takes a long time for the system to reach steady state operating condition, and the process is accompanied by a change in the selectivity of hydrogenation reaction from methyl-formate to formaldehyde.

Along with the main reaction, there takes place the formation of dimethyl ether, methane as well as methanol decomposition accompanied by isolation of carbon. The catalysts with zinc oxide only are less susceptible to the presence of a gaseous mixture of carbon oxides. No methyl-formate is formed in this case, and in the presence of hydrogen the reaction route of free carbon allocation is markedly depressed. Copper-zinc applied catalysts are more active towards formaldehyde, but the increase in hydrogen concentration in a reaction mixture deactivates the catalysts at high temperature (~500 0C) and minimizes the effect of copper. Hence, it is the right choice of the applied components ratio that is responsible for activity and stability of a catalyst performance.

The process of reaching catalyst steady state consists both in reducing oxide copper compounds and the formation of hydrocarbon species on its surface. Mutual influence of reducing agents - hydrogen and carbon monoxide, leads to an increase in the degree of reduction of oxide compounds, and changes in reaction selectivity as to the reaction products: methyl formate - formaldehyde.

PP-III-73

Effect of B-Cation Substitution on the Activity of $LaCrO_3$ and $LaNiO_3$ Perovskites for Autothermal Reforming of Methane

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Perovskite-type oxides (ABO_3) are perspective catalysts for hydrocarbon conversion to CO and H_2 [1]. Partial substitution of the A- or B-cations with other metals modifies the catalytic performance due to the variation of redox properties and oxygen mobility [2]. The aim of this work is to study the effect of B-cation substitution on the activity of $LaCrO_3$ and $LaNiO_3$ perovskites for autothermal reforming (ATR) of CH_4. Substituted $LaCr_{1-x}B_xO_3$ (B = Ni, Fe, Ru, Co, Mn, x = 0.15), prepared by Pechini method, and $LaNi_{1-x}B_xO_3$ (B = Pt, Pd, Re, Sn, Mo, x = 0.01-0.05), prepared by citrate sol-gel method, were characterized by DTA-TG, XRD, N_2 adsorption (BET), TPR, XPS, HRTEM and tested in the ATR of CH_4 in a fixed-bed reactor with mass-spectrometric gas analysis. XRD showed that all the $LaCr_{1-x}B_xO_3$ and $LaNi_{1-x}B_xO_3$ samples have the $LaCrO_3$ and $LaNiO_3$ perovskite structures, respectively. Initial $LaCrO_3$ catalyst exhibits low ATR activity and gives mainly CO_2 at CH_4 conversion ~ 36 % (T = 850°C). The substitution of Cr by Ni, Fe, Co or Mn has practically no effect on the product yield. On the contrary, using Ru the highest H_2 (~ 45 %) and CO (~ 65 %) yields at CH_4 conversion ~ 100% (T = 850°C) were observed. Remarkably, substitution of Ni by B-cations in $LaNiO_3$ leads to an increase of S_{BET} up to 2 times. We demonstrate that $LaNi_{1-x}B_xO_3$ catalytic performance in the ATR of CH_4 can be regulated by the type and content of B-cation. The particularities of ATR of CH_4 over $LaCr_{1-x}B_xO_3$ and $LaNi_{1-x}B_xO_3$ are revealed and correlated with the type of B-cation, structural and redox properties of these catalysts.

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MCP Transformation on Rh-M (M=Ge, Sn) Grafted Catalysts

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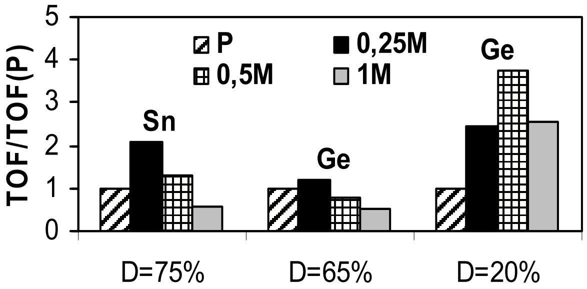
Increasing attention is paid nowadays to bimetallic ensembles prepared by "Controlled Surface Reactions" (CSR), so-called tailor-made catalysts [1, 2]. The full characterization of such catalysts requires combination of physico-chemical methods with catalytic tests [3, 4]. Our aim was to get closer to the understanding of Rh-Ge and Rh-Sn interactions and to examine the effect of particle size of the monometallic parent catalyst. Three 1% Rh/Al_2O_3 catalysts were prepared with dispersion of 75, 65 and 20 %, respectively. They were modified by adding heptane solution of $Sn(n\text{-}C_4H_9)_4$ or $Ge(n\text{-}C_4H_9)_4$ in Ar atmosphere at T=323 K, in amounts nominally to 1/4, 1/2 and 1 monolayers [4]. After drying (in Ar at 393 K), the samples were reduced in H_2 at 473 K for 4 h. The catalysts were characterized by H_2 chemisorption, TEM, CO-FTIR, ^{119}Sn-Mössbauer spectroscopy and in transformation of methylcyclopentane (MCP) in a closed loop reactor [4].



Activity of 1%Rh/Al_2O_3 catalysts with different dispersion and activity change of bimetallic samples after Sn or Ge grafting in methylcyclopentane reaction, p(MCP)/p(H_2)= 1,3/32 kPa, T=483K.

In the case of the parent catalyst (P), the activity related to one surface Rh atom (TOF, h^{-1}) increased with decreasing dispersion. Larger Rh particles produced also more fragments. Addition of second metal in small amounts increased the catalytic activity (per surface Rh atoms determined by H_2 chemisorption). For samples with high dispersion addition of 1/4 monolayer while with low dispersion 1/2 monolayer provided the highest activity. Changes were more pronounced on large particles and the effect of Sn addition was more important then that of Ge. Correlating the catalytic behavior with the observed selectivity pattern we suggest that small amount of the second metal deposited selectively on low-Miller-index micro-facets increasing the introduced amount leads to deposition on bigger on high-Miller-index sites (random deposition). The formation of different inter-metallic compounds is also suggested.

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PP-III-75

Influence of the ZrO_2 Phase Composition, Steady-state Y_2O_3 on CO Oxidation on Supported Palladium Catalysts

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In this paper we give study of the influence of phase composition - ZrO_2-Y_2O_3 , derived using EB-PVD method, on physico-chemical properties and catalytic activity of supported palladium compounds in the CO oxidation

X-ray amorphous ZrO_2- 6,5%Y_2O_3 consists of superfine randomly oriented crystallites, which size is 3-5 nm. The samples, that contain 9,5% and 15%Y_2O_3 are cubic ZrO_2 (JCPDS № 81-1550), with average crystallite size, calculated to Scherrer equation 14 and 18 nm. Palladium was supported by impregnation with $Pd(NO_3)_2$ solution and additional recovery with formaldehyde. In the case of amorphous sample, Pd is mainly situated in meso- and macropores, and in crystallic samples significant amount of Pd is situated in micropores. Such dependencies are also observed in the samples, that were used in catalysis.

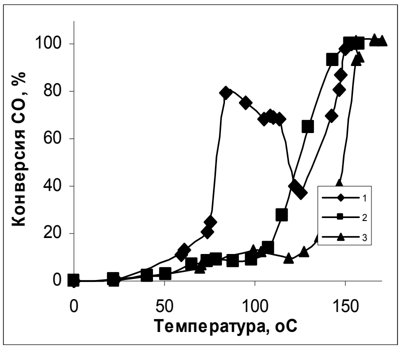

Fig. 1. Dependence samples catalytic activity on the temperature in the reaction of CO oxidation: 1 - ZrO_2-6,5%Y_2O_3 +1% Pd, 2 - ZrO_2-9,5%Y_2O_3+1% Pd, 3 - ZrO_2-15%Y_2O_3+1% Pd

The plot of temperature dependence of catalytical activity (fig. 1) can be roughly divided into two domains. First is domain of transient activity (up to a temperature 120°C) and II - the region of stationary activity - above 120°C. In the first domain, activity was measured after 10 min after entering the mode. At the temperatures above 70°C it decreased over time. The reason could be enlargement of the palladium particles. Domain of transient activity is observed in cases of all studied samples, but it is much more in the case of amorphous carrier, probably due to some stabilization of active clusters of finely dispersed Pd. In the second domain the ZrO_2-15%Y_2O_3+1% Pd is more active, since it is known that the increase of yttrium oxide in ZrO_2 leads to an increase in the mobility of oxygen, and thus to an increase in activity.

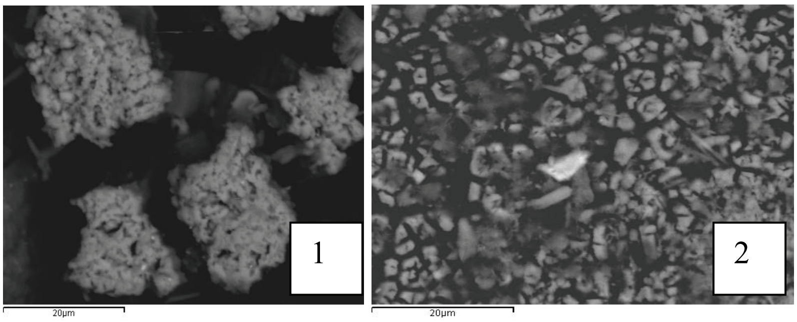

Fig. 2.
1- ZrO_2-6,5%Y_2O_3+1% Pd catalyst after use,
2 - ZrO_2-15%Y_2O_3+1% Pd catalyst after use.

According to electron microscopy (Fig. 2) in the ZrO_2-6, 5% Y_2O_3 +1% Pd catalyst after working as a metalcatalyst after working as a metal, significant amount of Palladium is situated on the inner surface of the sample, while in the ZrO_2-15%Y_2O_3+1%Pd catalyst amount of Palladium on the inner surface is insignificant.

PP-III-76

Mechanism of Catalytic Elimination of 1.2-Dichloropropane into Allene and Methyl Acetylene

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The purpose of this research was the study of kinetic regularities of reaction dehydrochlorination of 1.2-dichloropropane into allene and methyl acetylene in the presence of catalysts CaX, γ-Al_2O_3 and expanded clay, as well as discussions of possible routes for the formation of the reaction products [1.2].

It is found that the speed of the dehydrochlorination reaction of 1.2-dichloropropane in these conditions is satisfactorily described by the first order to 1.2-dichloropropane. Calculated according to experimental data values of apparent activation energy of dehydrochlorination reaction of 1.2-dichloropropane in the presence of catalysts γ-Al_2O_3, CaX and expanded clay were 93.44 kJ/mol, 77.18 kJ/mol and 54.9 kJ/mol. Quality comparison of selectivity of formation of hydrocarbons C_3H_4 with conversion degree of 1.2-dichloropropane has shown that process indicators have the highest value in the presence of expanded clay.

According to the author [3] classification for the obtained values ($k_0 = 1.27 \cdot 10^{11}$ s^{-1}), the investigated reaction is refers to the monomolecular in the adsorption layer.

The using of BOTH allowed to us to identify the number of active centers as ratio of calculated k_0 to the pilot. The result of calculations on the number of active points on the surface (sm^{-2}) show that tested catalysts settle in the following sequence:

$$\gamma\text{-}Al_2O_3 \quad < \quad CaX \quad < \quad \text{Expanded clay}$$
$$0.2\cdot10^3 \quad < \quad 0.6\cdot10^4 \quad < \quad 0.4\cdot10^6.$$

In the case of γ-Al_2O_3 preferential formation of allene with the subsequent isomerization to methyl acetylene is consistent with the participation of the Lewis acid and basic centers, while CaX and expanded clay Lewis and Bronsted acid centers fit an agreed mechanism for joint participation in the formation process of allene and methyl acetylene.

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PP-III-77

Mechanisms of Heterogeneous-Catalytic Reactions of Ethylene Monooxidation by Hydrogen Peroxide

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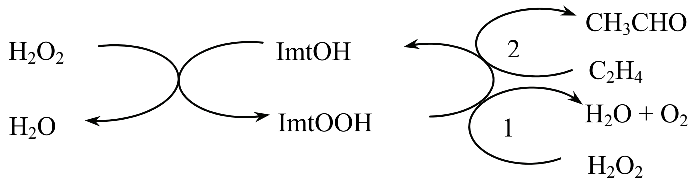
The biomimetic catalyst per-FTPhPFe^{3+}OH/Al_2O_3 indicated extremely high resistance to the effects of oxidant and their intermediates and relatively high temperature [1]. Owing to the mentioned properties of the biomimetic catalyst, the gas-phase monooxidation of ethylene by hydrogen peroxide on this catalyst was studied under comparatively mild conditions. The products of ethylene monooxidation reaction (C_2H_5OH and CH_3CHO) are the end ones, therefore selectivity of reaction taking into account these products in the conditions of the highest yield of ethyl alcohol (15.4 mas.%) and the least yield of acetaldehyde (12 mas.%) made up practically 100% and vice versa, in case of obtaining the highest yield of acetaldehyde (34.6 mas.%) and the least one of ethyl alcohol (4.6 mas.%) selectivity made up 87% owing to formation of by-product CO_2. Biomimetic per-FTPhPFe^{3+}OH/Al_2O_3 has demonstrated unique steadiness to both oxidant effect and high temperatures while retaining its activity [2].

From the experimental data follows that two synchronous reactions, catalase (primary) and monooxygenase (secondary) reactions, interact with each other. As a result, chemical interference is observed in the system, and the primary reaction strengthens the secondary one, which, in turn, decelerates the primary reaction. According to the generally accepted mechanism [1], these coherent-synchronized reactions can be written as:



where ImtOH is the per-FTPhPFe$_3$+OH/Al_2O_3 biomimetic and ImtOOH is an intermediate compound, 1 is the catalase (primary) and 2 is monooxygenase (secondary) reaction.

Both reactions occur via a common intermediate, per-$FTPhPFe_3^+OOH/Al_2O_3$, which transfers the inductive action of the primary reaction to the secondary one; that is, the process occurs under bifurcation conditions.

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Kinetic Regularities of 1-Decene Polymerization on Supported Titanium-Magnesium Nanocatalysts (TMNC) and Molecular Weight Characteristics of Obtained Polymers

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Synthesis of high molecular weight polydecene (PD) on TMNC developed at the TIPS RAS was studied [1]. It is shown that the process takes place under mild conditions (20-60°C and atmospheric pressure) in aliphatic solvent. In order to establish the possibility of regulation of the catalyst stereospecific ability and activity and molecular weight of PD TMNC was used both itself, and being modified with internal (9,9-bis(methoxymethylen)fluorine) and/or external (cyclohexylmethyldimetoxysilane) electron donor (ED).

It was found that the most active catalyst is unmodified (or basic) TMNC. The introduction of external ED reduces the system resulting activity in 3.8 times (initial activity drops in 14 times). Such a change in activity is typical in most cases of polymerization on titanium-magnesium catalysts modified with ED [2, 3]. Thus the ED does not change the monomer second order up to the end of polymerization. The introduction of internal ED in any combination with an external one or without it gives the first order. A notable violation of the first order is observed with increasing process temperature above 30°C. The activation energy of 1-decene polymerization is 91 kJ/mol e.g. very high and defines much lower rate of 1-decene polymerization, compared with shorter α-olefins.

TMNC is able to produce PD with molecular weight up to 4 mln and more, and with the ED introduction the shift in molecular weight to higher values and the disappearance of the polymer chains with a weight less than 700000 is observed. Similar effect is in a good agreement with the theory of blocking with ED of active sites producing non-stereoregular low molecular weight polymer chains.

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PP-III-79

The Nature of Synergistic Effects in Catalysis by Au-NiO Nanoparticles

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In the present work some monometallic M (M = Au, NiO) and bimetallic Au-M particles with different sizes (3-100 nm) supported on Al_2O_3, SiO_2, ZrO_2, TiO_2 and ZnO were synthesized with application of deposition-precipitation and impregnation techniques [1]. Structural and physicochemical properties of synthesized nanocomposites were investigated via TEM, XPS, DRIFT and XAS. The catalytic properties of supported nanoparticles were studied in the processes of: the purification of ethylene feedstock for polymerization by selective hydrogenation of acetylene in the presence of ethylene at 273-423K; the utilization of bioglycerol by steam reforming of glycerol into the synthesis gas at 373-793K; the migration of C=C bond in olefin compounds at 443K.

A strong synergistic effect of the activity was revealed for Au-NiO catalysts: Their activity in hydrogenation, isomerization and glycerol conversion was higher than the sum of conversions on Au and Ni catalysts. According to obtained structural and physicochemical data synergistic effect could be explained in terms of: 1) formation of new $Au^{\delta+}$ catalytic sites due to electron transfer from electron-rich gold to electron-deficient nickel; 2) decreasing in supported clusters aggregation; 3) formation of additional adsorption sites near catalytic centers.

This work was supported by Russian Foundation for Basic Research grant № 11-03-00403 and Council of President of Russia grants for the young scientists (MK 107.2011.3, MK-2917.2012.3, MK-1621.2012.3)

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Enantioselective Hydrogenation of C=C-Bound on Colloidal Palladium Catalyst Modified by (-)-Cinchonidine

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The colloid metals are well known as the effective and stereoselective catalysts for C-C-bond formation, ketones and olefins hydrogenation. The metal colloids stabilized by the optical active molecules and ions are applicable in the enantioselective transformations of prochiral molecules, in particular, in the enantioselective hydrogenation of methyl pyruvate that is catalyzed by the colloidal platinum modified by dihydrocinchonine [1]. The highly dispersed transition metals in colloidal suspension allow one to study the catalytic properties of the small metal particles in an absence of solid supports.

In this work, for the enantioselective hydrogenation of dimethyl itaconate (DMIA) and methyl α-acetamido cinnammate, we used the chiral cinchona alkaloid such as the widely applied (-)-cinchonidine (Cin) to modify the system $Pd(acac)_2$-H_2 that showed the catalytic activity in the unsaturated C=C-bonds hydrogenation.

At ambient temperature, P_{H2} = 5 bar and 100% conversion after 20 hour, the enantiomeric excess (*ee*) of methyl *R-(-)*-N-acethyl-α-phenylalanine achieved 78% *ee*. The figure presents the dependence for *ee* of methyl *R-(-)*-N-acethyl-α-phenylalanine on (-) Cin/Pd ratio. For dimethyl itaconate hydrogenation, one obtains a moderate result only.

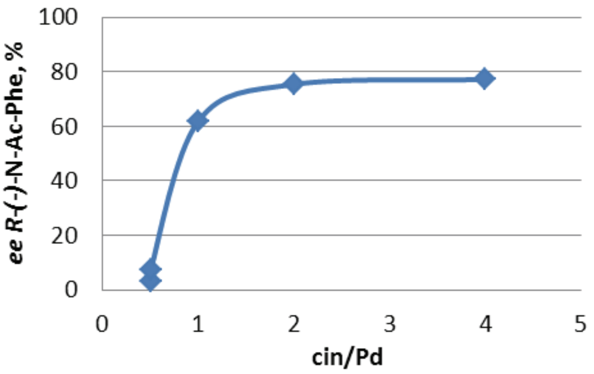

Figure. The (-) Cin/Pd ratio influence on the yield of methyl *R-(-)*-N-acethyl-α-phenylalanine

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PP-III-81

Influence of the Way of Active Sites Formation in Pt/MgAlOx Catalysts on their Catalytic Properties. XPS Study

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Catalysts Pt/$MgAlO_x$ synthesized with the use of layered magnesium-aluminum double hydroxide (MgAl-LDH) as a support precursor are the object of intensive studies, since they are important for the base catalysis and hydrocarbons conversion [1]. This relates primarily to dehydrogenation of light alkanes. The growing demand for C_2-C_4 alkenes in the production of polymers raises interest in catalytic dehydrogenation and initiates the development of new catalytic systems.

Investigation of the interaction of chloroplatinic acid as a platinum precursor with MgAl-LDH showed that the amount of anionic complexes of Pt(IV) adsorbed from an aqueous solution and their localization in the support structure are strongly determined by the nature of interlayer anions in LDH and ability of the anions to ionic exchange. Thus, the exchange of interlayer OH^- anions for $[PtCl_6]^{2-}$ was more pronounced as compared to that of CO_3^{2-} anions, with predominant localization of metal complex in the interlayer space. As a result, platinum reduction under constrained conditions of the layered structure was accompanied by the formation of particles with unusual planar morphology [2]. As a consequence, catalysts of the same chemical composition but prepared using LDH with different interlayer anions OH^- or CO_3^{2-} differed in the activity of propane dehydrogenation.

The localization of platinum in the structure of the support and its electronic state were studied depending on the LDH nature by XPS with analysis of $Pt3d_{5/2}$ level using Ag L_α irradiation. It was found that the surface concentration of platinum decreased more than 3-fold when interlayer anion $CO_3^{2-}$was replaced by OH^- at the same metal content. This observation agrees with data on the fixation of platinum complexes in the interlayer space of LDH.

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New Capabilities for XPS Studies of Ziegler-Natta Catalysts Using a System of Sample Loading in Inert Atmosphere

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A lot of efforts are made since the discovery of Ziegler-Natta catalysts to find an explanation for chemical and structural features of active sites that are responsible for polymerization of α-olefins. Several models suggested for the structure of the active sites are based on analysis of structure of polymers produced in the process. At the same time there is still no direct proof for one or another structure of the active sites. XPS is known to be highly effective method for studies of the nature of active sites of different heterogeneous catalysts. However, studies of Ziegler-Natta catalysts using XPS are limited due to low resistance of the catalysts to oxygen and water vapour resulting in complete deactivation during the sample loading into a vacuum chamber of a spectrometer. To resolve this problem, a special system is made in Boreskov Institute of Catalysis for loading samples into an X-ray photoelectron spectrometer SPECS in atmosphere of high-purity argon. The system makes possible to load a Ziegler-Natta catalyst from a sealed ampoule into an analytical chamber of the spectrometer in conditions eliminating a possibility of oxidation or hydration. In the present work, samples of catalysts for ethylene polymerization $TiCl_4/MgCl_2$ are studied at different steps of preparation.

It is established that the oxidation state of titanium – Ti^{4+} – remains unchanged after fixation of titanium tetrachloride on the surface of the support. Titanium reduces intensively to produce Ti^{3+} and Ti^{2+} states in the course of activation of the supported sample with triethylaluminum. A spectrum obtained by us for the activated catalyst is similar to that of model catalysts prepared in a vacuum chamber of an electron spectrometer without exposure to atmosphere [1]. In conclusion, based on these results, the technique developed allows us to obtain correct data studying samples of polymerization catalysts by XPS.

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PP-III-83

Mechanism of Butadiene Heterocyclization over Sulfided HDS Catalysts

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Afanasieva et al in 1970 published production of thiophene from butadiene and H_2S over La-K-Cr contained catalyst [1]. Thiophene hydrodesulfurization (HDS) reaction over Mo contained catalysts is resulting H_2S and C_4 hydrocarbons or directly [2] or via 1,3 butadiene as intermediate molecule [3]. Thiophene HDS over $H_2{}^{35}S$ sulfided Mo/Al_2O_3 catalyst resulted ^{35}S labelled thiophene [4]. This result shows that during HDS after the thiophene ring opening also recyclization takes place besides hydrogenation with another sulfur atom from the surface.

$$C_4H_4S + {}^{*}S_{cat} \rightarrow C_4H_4{}^{*}S + S_{cat}$$

Theoretically this mechanism can take place via two different pathways, a) as direct recyclization on the surface of sulfided catalyst (thiophene – thiolate - thiophene) and b) as a heterocyclization of intermediate butadiene and H_2S as products of the HDS [5] (thiophene – butadiene – thiophene). Butadiene conversion experiments have been performed in gas circulation apparatus (50mg catalysts were fed **a**; Butadiene + H_2S + H_2, **b**; Butadiene + H_2, **c**; Butadiene, + H_2S, **d**; pure butadiene) and in pulse system (10 mg catalysts fed butadiene in a; H_2, b; N_2 flow).

Results showed that in all cases thiophene was producted.

1) It shows simple butadiene can remove the sulfur from the MoS_2. This reaction can play an important part in decreasing of the surface sulfur during HDS.

$$C_4H_6 + S_{cat} \rightarrow C_4H_4S + cat + H_2$$

2) In presence of H_2 also thiophene production took place, and probably H_2 is absent on the surface of catalyst, so in condition of experiments H_2 adsorption and migration on the surface can be slower than heterocyclization. 3) Presence of H_2S resulted in higher amount of thiophene, consequently the well known poisoning effect of H_2S in HDS was not caused by the blocking of the active sites but from the supporting of the reverse reaction.

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Catalytic Reaction Dynamics Caused by Ions Mobility in Solids

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The mobility of ions and atoms in solid catalysts is manifested as the diffusion of oxygen in metal oxides (V, Cr, Mn, Fe, Mo); of carbon in metal carbides (Fe, Ni); and of hydrogen in metals and hydrides (Pd, Ti, La). It happens when reagents oxidize or reduce the surface layer of the catalyst. Then the solid bulk tends "to lick its wounds" by diffusion of atoms or ions from the bulk to surface (in reducing medium) or in opposite direction (in oxidizing medium). Certainly, ions mobility (for example oxygen) is marked only in oxides of variable level of metal oxidation (V_2O_3-V_2O_5, Cr_2O_3-CrO_3) in contrast to Al_2O_3 or SiO_2.

Since ions diffusion in bulk is caused by reaction on the surface, it affects the state of surface, and consequently affects the reaction dynamics. Because the capacity of bulk is much higher than that of the surface, ions mobility increases the working period of the catalyst. It makes acceptable the non-stationary cyclic regime of the process with the reaction period and the catalyst recovery period. In oxidation processes such a regime provides usually higher selectivity than the steady-state regime [1, 2].

In this report, the region in which the diffusion of ions in catalyst bulk affects the transient regime of catalytic reaction is examined, and corresponding ions diffusivity is estimated.

The complex effect of ions diffusion in catalyst bulk and reagents diffusion in pores is also considered. It is shown that the pellet effectivity is considerably affected by ions diffusion in a kinetic region of the reaction. On the contrary, in a diffusion region, the pellet effectivity only slightly depends on ions diffusion.

The considered problem, takes on a special significance in the case of reactor with a fluidized catalyst bed. Such a reactor is the most convenient option for cycle periodic regime of the process, with an internal or external circulation of the catalyst. The interval of ions diffusivity is estimated that affects total conversion in the reactor and average activity of the catalyst.

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PP-III-85

MgAlY Layered Double Hydroxides as Catalysts for Organic Syntheses Catalysed by Base Sites

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This contribution aims to bring new highlights concerning the effect induced by the incorporation of Y in the brucite-type layer of MgAl layered double hydroxides (LDH) structures on the basicity of these structures, the possibility of their reconstruction via the "memory effect" and their catalytic activities in organic syntheses mediated by base sites. A series of $Mg_xAl_{(1-y)}Y_y$-LDH compounds (where x = Mg/(Al+Y) = 1-10, y = 0.04-0.66) have been prepared by co-precipitation at constant pH = 10 under low supersaturation conditions using aqueous solutions of metal nitrates, NaOH and Na_2CO_3 according to a previously described method [1]. The obtained solids were calcined at 460 ^oC for 18 h, yielding the corresponding mixed oxides $Mg_xAl_{(1-y)}Y_y$-MO. The reconstruction of the LDH phases via "memory effect" was performed by hydration of the mixed oxides at different temperatures in the range 25-100 ^oC, yielding $Mg_xAl_{(1-y)}Y_y$-$LDHR_T$ (T = temperature). All the solids have been characterized by XRD, DRIFTS, DR-UVVis-NIR, and BET. The surface base sites of the catalysts were determined using a method suitable for both dried and calcined samples consisting in the irreversible adsorption of organic acids with different pK_a [2]. The catalytic activity of the samples was tested in two types of base-mediated organic syntheses: *i)* cyanoethylation of ethanol and *ii)* selective oxidation of cyclohexene by molecular oxygen in the presence of isobutyraldehyde. The characterization results showed that both surface areas and crystallinities of $Mg_xAl_{(1-y)}Y_y$ materials decreased with the increase of Y content in the range y = 0.01-0.66 for all x values in the range 1-10. Meanwhile, the basicity followed the opposite trend. The reconstruction of the LDH structure was possible only for the samples with lower content of Y (e.g. y = 0.04-0.33) and the heating during the rehydration process had beneficial effects on the crystallinity, the texture and the basicity of the materials. The catalytic activity of $Mg_xAl_{(1-y)}Y_y$ materials for both catalytic processes investigated was higher than that of the corresponding Mg_xAl materials, indicating the importance of the basicity increase following the incorporation of Y in the brucite-type layers.

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PP-III-86

FTIR Study of Adsorption and Transformations of HCN on Oxide Adsorbents

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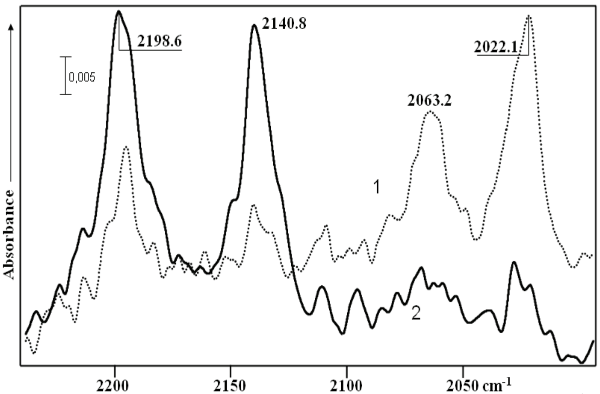
In spite of a great importance of HCN for organic synthesis, the mechanism if its adsorption and transformations on the surface of oxide catalysts is far of being understood. It has been shown earlier that ^{13}C- and ^{15}N- isotopic substitution can be helpful to distinguish the products of HCN dissociation on silica [1] and alumina [2], while DCN adsorption enables us to clarify the structure of molecular complexes of hydrogen cyanide [2, 3]. In the present work isotopic substitution was used to determine the forms of HCN adsorption on TiO_2, γ-Al_2O_3 and MgO. Experimental results we compared with calculated isotopic shifts for model structures.

Spectra of adsorbed DCN enable us to distinguish between the bands of molecular adsorption and those of dissociation products. Using of ^{13}C and ^{15}N substitution, we have proved that coordinately adsorbed on TiO_2 and γ-Al_2O_3 cyanide has HCN configuration, but not isomeric HNC form. Both quantum mechanical calculation and normal coordinate analysis of a model system show that C- and N-bonded forms of CN^- ion should have deviations in the isotopic shifts on ^{13}C and ^{15}N substitution from the value predicted of the reduced mass ratios. This was used for band assignment in the spectra of dissociated HCN.



Spectra of adsorbed H^{13}CN on MgO are shown in the figure. Bands at 2063.2 and 2022.1 cm^{-1} (curve 1) are the first to appear after heating the sample with adsorbed isotopic mixture above room temperature. Their separation is about 2 cm^{-1} smaller than follows from the reduced masses, while for the 2198.6 and 2140.8 cm^{-1} bands, growing on further heating (curve 2) or higher, on the contrary, the shift is about 10 cm^{-1} above the predicted value. This means that HCN dissociation first leads to N-bonded CN^- ions with further isomeric transition to C-bonded form. Analogous results, obtained for alumina, are in accordance with the earlier interpretation [2].

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PP-III-87

Study of the Mechanism of Nitrogen-Containing Carbon Nanofibers Growth on Metal Catalysts

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Presently nitrogen-containing CNFs (N-CNFs) receives a large interest because the introduction of nitrogen atoms into CNF structure leads to unique bulk and surface properties of N-CNFs [1-2]. Catalytic pyrolysis of carbon- and nitrogen-containing compounds is one of the good possibilities for efficient N-CNF synthesis [3]. This work is devoted to the study of mechanism of N-CNF growth on metal catalysts (Ni, Ni-Cu) by means of in situ XRD technique.

The decomposition of 75%C_2H_4/25%NH_3 and 25%NH_3/He mixtures on Ni and Ni-Cu catalysts at 550°C were carried out in a high-temperature reaction chamber equipped with a diffractometer of the Siberian Center for Synchrotron and Terahertz Radiation, X-ray diffraction patterns were recorded every 30 s [4].

The initial Ni-Cu catalyst consists of $Ni_{0.87}Cu_{0.13}$ (a=3.563 Å) and $Cu_{0.93}Ni_{0.07}$ (a=3.609 Å) alloys. It was shown that decomposition of 75%C_2H_4/25%NH_3 mixture on Ni-Cu catalyst proceed via dissolution of carbon in $Ni_{0.87}Cu_{0.13}$ alloy, while $Cu_{0.93}Ni_{0.07}$ alloy remains unchanged in the course of the reaction. In the case of Ni catalyst the carbon is dissolves in catalyst particle with the formation Ni_3C. It was found that N-CNFs grown during 15 min contain 1 wt.% of nitrogen.

When 25%NH_3/He mixture was passed through the Ni-Cu catalyst there were no changes in the X-ray diffraction patterns of the catalyst although the formation of nitrogen and hydrogen is registered. It was shown that ex situ treatment of pure CNFs by 25%NH_3/He at 550°C does not lead to the incorporation of nitrogen atoms into the carbon structure.

Based on the results obtained the mechanism of N-CNF growth on Ni and Ni-Cu catalysts is proposed.

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A DFT Study of Electronic and Steric Effects of Alkoxy Ligands for Dialkyl Carbonate Formation from CO_2 and *n*-$Bu_2Sn(OR)_2$

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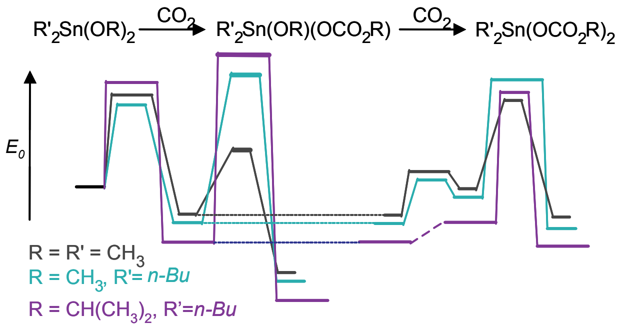
The current interest in the catalytic coupling of CO_2 and alcohols to dialkyl carbonates arises from CO_2 conversion to entering the chemical value chain. It is a challenging reaction and the mechanism is poorly understood. Here, we report on a DFT study of electronic and steric effects for CO_2 insertion into the Sn-OR bonds of tin (IV) complexes, $(R')_2Sn(OR)_2$ (R = Me, Et, iPr; R' = Me, *n*-Bu) [1,2]. DFT calculations were performed with ADF software, a TZP basis set, and PBE as GGA exchange-correlation functional.

The reaction pathways are exothermic and the driving force for CO_2 insertion is assigned to a charge-transfer between the HOMO of the tin complex, mainly localized on the oxygen atom of the alkoxy ligands, and the LUMO of CO_2. Results nicely point out that the steric effect of the R group does increase the concentration of mono-hemicarbonato species, which further reacts with CO_2 to the bis-hemicarbonato species (Scheme 1). Unexpectedly, the energy barrier of the second CO_2 insertion step is much lower than the first one. The steric effect is evidenced for the rotation step of the hemicarbonato group leading to a kinetically and thermodynamically stabilization vs extrusion of CO_2, as found experimentally [3].



Scheme 1. Energy profile of CO_2 insertion into Sn-OR bond.

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PP-III-89

Oxygen Isotope Exchange of $(1\text{–}y)\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{MnO}_{3\pm\delta}\cdot y\mathrm{Zr}_{0.82}\mathrm{Y}_{0.12}\mathrm{O}_{1.91}$

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Composite lanthanum-strontium manganites based materials are successfully used as cathode materials in Solid Oxide Fuel Cells. Unfortunately, the oxygen exchange mechanism has not been fully understood. In this study oxygen isotope exchange method with gas phase analysis have been used for the oxygen exchange mechanism investigation at T = 650—850°C and Po_2 = 1—10 Torr for *i*) $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{MnO}_{3\pm\delta}$ with different strontium content and porosity; *ii*) $(1\text{–}y)\mathrm{La}_{0.6}\mathrm{Sr}_{0.4}\mathrm{MnO}_{3\pm\delta}\cdot y\mathrm{Zr}_{0.82}\mathrm{Y}_{0.12}\mathrm{O}_{1.91}$ with y = 0—1. The method allows working with porous materials as opposed to the depth profiling techniques [1, 2].

The interphase exchange rate is shown to increase with strontium content in $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{MnO}_{3\pm\delta}$ as in the case of $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{CoO}_{3-\delta}$ investigated in [3], see fig. The oxygen exchange processes in $(1\text{–}y)\mathrm{La}_{0.6}\mathrm{Sr}_{0.4}\mathrm{MnO}_{3\pm\delta}\cdot y\mathrm{Zr}_{0.82}\mathrm{Y}_{0.12}\mathrm{O}_{1.91}$ composites take place both on the individual components of the composite material and on triple-phase boundaries (TPBs), according to a model suggested in this work.

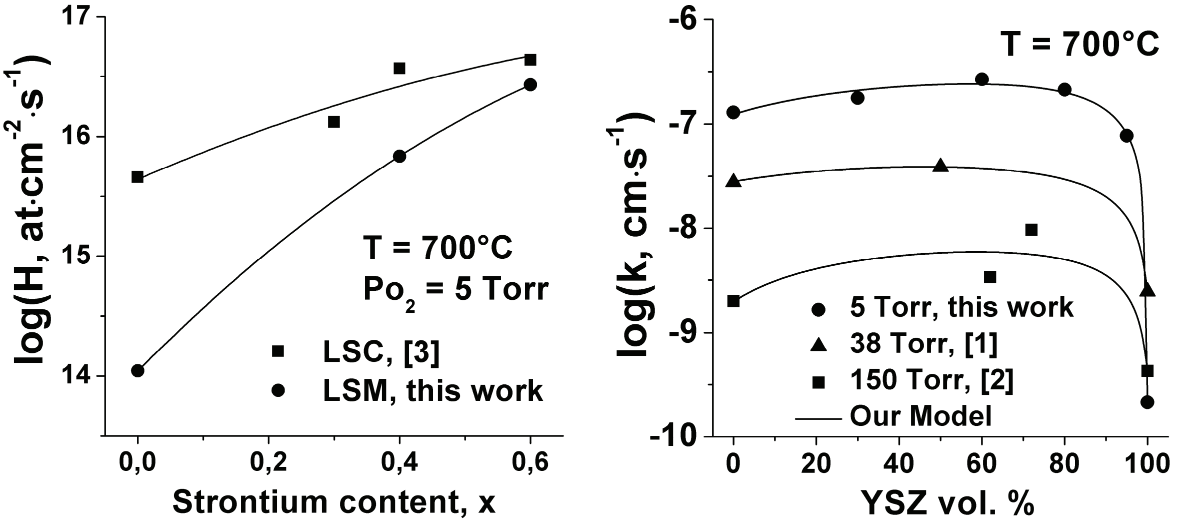

Fig. 1. The interphase exchange rate dependences as functions of Sr content for LSM and LSC oxides and YSZ vol. % for LSM—YSZ composite materials.

This work is partly supported by the grant for the young scientists of Ural Branch of Russian Academy of Sciences in 2012.

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Features of the Alcohols' Dehydrogenation on the NZP – Catalysts Depending on the Location of the Ion - Modifier

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Zirconium phosphates with NZP–framework have a flexible structure that allows for heterovalent substitution in the cation and anion positions in the lattice without destroying it. This allows to vary the redox and acid-base properties of NZP catalysts, which makes them promising catalysts.

The purpose of this work was to study the influence of the replacement of Na^+ or Zr^{4+} ions in $NaZr_2(PO_4)_3$ by zinc, cobalt, nickel, and copper ions (M^{2+}) at various ratios and the M1–M2 transition and red-ox properties of M^{2+} on the catalytic activity of NZP in the model reaction of alcohols dehydrogenation.

NZP catalysts were tested using a flow unit. The reaction mixture was analyzed by a FID chromatograph.

In case $Na_{1-2x}M_xZr_2(PO_4)_3$ in which Na^+ ions were replaced by $M^{2+} = Co^{2+}, Ni^{2+}, Cu^{2+}$, the experimental dehydrogenation activation energy E_a decreased in passing through the T* = 310–340°C temperature; above this temperature, the electrophysical and crystallographic phosphate properties changed. These changes were explained by the reversible transfer of Me^{2+} ions from position M1 to M2 in the NZP lattice. Me^{2+} centers with different alcohol adsorption forms participated in the dehydrogenation reaction. For the first form, E_a and the logarithm of the pre-exponential factor linearly correlated with the ionic radius of M^{2+} (fig.1).

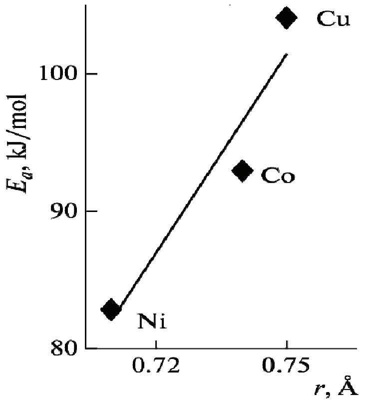

Fig.1. Correlation of the activation energy of formation of acetone with atomic radii at 200–300°C (T < T*) for samples $Na_{1-2x}M_xZr_2(PO_4)_3$ with x = 0.25

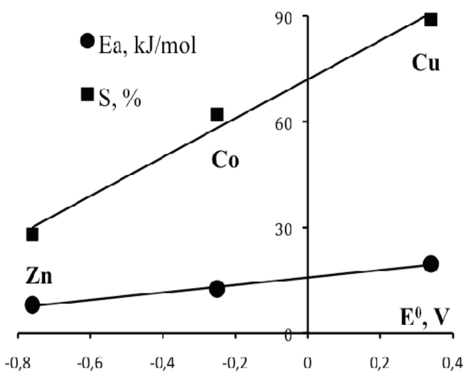

Fig.2. Correlation of the dehydrogenation activation energy and selectivity of MEK formation with standard red-ox potentials for samples $Na_3ZrM(PO_4)_3$

In case of $Na_3ZrM(PO_4)_3$ in which Zr^{4+} ions were replaced by $M^{2+} = Co^{2+}, Zn^{2+}, Cu^{2+}$, based the linear correlations of catalytic and adsorption characteristics of phosphate with standard red-ox potentials (E^0) of ion-compensators was observed that indicated the importance of reversible changes in the charge state of the active site M^{2+} in alcohols dehydrogenation as red-ox type reaction. The overall reaction with the participation of the M^{2+} active center can be written as

1) $Cu^{2+} + 2C_4H_9OH \rightarrow Cu^0 + 2H^+ + 2C_4H_9O^-$, 2) $2H^+ + Cu^0 \rightarrow H_2 + Cu^{2+}$

Thus, the activity of doped M^{2+} centers depends on its location in NZP-framework, so the catalytic activity in aliphatic alcohol conversion to aldehyde is determined not only by the ion (atom) size but of the surrounding of M^{2+} that also influenced the adsorbed alcohol state.

Direct Synthesis of Heterogenized Nickel- or Cobalt-Containing Catalytic Dithiosystems for Polymerization of Butadiene

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Nickel- or cobalt-containing dithioderivatives in combination with aluminorganic compounds (catalytic dithiosystems) show very high catalytic activity and selectivity in butadiene homogeneous polymerization process.

It is know that an ideal catalyst combines the advantages of both homogeneous and homogeneous catalysis. With this purpose we carried out an unusual method of heterogenization of homogeneous catalysts for butadiene polymerization. The nickel- or cobalt-containing dithioderivatives were directly synthesized on OH-group of support (such as silicates or zeolites).

We carried out the reaction of direct phosphorosulfuration with P_2S_5 of OH-groups of zeolite such as HLaY or HY. For it zeolite gel was released from excess of water by heating 150-200°C. Reaction of phosphorosulfuration in the medium of xylene solvent was out at 80-120°C. Using received dithiophosphorus fragment on the support and corresponding chloride, nitrate or sulphate salts of Ni and Co their heterogenized compounds have been synthesized. The received compounds were identified by phosphorus content, also with the methods of IR-spectroscopy, DTA and X-ray analysis.

Catalytic activities of synthesized heterogeneous dithiocompounds of Ni and Co in combination with aluminum organic compounds have been tested in reaction of solution, gas phase or block polymerization of butadiene. It was show, that against the homogeneous analogue, heterogenized compounds of Ni and Co show very high catalytic activity and selectivity in relation to formation of high stereoregular 1,4-cis polybutadiene. It was established, that even in the presence of nickel compound it is possible to synthesize the high-molecular polybutadiene with intrinsic viscosity $[\eta] = 1{,}0\text{-}2{,}5$ dl/g and 1,4-cis isomer content 93,0% and higher, against $[\eta] = 0{,}1\text{-}0{,}55$ dl/g and 1,4-cis isomer content no more than 80% in homogeneous catalyst. In the presence of cobalt containing heterogenized catalysts is in range of 500,0-1500,0 kg PBD/g M. hour, against 40.0-100.0 kg PBD/g M. hour in a homogeneous variant.

These new heterogenized nickel or cobalt-containing catalysts can be used in the solution, bulk, slurry (suspension) and gas phase polymerization processes of dienes.

PP-III-92

Effects of Nanostructuring of Ti-MCM-41 by Supporting of Vanadium Oxide on the Process of Dehydrogenation of Propane

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In connection with the considerable increase of demand on clean propylene, research of possibility of increase of propylene yield in the endothermic process of catalytic dehydrogenation (DH) of propane and development of exothermic process of its oxidative dehydrogenation (ODH) becomes an actual task presently. It was shown that a greater yield of propylene has been reached on catalysts supported on porous supports with the developed active surfaces. It is known also, that the system of unidimensional pores of мesoporous silicon dioxide can be used as solid-phase nanoreactor for the synthesis of well-organized arrays of unidimensional nanostructures of connections of transitional metals. Thus the reactionary zone limited to the walls of pores creates terms for the synthesis of nanophases.

In this work vanadium oxides supported on mesoporous system Ti-MCM-41 were investigated as catalysts of processes of DH and ODH of propane. This system has been obtained by hydrothermal template, alkaline synthesis from pyrogenic titanairosil (TAS), which contains Ti ions only in the form of isomorphic replacement of Si ions by its in SiO_2 matrix. Its quantity corresponded ~ 2,5 wt. % TiO_2. Catalytic activity of the received supported systems has been measured in a flowing quartz reactor with length of 30 sm in and internal diameter of 0,5 sm, using particles in the size of 0,25-0,5 mm, not filling an inactive packing the empty volume of a reactor before and after a layer of the catalyst. The reaction mixture contained 7 vol.% C_3H_8 in Ar (DH) or 7 vol.% C_3H_8 and 3,5 vol.% O_2 in He (ODH). The time of contact of the reaction mixture with the catalyst – 2,5 s. It is established that the obtained mesoporous system contains isolated strong acidic sites and shows comparatively larger catalytic activity in the processes of dehydrogenation of propane to propylene at presence and absence of oxygen in the reaction mixture. The yield of propylene was ~ 20 mol. % at 650-675 ^{o}C.

The vanadium oxides were supported on surface H-Ti-MCM-41 by impregnation its water solution of vanadium oxalate complex or a solution of acetylacetonate vanadyl in acetonitrile with the subsequent drying and calcination in an air atmosphere. Systems containing 5÷25 wt. % V_2O_5 / H-Ti-MCM-41 and 2÷30 wt. % VOx / H-Ti-MCM-41 were obtained, accordingly. It was shown that at supporting of vanadium oxide on H- Ti-MCM - 41 order of mesoporous structure has been violated, a diameter and volume of its mesopores has been decreased and micropores has been generated. But diameter of mesopores remained in limits that is typical for mesoporous materials. In the processes of dehydrogenation of propane the obtained catalysts has shown high activity. In the process of DH at 650-675 ^{o}C the maximal yield of propylene was ~ 70 mol. % and it was 50 mol. % in the process of ODH. The maximal yield of propylene extremely depended on the formed volume of pores and its correlation with acidity of active sites on the surface of the systems and it corresponded to a certain optimal turn-down of these values, regardless of method of supporting of vanadium oxide. Being based on these data, it was supposed that for effective work of catalyst in the processes of dehydrogenation of propane it is necessary to provide optimal frequency of co-operation of propane with active catalytic sites on the surface of walls of mesopores, which cause activating of propane with continuation of chain reaction in the volume of pores. It is assisted by certain, depending on the concentration of mixture, time of its contact and concentration of active sites, optimal size of diameter and volume of pores of support.

PP-III-93

Direct Synthesis of Hydrogen Peroxide on Model Pd Surfaces

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We experimentally demonstrated that model catalysts in the form of ideal Pd surfaces, either single (100) or poly crystalline, are active in H_2O_2 direct synthesis at 15 °C and pressure in excess of 20 bars, in methanol. Activity scaled on the available surface is much larger than some of the best powder catalyst suggested so far (Pd-Au on sulphated zirconia).

The surface with a long range order, i.e. single crystal Pd (100), was far more active that the corresponding polycristalline surface, suggesting an actual correlation between structure and reactivity, extremely relevant for performances.

Prereduction treatments and corresponding X-ray photoelectron spectrocopy of the surfaces confirmed the presence of surface oxidized specie, which structure appear to be related to the underlying Pd texture.

These results, well validated, open new perspectives for an effective catalyst design, taking surface science speculations, based on either ultra high vacuum experiments in the gas phase and DFT calculations, closer to an experimental validation. This contribution goes well beyond the investigation of the H_2O_2 direct synthesis mechanism.

Effect of Dopants upon the Acidic Properties of Oxides

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Catalysts modified by various acidic dopants exhibit high activity and selectivity and are widely used nowadays. To understand the mechanism of the promoting action is of a great interest for the creation of new catalytic systems.

Co-adsorption of acids with basic test molecules leads to mutual enhancement of adsorption. This can be demonstrated, when in the presence of SO_2, NO_2, or H_2S, protonation of such bases as NH_3, pyridine or 2,5-dimethylpyridine (DMP) occurs on silanol groups that never manifest any Brønsted acidity at normal conditions [1]. The effect suggests a new explanation of the promoting action of the above gases in the reactions catalyzed by Brønsted sites [2]. On the other hand, adsorption of bases increases the basicity of oxygen atoms, revealed by the spectra of adsorbed fluoroform [3].

Lewis acidity of oxides can also be influenced by adsorbed acidic molecules. This effect is illustrated by IR spectroscopic study of low-temperature CO adsorption on the modified CaO surface. The most high-frequency bands of CO adsorbed on CaO pre-exposed to CO_2, CCl_4, SO_2, SO_3 move from about 2157 up to almost 2190 cm^{-1} [4]. The dopants exist here in the form of surface CO_3^{2-}, Cl^-, SO_3^{2-}, or SO_4^{2-} ions, and one can consider such surface as a layer of corresponding salts, which exhibit higher electron accepting ability of surface cations, as compared with oxides. This effect is consistent with superacidity of oxides doped with SO_4^{2-} and explains the extremely high Lewis acidity of cationic sites in zeolites as compared with that of oxides of the same elements. The increase of catalytic activity of modified catalysts is illustrated by the reaction of 2-propanol decomposition over pure and sulfated CaO surfaces.

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PP-III-95

Soot Combustion in DPFs Catalyzed with Ceria Nanofibers

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Ceria nanofibers were prepared and deposited on SiC diesel particulate filters (DPFs), aiming at improving the soot-catalyst contact conditions and promote soot combustion at lower temperatures than in the non catalytic case. In particular, the nanofibers have been found to be very active with respect to other ceria catalyst morphologies, due to their arrangement in a network which enhances the number of soot-fiber contact points.

This effect was initially elucidated in a series of tests of soot temperature programmed combustion, which were carried out on the catalysts powders mixed with soot in loose contact conditions [1]: a specific sub-set of nanofibers exhibited a 112°C anticipation of the onset oxidation temperature (10% of total soot combustion) with respect to the non-catalytic test, and 38°C with respect to ceria nanopowders obtained with the so-called Solution Combustion Synthesis (SCS) [2], which instead are characterized by inner porosities hardly accessible to soot particles.

The nanofibers were then supported on Alumina washcoated DPFs, which were loaded with soot for 1 h, and subsequently subjected to a progressive temperature increase to induce soot ignition. Both CO_2 concentration in the outlet gas, and the pressure drop, were recorded during these tests. The main advantage given by the nanofiber catalyzed DPF, with respect to the other investigated morphologies, was not related to the maximum rate of soot oxidation, which was similar for all ceria catalysts, but again to the onset temperature. In fact, the pressure drop curve started to decrease more than 50°C before the DPF catalyzed with ceria through *in-situ* SCS. This behavior could greatly improve the soot oxidation activity especially for DPF passive regeneration purposes.

Such investigations led to a definition of the role of catalyst-to-carbon contact conditions on the conversion rate, which was carried out through the determination of the prevalent kinetic parameters (activation energy, oxygen reaction order, pre-exponential kinetic constant).

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Mathematical Modelling of Oxygen Regeneration of Catalysts

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Catalytic cracking plays a key role in the refining industry. Catalytic cracking breaks complex hydrocarbons into simpler molecules in order to increase the quality and quantity of lighter, more desirable products and decrease the amount of residuals. In this work investigations of a moving-bed and fixed-bed reactor were carried out. For the optimum control of this process it's necessary to work out a mathematical model and to investigate the effect of possible changes in the operation by means of calculations with the model on high-parallel computers. In [1] it was shown that a mathematical model describing the industrial regeneration of silica-alumina catalyst in a moving bed can be deprived by writing the equations that represent the mass balances of coke and oxygen, and the beat balance for an infinitely thin regenerator slab. Fixed bed catalyst regeneration in an adiabatic reactor may be described by a system of differential equations representing the material and thermal balances with respect to oxygen, coke and temperature with boundary condition.

Solution for optimization of process of oxygen regeneration was derived by using genetic algorithm. The program that allows calculating the temperature and coke content variation was created. It has the user-friendly input/output interface for investigation of consumption, concentration and temperature of oxygen-containing gas influence. Utilizing the mathematical model proposed, we have found the optimum control over fixed-bed catalyst regeneration by genetic algorithm. Future work is also needs to extend the parallel genetic algorithm for a moving bed reactor by implementing the same methodology.

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PP-III-97

Synthesis of Olefins from Carbon Oxides and Hydrogen on Iron-Manganese Nanosystems at Atmospheric Pressure

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An important task for the creation of an industrial process of olefins synthesis from carbon oxides and hydrogen is the development of high-efficiency and low- carbonation catalytic systems and to study the mechanism of this reaction. It is known [1-3] that the Fe-Mn bimetallic catalysts deposited on different carriers are very promising for obtaining olefins from CO and H_2. However, the published data on their use is inconclusive, but the mechanism of the influence of Mn on the formation of olefins is not fully understood. To further complicate the task of optimization of such systems for use in the hydrogenation of mixtures of CO and CO_2.

To solve this problem were carried out two series of experiments. The first - the hydrogenation of CO was carried out on catalytic systems, which are iron nanoparticles deposited by plasma-chemical method on the surface of γ-Al_2O_3 or Mn/Al_2O_3. The second catalyst systems have a layered structure and consisted of layers of Fe and Mn nanoparticles in inert supporters and they were separated by an isolation.

It was found that the selectivity to olefins increased significantly with the introduction of manganese in both types of catalysts. However, for the first series of catalysts, the yield of products decreased significantly. When the Fe nanoparticles are separated by an insulating layer from the Mn, the conversion of reactants is comparable with the results obtained in the Fe/ZrO_2 и Fe/Al_2O_3.

The adsorption of hydrogen on iron can be either molecular or dissociative, the manganese has practically no atomic hydrogen. C^* and CH_X-radicals formed by dissociative mechanism may be hydrogenated on iron centers as to olefins and paraffins up. At the same time, some of CH_X - radicals can move through the gas phase to the surface of manganese. Since its surface has no atomic hydrogen, the further hydrogenation of CH_X -radicals to alkanes does not occur, and there is a joint recombination of these particles mainly to olefins.

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Different Catalytic Activity of Zeolites Modified by Transition Metal and Aluminum Chloride on Liquid- and Gas-Phase Conversion of Alkanes

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Earlier we have established that complexes of transition metals and aluminum halides can activate alkanes at low temperatures (170-230K) providing the products of isomerization and metathesis reactions [1]. In this work the synergetic effect of transition metal cation and Lewis acid immobilized on oxide surfaces is tested. High silica zeolites (ZSM-5, BEA) modified by the transition metal (Co, Ni, Cu) and aluminum salts catalyze of paraffin (C_7-C_{12}) conversion in soft conditions at 370-430K temperatures. The activity of the modified supports depends strongly on a phase state of the reagents. In a liquid the efficiency of catalysts exceeds one of initial zeolites in 5-10 times while in a gas phase the activities of two systems are comparable. The reaction products consisted in all cases of isomers and alkanes with both lower and higher molecules than the feed; no alkenes were seen. A similar influence of the aggregate state of the reactants on the alkane transformations on zeolites ZSM-5 and MOR at moderate temperatures was noted in [2], where the conversion of 3-methylpentane was higher than that of n-hexane on the order in liquid, but in the gas phase inverse relationship was obtained.

Based on DRIFT spectral studies of adsorbed probe molecules (carbon monoxide, ethane) and data of EPR and UV/vis spectroscopy new active sites of transitional metals including coordination with immobilized aluminum chloride are formed by modification of oxide support with different additives. For example, new intensive band at 490 nm is recorded in electronic spectra of Cu(Al)BEA and changes in the EPR spectra are registered at the same time. The mechanism of alkane transformation appears to be different on the zeolite catalysts in the liquid- and gas-phase processes. Adsorption phenomena linked to the confinement effects of zeolites are decisive in the gas-phase reactions, but the mutual influence of red-ox properties of transition metals and immobilized Lewis acids is crucial in liquid.

This work was supported by RFBR (12-03-00595a and 11-03-00403a).

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PP-III-99

Turpentine Isomerization over Nature Catalysts

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Turpentine processing allows to obtain a number of the valuable products used in the pharmaceutical and perfumery industry.

Catalytic turpentine isomerization over Belarussian natural catalysts, glauconite and aluminosilicate (named Al-Si RB) containing montmorillonite, kaolin, muscovite and anorthoclase (from "Stalnoye" deposit) was investigated.

It was established earlier [1] that Al-Si RB modified 50 ml/g of 10 % HCl shows the highest activity in α-pinene isomerization. Glauconite was treated by 10 % HCl for 3 h (50 ^{o}C, 25-175 ml/g of modifier) to activate it.

Turpentine was isomerizated at 140 ^{o}C in presence 1 wt % of catalyst.

It was established that at turpentine conversion over initial catalysts only α-pinene transformed, and over modified ones 3-karen also reacted. The main isomerization products were camphene and dipentene, minor ones were mainly α- and γ-terpinenes, terpinolene and p-cymene.

Low α-pinene conversion (10-12 %) was observed over untreated aluminosilicates. Al-Si RB modified by 50 ml/g 10% HCl shows the highest catalytic activity. α-Pinene conversion after 1 h of reaction was 90 % and selectivity to camphene and dipentene was 47,5 and 29 % respectively.

Among the modified glauconite samples the one activated by 50 ml/g of 10 % HCl was proved the most active (α-pinene conversion was 94 % after 5 h of reaction). Selectivity of reaction toward camphene was 37 %, and to dipentene was 23 %. Conversion of 3-karene was 15 and 23 % on Al-Si RB activated by 50 ml of 10 % HCl and glauconite respectively. Monocyclic products were thus formed.

It was established [1], that α-pinene transformation proceeds to form bicycle products (camphene) on the weak acid sites, and to form monocyclic ones (dipentene and others) on the strong sites. Low selectivity of glauconite to camphene and substantial conversion of 3-karene might be caused by prevalence of strong acid sites on its surface.

Possibility of the use of natural Belarussian aluminosilicates as turpentine isomerization catalysts was shown.

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Impact of Activation Conditions on the State of the Active Cobalt Surface in Co-Al Catalysts of Fischer-Tropsch Synthesis

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Co-based catalysts are well-known as effective catalysts for Fischer-Tropsch synthesis (FTS) from hydrogen-rich syngas. To a great extent activity of the catalysts is determined by the dispersion of Co^o particles formed on the surface of the catalysts after reductive activation. Our work was aimed at exploring the possibility of controlling the dispersion of Co^o particles formed in the course of reductive activation of oxide precursors of Co-Al catalysts. Temperature-programmed reduction (TPR) was used for investigation of the reduction dynamics of oxide precursors formed during the thermal treatment of combined CoAl hydroxo-nitrate-carbonate compounds having a hydrotalcite-type structure in the inert atmosphere and in the inert atmosphere containing 3-4% vol. NO. It was shown that the reduction occurs in two main stages, that, according to the XRD data [1], correspond to the reduction of Co (III) to Co (II) and then to Co^o. The character of reduction depends on the oxidative properties of the gas during thermal pretreatment, particularly at the stage of formation of Co (II) (Figure 1). The specific surface area of Co^o was measured by N_2O titration method. The catalysts pretreated in NO-containing Ar have higher specific Co^o surface area (Table 1). The catalytic tests of obtained catalysts in FTS were performed at 0.1 and 2.1 MPa, H_2:CO:N_2 = 6:3:1, at 210°C in a fixed bed reactor.

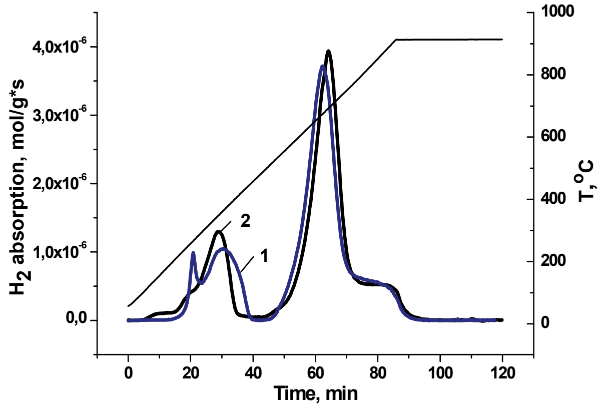

Figure 1. TPR curves of the oxide precursors of sample 1 (Table 1) after their calcination: (1) in 3% vol. NO containing Ar; (2) in pure Ar. The temperature increment rate 10 K/min.

Table 1. The specific surface area of Co^o.
Thermal treatment at 250°C, reduction at 600°C.

№	Support	Co:Al, atomic fractions	S_{Co}, m^2/g	
			He	Ar+3% vol. NO
1	γ-Al_2O_3	0,29	23	44
2	δ-Al_2O_3	0,12	11	15
3	δ-Al_2O_3	0,22	20	35
4	δ-Al_2O_3	0,43	24	46

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Study of the Hydrogen/Iron- Nickel Catalyst Interactions

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The world's oil reserves are being rapidly depleted; therefore the supply of hydrogen remains virtually unlimited and produces no air pollutants. Hydrogen can be produced from several sources, reducing our dependence on petroleum. Hydrogen can be obtained from renewable sources through thermal or catalytic processes. Iron promoted nickel based catalyst has been developed for high yield hydrogen generation [1]. Investigations have reported that binary Fe- Ni decreased the decomposition temperatures and yielded 70-90% hydrogen in the temperature range of 650 to 800°C [2].

We have analyzed at theoretical level, the adsorption of H on a FeNi(111) catalyst by tight binding calculations [3]. Different sites on the surface were selected in order to establish the preferential H adsorption location and the optimum H-surface distance. The two most stable sites for H on FeNi(111) are those where H bonds are on top Fe at 1.50 Å to the surface and the H bonds are on the Fe-Fe bridge site at 0.70 Å above the surface. We found that the minimum energy site corresponds to the H bonding on top Fe. Fe-H bond is formed on the FeNi surface and the interaction is mainly due to the overlaps between the H s orbital with the p_z, s, d_z^2 and p_y Fe orbitals. As a consequence, it is observed a Fe-Fe bond weakening of 12 %. On the other hand, when the H is located on the Fe-Fe bridge site, the Fe-H interactions weaken the Fe-Fe nearest bonds to about 33% with mainly participation of p_z, p_y, s and d_{yz} Fe orbitals. In general, after H adsorption, the Fe-Ni and Ni-Ni bonds are slightly affected. The Ni-H interaction is not evidence on the FeNi(111) surface.

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PP-III-102

CO_2 Tolerancy of Highly Productive Composite Fischer–Tropsch Co Catalyst

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Fischer–Tropsch synthesis (FTS) is often considered as an important step in catalytic processing of renewables or of stranded fossils. It is a process of catalytic conversion of CO-H_2 mixture (syngas) into liquid hydrocarbons [1, 2]. The syngas production technologies never provide CO-H_2 only; actual CO_2 content may reach up to 30% [3, 4]. Although CO_2 removal before FTS is considered an obligatory step, recent literature discusses a potential cost advantage if CO_2 is not removed [5]. Indeed, if CO_2 is hydrogenated along with CO or tolerated in the FT reactor, the expensive CO_2 removal step may be eliminated. Literature reports here very contradictive data on the subject. It is therefore interesting to investigate the effect of carbon dioxide on a cobalt highly productive composite catalyst under FTS conditions.

The effect of CO_2 on Fischer–Tropsch synthesis (FTS) on a cobalt based highly productive composite catalyst was investigated in fixed bed reactors at laboratory scale and pilot scale. Two types of feed gas, i.e. H_2:CO:N_2 and H_2:CO:CO_2:N_2 were used. It has been shown that CO_2 acts as an inert diluting agent if its concentration is below 30 vol. %. Testing of the highly productive composite catalyst has confirmed that this catalyst is tolerant to carbon dioxide. The results could have implications for the design of XTL processes (anything-to-liquids is a process that converts carbon and energy containing feedstock to high quality fuels). In particular, it might be advantageous to keep some carbon dioxide in the syngas feed to the FTS process. The mechanism of this specific tolerancy towards CO_2 is not yet clear, possible options are discussed in the paper.

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Results of Thermodynamic Modeling for Some Catalytic Processes

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Proposed thermodynamic methodology allows to simulate different stages of catalysts preparation and operation, to take into account thus both chemical and phase transitions – with the quantitative account of synthesis target- and by-products leaving reactionary space (i.e. those, on which the system becomes open), catalysts ageing effects, etc.

Realization of the method has allowed correctly and effectively to solve the put problems for various classes of catalytic materials. E.g. for industry oxidization of ammonia a catalyst on the base of system Fe_2O_3 - Mn_xO_y is one of most interesting and promising one but investigated insufficiently. The catalyst is prepared by thermal decomposition in a nitrogen atmosphere of the equimolar mixtures of hydrated nitrates of iron(III) $Fe(NO_3)_3{\cdot}9H_2O$ and manganese(II) $Mn(NO_3)_2{\cdot}6H_2O$. The heat treatment of this mixture is carried out under 1173 K. A process of this mixture heat treatment was investigated by thermodynamic modeling method, which gave the following series of phase-chemical transformations (as a function of composition and temperature of the system):

298 K: $Mn(NO_3)_2 = MnO_2 + 2O_2 + N_2$

$4Fe(NO_3)_3 = 2Fe_2O_3 + 15O_2 + 6N_2$

793 K: $4MnO_2 = 2Mn_2O_3 + O_2$

1374 K: $6Mn_2O_3 = 4Mn_3O_4 + O_2$

1461 K: $6Fe_2O_3 + 2Mn_3O_4 = 6MnFe_2O_4 + O_2$

The obtained data about the thermodynamic properties and phase transformations in this system can be used for development of effective modified catalysts for ammonia oxidizing.

On this basis the calculation of chemical and phase transformations occurring in catalytic systems $ZnO–Al_2O_3–CuO$, $V_2O_5–K_2O–SiO_2–Al_2O_3–SO_2\text{-}O_2$ etc. is carried out too. It describes and simulates processes occurring in thicker, cells and liquid phase of corresponding catalysts. Multiplan picture of temperature and composition influence on phase and chemical transformations in the systems is received.

Received theoretically and by calculation way the results are not only well agreed with known experimental data, but also give qualitatively and quantitatively richer information on catalysts processes mechanisms of different compositions and purposes.

PP-III-104

Cr, V and Pt in O_2-Free Propane Dehydrogenation: Who Wins and Why?

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Continuously growing demand for propylene drives intense exploration of new production processes or improving the existing ones. Catalytic non-oxidative dehydrogenation (DH) of propane is a promising alternative to FCC currently used for commercial production of propylene. In this study we explore the potential of highly dispersed VO_x species supported on alumina, silica and various Si-Al mixed oxides in the DH reaction. Particular attention was paid to the fundamental factors governing catalysts stability within a single DH stage and over several DH/regeneration cycles. In this context, the influence of the support acidity on catalytic performance was studied.

Compared to industrially relevant CrO_x- and Pt-SnO_x-based catalysts (also prepared in this study), several catalysts containing supported VO_x species showed higher activity and better on-stream stability. For instance, an initial propylene yield above 20% was achieved on VO_x/MCM-41 and even above 25% on VO_x/Siral-10 (Figure). Moreover, VO_x/Siral-10 showed higher on-stream stability in shorter DH stages (5 h) than all other catalysts.

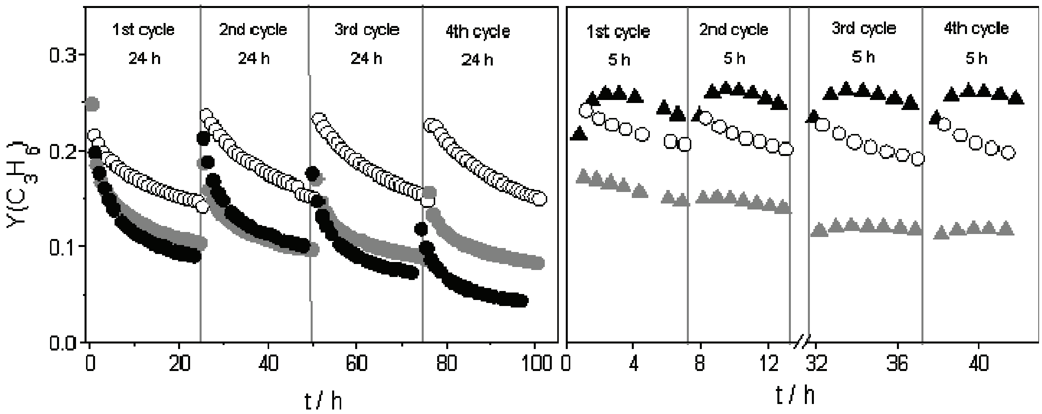

Figure **C_3H_6 yield in 24h-DH cycles over VO_x/MCM-41 (○), CrO_x/MCM-41 (●), Pt-SnO_x alumina (●) and in 5h-DH cycles over VO_x/Siral 10 (▲), VO_x/MCM-41 (○), VO_x/Siral 70 (▲) at 823 K.**

In-situ UV/Vis and TPO experiments indicate that buildup of coke and structural changes in the active metal oxide species are the two phenomena responsible for the catalysts deactivation in a single DH stage and over a sequence of DH/regeneration cycles. The catalytic performance will be discussed in light of characterisation results to elucidate fundamental structure-activity relationships in the DH process.

Oligomerization of Ethylene over Ga^+ /ZSM-5 Zeolite from Diffuse Reflectance IR and Quantum-Chemical Data

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Diffuse reflectance IR spectroscopy and quantum-chemical calculations were used to study adsorption and subsequent ethylene transformations on gallium cations in gallium-modified ZSM-5 zeolite. Modification of HZSM-5 zeolites with gallium cations was carried out via anchoring of trimethyl gallium (TMG) or by incipient wetness impregnation with a solution of gallium nitrate. Both ways of preparation result in similar quantitative substitution of all acidic protons by Ga^+ ions. DRIFTS measurements of ethylene adsorption on both samples of Ga^+ /ZSM-5 at 300 K show the similar results of decreasing the intensity of the bands at 3091 and 2990 cm^{-1} related to adsorbed ethylene and increasing the intensity of the bands at 2860 and 2937 cm^{-1} related to growing oligomer chains. These bands could not be removed by evacuation with heating up to 773 K. This data indicate on ethylene oligomerization on gallium cations Ga^+ without participation acidic protons even at room temperature. The rate of ethylene oligomerization on Ga^+ /ZSM-5 was some times smaller than in the case of HZSM samples in the same conditions.

Quantum-chemical calculations of adsorption and subsequent ethylene transformations on Ga^+ exchanged cation of zeolite lattice were carried out using density functional theory with a B3LYP functional in the 6-31G basis set and the GAUSSIAN 03 program. Three kinds of ethylene activation on gallium cation were analyzed: activations which accompanied by cleavage of C-H or C=C double bond and weak ethylene adsorption. It is found that activation of one ethylene molecule connected with cleavage of C-H or C=C double bond required high activation energy (~ 60 kcal/mol). On the other side the synchronous connection of two ethylene molecules with formation 5-membered heterocycle of $Ga\text{-}C_4H_8$ can occur with smaller activation energy (~ 20 kcal/mol). However it was found that removal of these structures from zeolite surface is energetically complicated. Process of hydrogenation of a heterocycle with formation of butane molecule was also considered and it was estimated activation barriers of this process (~ 30 kcal/mol) were estimated.

Thus, one expects that Ga cations may also be involved in the secondary reactions of olefins formed upon alkane dehydrogenation over Ga/ZSM-5 zeolite during process of aromatization of light alkanes.

PP-III-106

Unusual DRIFT Spectrum of Ethane Adsorbed by Mo/Y Zeolite Prepared by CVD Method from Molybdenum Hexacarbonyl

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Recently, we presented evidence that the intensity of IR bands of paraffins adsorbed by zeolite reflect the polarization and activation of a chemical bonds upon adsorption [1, 2]. The most strongly perturbed vibrations are the initially fully symmetric C–H stretching vibrations if paraffins adsorbed by isolated bivalent cationic forms of zeolites. The strongest polarization of ethane by Zn^{2+}/ZSM-5 leads to activation and the subsequent heterolytic dissociation of ethane at moderately elevated temperatures [3]. In presented work the adsorption and activation of ethane by isolated, incorporated in Y zeolite molybdenum cations were investigated by DRIFTS.

Modification of Y zeolites with molybdenum cations was carried out by chemical vapour deposition (CVD) method via chemical reaction of the hydrogen form of zeolite Y with molybdenum hexacarbonyl vapor without oxygen atmosphere. Zero valency molybdenum species substitute acid protons removed as hydrogen, oxidize and stabilize as isolated cations in cationic positions, more possible as Mo^{n+}(n=2 or 3). This preparation results in similar quantitative substitution of all acidic protons.

Ethane adsorption by Mo/Y leads to appearance a very high relative intensity of low frequency band at 2734 cm^{-1} from initially symmetric C-H stretching vibration in comparison with other C-H bands in DRIFT spectra. The obtained spectrum is very similar to the spectrum of ethane adsorbed by Zn^{2+}/ZSM-5 [3] and indicates strong polarization of ethane in the result of interaction with molybdenum cations. Such strongest polarization of ethane leads to chemical activation and to subsequent chemical transformations of ethane at moderate temperatures resulting in the heterolytic cleaving of proton from ethane and formation of acidic hydroxyl groups. Also new bands in the regions of C-H bands higher then 3100 cm^{-1} appear. The appearance of these bands is connected with C-H bands of acetylenic fragment. This result cat be explained assuming that ethyl fragment obtained after cleaving of proton from ethane decomposed with simultaneous formation of molybdenum hydride fragments (via homolytic oxidative addition of the hydrogen) and stable as acetylenic species coordinated to the molybdenum.

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Identification of Surface Structures Responsible for Activity and Selectivity of Cobalt-Based Catalyst in Fischer-Tropsch Synthesis

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Performance of catalysts of Fischer-Tropsch synthesis (FTS) represent sophisticated function of both reaction conditions and the nature of catalyst proper. Both porous system and heat capacity of the catalyst influence heat- and mass- transfer. Chemical properties and surface acidity of a support determine the degree of strong interaction. The controversial influence of these factors often hinders investigation of reliable correlations between the yield of liquid hydrocarbons and process parameters. It means that the variety of phases and structures occurring in a catalyst leads to absence of understanding of their contribution into optimization of FTS. The use of Raney cobalt as a catalyst with unchangeable porous structure and heat capacity allowed us TPR identification of cobalt-oxide structures responsible for activity and selectivity in FTS.

The position of maxima in TPR curves measured for reduced catalysts (technique TPR-aR) is determined by kinetic characteristics of a system. In order to identify surface and bulk oxides correctly it is necessary to keep all the experimental parameters (particle size, flowrate of gas, heating rate, etc.) constant. The samples of Raney cobalt in pristine or modified with 1.5% Mn_2O_3(Cr_2O_3) form were reduced in the TPR cell at ambient pressure as describe elsewhere in detail [1]. It is shown that there is linear correlation between C_{5+} yield and the content of certain cobalt oxide structures, which are reducible with TPR-aR maximum positioned in the range 500-800°C. Similar results were also received for 20%Co/$CoAl_xO_y$.

It was found that the activity and selectivity in Fischer-Tropsch synthesis are primarily determined by immobilized surface cobalt oxide structures, which can be characterized by TPR-aR curve with a maximum of hydrogen consumption in the range 500-800°C. These structures contain partially reduced cobalt (effective charge δ+) on oxide support.

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PP-III-108

Acidic Properties and Location of Zn Cation in Mordenite by IR Spectroscopy and DFT Simulations via CH_4 Adsorption

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In many cases chemical activation of different molecules adsorbed by cation exchanged zeolites results from their polarization by cations. In ZSM-5 where the negatively charged [AlO_4] tetrahedra are strongly distantly separated from each other only one half of them is neutralized by bivalent cations resulting in superacidic adsorption Lewis sites while the second part of negatively charged [AlO_4] tetrahedra is free. For Zn^{2+} cations in ZnZSM-5 zeolite the unusual type of cationic positions results to dissociative adsorption of CH_4 molecule with the formation of bridged hydroxyl group and Zn-CH_3 structure [1]. In this work we presented evidence by IR spectroscopy that dissociative adsorption of CH_4 molecule occurs on Zn^{2+} cations in mordenite with small Si/Al (Si/Al =6). To explain the obtained results acidic properties of Zn^{2+} cations in dependence of location of these cations in structure of mordenite with different membered rings were studied by DFT simulation of adsorption of CH_4 in mordenite. This provide the vibrational frequencies, intensities of IR bands and binding energies of adsorbed CH_4 molecule with Zn^{2+} cations located in different positions in different-membered rings of mordenite. The main attention was paid to theoretical studies of adsorption of CH_4 on Zn^{2+} in 12-membered rings in main channel with far distance Al atoms in this rings and preferred location of Zn^{2+} near one of this.

It was found that adsorption of adsorption of CH_4 on Zn^{2+} location near one of Al atom of Al in 8-membered rings with far distance of Al atoms and in 12 -membered rings with near distance of Al atoms leads to hydrogen-bonding of CH_4 with oxygen of lattice. This results could lead to increasing to shift of vibrational frequencies, intensities of IR bands that not supported by IR spectroscopy of adsorbed CH_4. Nevertheless the experimental data of vibrational frequencies, intensities of IR bands of adsorbed CH_4 are in good agreement with theoretical calculation of adsorbed CH_4 on 12 -membered rings with far distance of Al atoms. It was calculated that adsorption of CH_4 on mordenite in this case could occur to dissociative adsorption of CH_4 molecule at moderately elevated temperatures.

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High Active Sulfate-Dopped Zirconium Oxide Catalysts for Skeletal Isomerization of C_4-C_6 Alkanes. Role of Electronic Properties and Surface Acidity in n-Alkane Activation

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Catalysts based on sulfated zirconia (SZ) are widely used in oil refining to isomerize C5-C6 hydrocarbon fractions, showing activity in this process close to that of chlorinated alumina [1]. However, for the discussed class of catalysts up till now there is no clear knowledge of the nature of their active centers and the mechanism of isomerization process on them as well [2].

In the present work catalytic properties of sulfated zirconia of various composition were studied in n-pentane isomerization and compared with their acidic properties revealed by IR spectroscopy of adsorbed CO. It is shown that the nature and strength of acid centers on a surface of the sulfated oxides not always defines their catalytic activity and the existing views on the isomerization mechanism on SZ, and the activation stage of n-paraffin in particular, should be updated.

Change of electronic state of sulfated zirconia upon either hydrogen or butane adsorption was studied by EPR, ESDR and magnetic susceptibility. On basis of the obtained data it is drawn a conclusion that during SZ preparation a formation of bulk defects with excess electron density takes place. Comparison ESDR and catalytic activity of various SZ samples allowed to find out a reverse correlation between the SZ catalytic activity and the energy gap width. The mechanism of n-paraffin activation with participation of delocalized electrons in regions with excess electron density is offered. The proposed mechanism does not require interaction of n-paraffin with both localized electrons (Zr^{3+}) and acid centers. The role of the acid centers in the isomerization reaction on SZ consists in stabilization of the activated state of n-paraffine.

Investigation of dependences of SZ isomerization activity for individual C_4-C_6 paraffins on their partial pressure has revealed that the bimolecular mechanism is realized for C_4 isomerization reaction, while for C_5-C_6 isomerization the monomolecular mechanism takes place.

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PP-III-110

The Composition, Structure and Catalytic Activity of Some Metal-Oxide PEO-Coatings on Aluminum

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By X-ray photoelectron spectroscopy we have studied the features of chemical composition and structure of several coatings formed by plasma electrolytic oxidation (PEO) on aluminum. Such coatings possess various attractive properties. Among them a significant catalytic activity in oxidation of CO to CO_2 [1-3], which was the subject of our present research. The variety of coatings was determined by the composition of used electrolytes, oxidation conditions and further treatment. So there were formed structures containing different combinations of elements of the substrate, electrolyte and environment (Al, Mn, Fe, Co, Ni, Cu, C, O, P and others).

The catalytic activity of the investigated coatings depends strongly on their composition and structure. Thus, for explaining of its nature, detecting of factors responsible for activation, degradation, deactivation, and identifying of some features of catalytic processes there have been studied some systematic series of samples with various composition, structure and stage of catalytic process. Namely, we have studied such samples as: the initial metal substrate, the PEO-coatings formed in electrolytes containing certain components in appropriate quantities, the coatings unexposed to catalytic tests, and the coatings which have passed through various stages of the catalytic process.

On the basis of the data comparison of the catalytic activity, kinetics of the processes, chemical composition and state of surface layers of the studied systems, the conclusions were made on the nature of active centers and the impact of noted features on the catalytic properties.

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Cluster Modeling of Metal Oxide Structures on Al and their Interaction with CO

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Some coatings formed by plasma electrolytic oxidation (PEO) on aluminum exhibit a catalytic activity in the conversion of CO to CO_2. Thereby we have performed quantum chemistry modeling of some metal oxide systems to define the nature of such activity. The studied model metal oxide systems are isostructural with formed coatings.

Ab initio and density functional theory calculations were performed by the restricted Hartree-Fock method within the Gamess US code. Modeling was carried out in agreement with the three basic principles: neutrality, stoichiometry and coordination. Cluster geometry was fully optimized with the 3-21G basis set and with the use of 6-31G basis set refined. Electronic structure and thermodynamic characteristics of model systems were calculated in experimental and optimized geometry.

The studied metal oxide clusters were: Al_2O_3, Al_4O_6 and Al_6O_9. Values of bond lengths (Angstrom) were obtained as follows: Al-O bond: 1,864; 1,981 (1,855; 1,971 – experimental); Al-Al bond: 2,669; 2,805 (2,655; 2,791 - experimental); O-O bond: 2,632; 2,881 (2,620; 2,866 - experimental). There is a good agreement between experimental and optimized geometry.

On the basis of the calculations the interaction between CO and active centers of the clusters, namely, aluminum atoms on the various faces, was estimated. According to the obtained data, the optimal position for the interaction is the “zenithal” position of CO, relatively to the all considered centers.

Nickel- and copper-containing PEO-coatings were modeled by replacing of Al atom to NiH or Cu in the studied clusters, energy of their interaction with CO was defined. Similar to the above calculations were also carried out for various cluster configurations of nickel and copper oxides.

The obtained results were used to explain the differences of catalytic activity of the PEO-coatings on aluminum of various compositions and structure, and to describe the features of the catalytic process, activation/deactivation mechanism and catalyst poisoning.

PP-III-112

Chemisorption and Oxidation of SO_2 at Pt-Containing Fiber-Glass Catalysts

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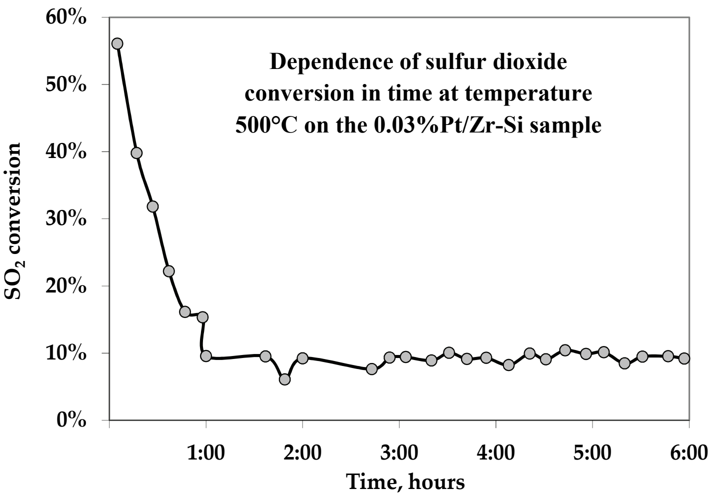
Pt-containing catalysts on the base of the fiber-glass supports (Pt-GFC) are the prospective catalysts for application in SO_3 production facilities for conditioning of the flue gases from coal-fired power plants [1,2] as well for SO_2 oxidation in conventional reactors. This study was dedicated to investigation of SO_2 chemisorption and oxidation reaction dynamics.



Dynamic experiments with the catalyst containing 0.03% mass Pt at ZrO_2-SiO_2 fibrous support showed the transient decrease of observed SO_2 conversion in the beginning of experiment down to the steady-state value. It was shown that the transient behavior is connected with intensive sorption of sulfur dioxide.

It is possible to conclude that Pt-GFC are able to sorb the SO_2 in significant quantities (more than 20% mass of GFC). As soon as the unit surface area of the glass fibers is negligible, such sorption capacity may be explained only by the absorption in the glass bulk. From the other hand, the SO_2 sorption is possible only in presence of oxygen in the GFC bulk – either absorbed from reaction mixture or pre-absorbed in the GFC structure. It gives the ground to propose that SO_2 absorption, in particular, and the SO_2 oxidation reaction, in general, occurs via the interaction of sulfur dioxide and oxygen with formation of the intermediate species (probably - bulk sulfates) in the Pt-GFC structure.

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Features of the Mechanism of Partial Oxidation of 3- and 4-Methylpyridines on the Modified V-O-Catalysts

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The partial oxidation of 3- and 4-methylpyridine in V_2O_5 and modified by addition of TiO_2, SnO_2, ZrO_2 and Al_2O_3 binary vanadium oxide catalysts are studied. A direct relationship between the reactivity (R) of isomers and their CH-acidity in the gas phase, calculated with nonobservational quantum-chemical method is established. 3-Methylpyridine is characterized by a low R, the main product of oxidation is nicotinic acid, and pyridine-3-aldehyde is formed in small amounts or absent. 4-Methylpyridine have a higher R of the products of its partial oxidation along with isonicotinic acid the presence of pyridine-4-aldehyde, which output is in the low-temperature experiments is comparable with the release of acid.

The difference in the mechanism of oxidation of 3- and 4-methylpyridine on the V-O-catalysts may be related to the chemisorption and activation of the starting compounds on the surface acid sites, as well as with different basicity in the gas phase and the adsorption capacity of intermediate pyridine aldehydes. As nonobservational quantum chemical calculations show [1], the pyridine-3-aldehyde sensitivity to proton nitrogen atom of the ring is much higher than that of pyridine-4-aldehyde. Therefore, 3-methylpyridine, in contrast to the 4-methylpyridine, converted to the acid without the intermediate aldehyde desorption into the gas phase.

Presumably, the promoting effect of these additions of oxides of V_2O_5 is associated with a change in the phase composition of the catalyst due to the weakening of V=O in the lattice of vanadium pentoxide and an increase in its R. Thus, we have established a correlation between the activity of the studied catalysts and the values of sensitivity to proton of vanadyl oxygen involved in the deprotonation of the oxidized methyl group, calculated by quantum-chemical method EHM/AP [2]. Active centers of the surface are modelled with clusters that contain fragments of V_2O_5 and oxides-modifiers.

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PP-III-114

Peculiarities of Ethane Aromatization over Bifunctional Metal-Containing Catalyst

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Modern oil refining and petrochemistry heavily rely on the use catalysts, based on synthetic zeolites. In order to develop general approaches to controlling and predicting their catalytic activity one has to know the mechanisms taking into account the state of every component in the catalyst system. The purpose of this study is to propose a staged scheme of ethane aromatization based on a detailed analysis of Pt and Ga states, their localization in Pt-galloalumosilicates, and the composition of ethane conversion products over this catalyst for different conversion rates.

According to the HRTEM data due to the introduction of more than 0.1% of platinum into Ga-AS, the gallium migrates to the outer surface of the zeolite particles, while platinum forms clusters in its channels. In addition, the decrease in the gallium content in the inner space of the carrier channels with increasing platinum content was registered by the EDX-analysis. This suggests the degradation of adsorbed Ga-Pt complexes resulting in the Ga displacement from the channels to the outer surface of zeolite crystals whereas Pt clusters remains inside the channels. The reduction of gallium ions results in the formation of amorphous spherical particles of metallic Ga on the surface of support.

Catalytic studies show that the introduction of platinum into galloalumosilicate leads to the acceleration of ethane dehydrogenation as a key stage in the process of conversion of ethane. The hydride-ion separates from the molecule of ethane to form ethylene with participation of Pt-Ga clusters. The galloalumosilicate supplemented with 0.3% Pt exhibits the highest activity and selectivity towards the formation of aromatic hydrocarbons from ethane, which is to be due to the increased concentration of platinum in its dispersed state and to the optimized composition and ratio between the catalytic centers of various origins.

Thus, a combination of such active metal components as gallium and platinum, on the one hand and interaction of acid sites of the zeolite support on the other ensure high aromatization efficiency of the catalyst during ethane conversion.

Phenol Oxydation by PP-CWAO Treatment with Cu/13X

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Water pollution is characterized mainly by the volume of waste to be treated and by the nature, concentration and toxicity of pollutants that form it. These parameters are all factors that have to be taken into account when choosing the treatment method to use. WAO (Wet Air Oxidation) is a phenol oxidation treatment method based on oxidation with air or oxygen, and is conducted at elevated temperatures (373-573 K) and pressures (1 - 20 MPa). With addition of homogeneous or heterogeneous catalysts, WO processes can be carried out at lower pressures and temperatures. If these processes use hydrogen peroxide as oxidizing agent, the process is called CWPO (Catalytic Wet Peroxide Oxidation), in which treatment is carried out at atmospheric pressure and temperatures below 373 K. To take advantages of the CWPO & CWAO process, and maximize the effectiveness of treatment, in this work, mixture of both oxidants (oxygen and hydrogen peroxide) was used.

Activity of synthesized and calcined Cu/13X catalyst was tested in the PP-CWAO (*Peroxide Promoted Catalytic Wet Air Oxidation*) reaction using batch reactor. The catalysts were characterized by different methods (XRD, AAS, BET surface area). The catalytic tests were carried out in a stainless steel Parr reactor in batch operation mode at the constant catalyst mass (0.1 g / 200 cm-3), different temperatures (333 - 353K) and air pressures (2 - 20 bar). The initial concentration of phenol was 0.01 mol dm^{-3} while the concentration of hydrogen peroxide varied from 0.01 mol dm-3 to 0.14 mol dm^{-3}.

Based on the results it has been concluded that the PP-CWAO process leads to higher pollutant removal conversions than the CWAO and CWPO processes. The results were influenced by the Ph: H_2O_2 : air molar ratio. A synergistic effect was found when H_2O_2 is combined with air which leads to higher mineralization of the phenol.

The stability measurements showed that thermal treatment stabilizes the Cu/13X catalyst from leaching.

PP-III-116

Theoretical Calculation of Hydroxyl Mechanism for Reforming of CH_4 with Supercritical CO_2 over Ni Catalyst

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The reforming reaction of CH_4 and CO_2 can not only transform natural gas into syngas, but also reduce the emission of a large number of CO_2, which can achieve the goal of transforming the trash into treasure. Supercritical CO_2 is a common supercritical fluid, its critical temperature is 304.13 K, critical pressure is 72.90 atm.

The hydroxyl mechanism of CH_4-Supercritical CO_2 reforming reaction was studied using DFT method at B3LYP/Lanl2dz level. The imaginary vibration mode of the transition states and Curves of IRC pathway were obtained. The process of hydroxyl reforming reaction over Ni catalyst were as follows:

$CH_4 + M \longrightarrow CH_3M + H\cdot$ step1
$CH_4 + M \longrightarrow CHM + 3H\cdot$ step2
$H_2 + 2M \longrightarrow 2H\text{-}M$ step3
$CO_2 + H\text{-}M \longrightarrow CO\text{-}M + \text{-}OH$ step4
$CH_3M + \text{-}OH \longrightarrow CH_3O + H\text{-}M$ step5
$CH_3M + \text{-}OH \longrightarrow CH_2OH + H\text{-}M$ step6
$CHM + \text{-}OH \longrightarrow CHO + H\text{-}M$ step7
$CH_2OH \longrightarrow CH_2O + H\cdot$ step8
$2CH_2OH \longrightarrow \text{-}CH_2 + HCHO + H_2O$ step9
$CHO \longrightarrow CO + H\cdot$ step10
$CHOH \longrightarrow CO + 2H\cdot$ step11
$CO\text{-}M \longrightarrow CO + M$ step12
$2H\cdot \longrightarrow H_2$ step13

It was found that the mechanism included 13 steps, the beginning of hydroxyl reforming was the reaction of methane with Ni catalyst. -OH, CH_3Ni, CHNi and $-CH_2OH$ were important intermediate products. We chose step 3, 4 , 5, 6, 7 for further exploration. Hydroxyl could attack CH_3Ni group from the side and the back, respectively. Hydroxyl was easier to attack CH_3Ni from para-position.

The activation energies of step 3, 4 , 5, 6, 7 were 201.1664, 360.1252, 102.6259, 61.5419, 126.3132 kJ·mol^{-1}, respectively. The rate determining step was hydroxyl's generative process as shown in step 4, hydroxyl played a significant role in the process of reforming reaction. It was competing that hydroxyl reacted with CH_3Ni, CHNi groups, respectively. Under supercritical CO_2 condition, the hydroxyl reforming reaction could proceed smoothly.

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Pt /Modified Kaolinite in the Isomerization of n-Hexane

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At present a large number of studies is devoted to the processes of isomerization of hydrocarbons to improve octane number of gasoline fraction. Application as the matrix of Pt-and Pd-catalysts, new materials - columnar clays based on natural clays is anactual direction in the synthesis of modern catalysts of isomerization of n-alkanes. Previously we showed high activity and selectivity of Al-pillared montmorillonite (AlNaHMM) in the isomerization of n-hexane. This work is devoted to the study of the catalytic activity of Pt-catalysts supported on Al-modified kaolinite clay of Ermakov deposit in Kazakhstan (HKE). Isomerization reaction was carried out in a flow reactor at atmospheric pressure of hydrogen in the temperature range 250-400°C. According to the XRD and EPR study kaolinite is a mixture of different mineral fractions. Kaolinite and montmorillonite are clearly fixed. Compared with MM in kaolinite observed high content of SiO_2, Fe_2O_3 (6%) and K_2O. The composition of kaolinites determines a lower acidity of the contacts. The total content of acid centers(a.c.) of activated kaolinite is no more than 100.5 mkmol NH_3 /g, 45.3% accounted for weak a.c. with $T_{des.}$ up to 200 °C and 29% of middle a.c. with $T_{des.}$ = 200-300°C. The total acidity of HMM is 224.5 mkmolNH_3/g. The quantity of weak a.c. - 27.7%, middle a.c. responsible for the isomerization, -39.9%. Specific surface area of kaolinite -177,3m^2 / g, NaHMM-245,1m^2/g The number of micropores is 22,8% for NaHMM,and 12,9 % for the HKE. The difference between the acid and textural properties of catalysts is effected in the activity and the products of the isomerization. The following table shows the data for Pt / Al (5,0)HKE and Pt/Al(5,O)NaHMM-catalysts.

Table. Isomerization of n-hexane on Pt-catalysts

Catalyst	T,°C	α,%	S_{C6},%	S_{C6+},%	Yields of reaction products,%								
					C_1-C_5	i-B	2MB	2,2DMB	2MP	3MP	2.4DMP	3,3DMP	2MG
Pt/AlHKE	350	47,9	97,7	100	-	-	-	41,9	2,9	1,3	0,9	0,1	0,1
	400	33,5	84,8	94,6	2,1	1,4	-	9,8	12,5	0,9	2,8	0,1	0.1
Pt/AlHMM	350	39,0	92,6	99,7	-	-	0,1	1,5	20,7	13,9	1,3	1.5	-
	400	46,8	79,7	98,1	0,9	-	-	1,9	21,1	14,4	3,0	5,6	-

The peculiarity of the synthesized catalyst on the base of kaolinite clay, as is evident from the table is the formation of significant amounts (41.9%) 2.2-dimethylbutane. The same conversion of n-hexane over montmorillonite catalyst did not observed. The formation a large amount of disubstituted isomers is probably due to the mechanism of the reaction. Increased quantity of mesopores and low content of strong acid centers in kaolinite increases isomerisation activity of catalysts The suggestion was made about different nature of a.c. on the AlNaHMM and AlHKE.

Support by the ISTC (grant No K-1476) is gratefully acknowledged.

Modification of Heterogeneous Titanium Catalyst in Turbulent Microreactor at the Synthesis of (co)Polydiene

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Stereoregular (co)polydienes are the products of large-scale production of synthetic rubber. The main monomers for the synthesis of polydiene are isoprene and butadiene and the polymerization is carried out on microheterogeneous titanium catalysts. Due to the fact that the catalytic system is represented by microparticles $TiCl_3$, then one of the possible mechanisms of influence on the rate of polymerization is a modification of the catalyst due to short-term intensive hydrodynamic effects. For these purposes, is proposed to use small-size tubular turbulent apparatus of diffuser-confusor design, which circulates through the reaction mixture. Changing the size of the particles microheterogeneous catalyst without changing the composition of the reaction mixture reveals the relationship of the surface structure of the catalyst and kinetic parameters of the process and the properties of the synthesized polymer. Because the synthesized polydienes characterized by a broad molecular weight distribution, the presence of titanium catalysts are of several types of active centers. At the centers of each type of polymer is synthesized with a specific molecular weight. It is shown that for large particles (8-50 microns), low polymerization rate is formed by polybutadiene of high molecular weight and broad molecular weight distribution. Fractions of the catalyst with average particle sizes (0,3-7,5 nm) with high speed and produce polymerized butadiene polymer with average molecular weights. At the smallest particles (30-95 nm) at a low rate of polymerization is formed by low molecular weight polybutadiene with narrow molecular weight distribution. The results on the effect of the titanium catalyst preparation conditions on the microstructure of the polymer, compositional heterogeneity, and microheterogeneity of copolymers of butadiene and isoprene. The examples of the introduction new technical solutions using tubular turbulent apparatuses in the industry.

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PP-III-119

Atomic Layer Deposition for Water Gas Shift Reaction over Bimetallic Catalysts

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Atomic layer deposition (ALD) uses self-limiting chemical reactions between gaseous precursors and a solid surface to deposit materials in a layer-by-layer manner. For the catalytic applications, this process results in a unique combination of attributes, including sub-nm precision, the capability to engineer surfaces and interfaces, and unparalleled conformability over high-aspect ratio and nanoporous structures. Keeping in mind these capabilities, ALD could have a certain impact in the design of catalytic materials with the desired properties. The presentation will survey the recent work applying ALD to heterogeneous catalysts for water gas shift reaction in particularly. We will consider supported catalysts as well as model catalysts prepared on a flat support.

Studing the Routes of Hydrocarbon Oxidation, Contained Cyclohexane Ring in the Presence of $H_2O_2/Cu_2(DMG)_2Cl_4$

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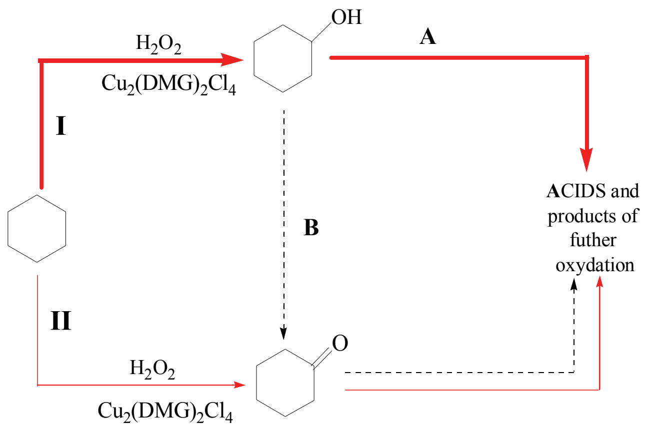
Studying of hydrocarbon activation processes and oxidation, and also investigation the catalyst function in redox processes under mild conditions in simple model reactions has a very great interest as regards to catalysis, biochemistry, biomimetics and medicine.

In this study possible ways of hydrocarbon oxidation, which contain the general structure fragment – cyclohexane ring (cyclohexane, decalin, tetralin, adamantane) are considered in mild conditions in the system $H_2O_2/Cu_2(DMG)_2Cl_4$.

As an example we indicate that in presence of $Cu_2(DMG)_2Cl_4$ oxidation process could be carried out selective both on cyclohexanol with output of near 15% in 5 minutes, and on adipic acid with output of more than 10% in 30 minutes.

Subject to received results we can suppose that cyclohexane oxidation by H_2O_2 in presence of $Cu_2(DMG)_2Cl_4$ is carrying according to the *scheme*, provided that the main route is carrying in the direction I-A.



In case of decalin, tetralin and adamantane oxidation in the discussed conditions alcohol and ketones were recorded.

The study is executed under FTP "Scientific and scientific-pedagogic personnel of innovated Russia" in 2009 – 2013 in the theme "Chemistry of high-molecular compounds. Petrochemistry. Catalysis" and Program of Education and Science Ministry of Russian Federation "The development of scientific potential", project DSP 2.2.1.1.2820, and also under governmental budget theme "Creation of next generation homogenous and heterogenous catalysts for the important petrochemical processes – hydrogenation, hydroformylation, carbonylation, oxidation" (No. of governmental registration 01.990001227).

PP-III-121

Catalysis on Zeolites: Solketal Formation Mechanism

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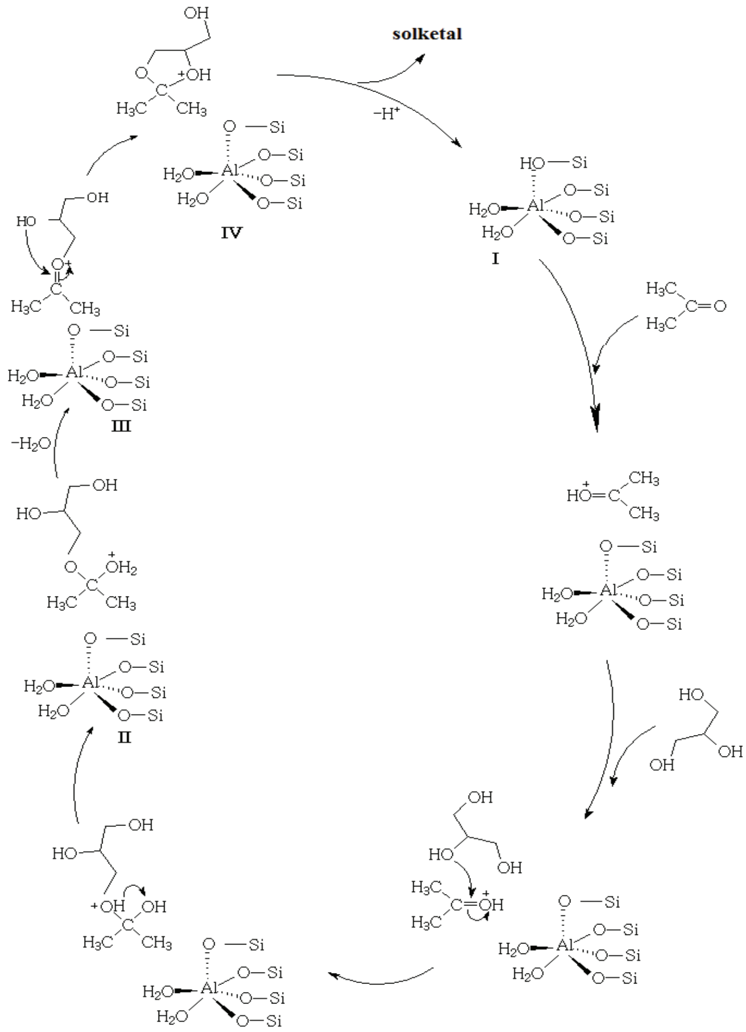
Based on reported data and received results in our studies, we suggest the following *mechanism* of solketal formation. The active acid centre in zeolite surface is represented as a fragment I. In its basis is an octahedral aluminum atom, which is connected with zeolite frame. Herewith the oxygen atom of acetone is protonated with localization positive charge on it. A glycerin molecule interacts with protonated acetone. As a result of electron density redistribution the intermediate II is formed, which loses water molecule with formation the cation III. The intermediate III is turned into the cyclic cation IV, which returns proton with regeneration of the active centre I, at that itself transforms in solketal.



The study is executed under partial finance support of Program RAS Presidium No.3 "Energetic aspects of advanced processing of fossil fuels and renewable hydrocarbon feedstocks" (program code 3P, executive code X9717).

The Mechanism of Methanol Conversion into C_2-C_3-Olefines on SAPO Catalysts

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C_2-C_3-olefines are large-scale products of chemical industry and can be used as initial substances for production of valuable chemical materials, such as polythene of low and high pressure, polypropylene, polyolefines, polystyrene, poly-α-olefines etc. At present, manufacture of C_2-C_3-olefine by traditional ways meets certain deficiency of raw materials and high expenses of this processing because C_2-C_3-olefine market cost exceeds 1000 USD per ton. In this connection, the methanol to olefine (MTO) process seems to be very attractive for future.

In Zelinsky Institute of Organic Chemistry, the SAPO zeolite catalysts have been found to be effective in methanol conversion into olefins C_2-C_3.

The method of synthesis of SAPO-zeolite catalysts comprises using triethylamine as a template structure agent, which forms colloid under in the presence of sodium, ammonium or hydrogen fluoride and crystallizes at 180-205° for 20-60 h. The prepared SAPO-34 zeolite has small size and high degree of crystallization.

On the basis of analysis of experimental data, the model of the mechanism of MTO-conversion is proposed.

1) Excess of temperature of MTO-conversion is higher 450°C is inexpedient in view of activization of the collateral processes overwhelming C_2-C_3-olefine formation

2) Process appreciably proceeds on the radical - chain mechanism

3) Methanol in dimethylether (DME) conversion is fast process, and further DME in primary stable hydrocarbon radicals conversion (methylen and others) is the rate limiting stage determining the general rate of process and character of distribution of reaction products

4) Increased DME-contents at intermediate stages blocks C_2-C_3-olefine formation

5) Catalysts such as SAPO do not promote aromatization of C_2-C_3-olefine

PP-III-123

One-Pot Hydrodebenzylation – Acylation over Pd/C: Mechanistic View on Catalyst Deactivation

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Catalyst Pd/C was found to be highly effective for the cleavage of N-benzyl bonds of isowurtzitane derivative followed by their acylation in the presence of molecular hydrogen. Thus a key step in the synthesis of 4,10-diformyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexa-azaisowurtzitan (the precursor of nitramine 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane) is one-pot hydrodebenzylation-acylation reaction of 2,4,6,8,10,12-hexabenzylhexaazaiso-wurtzitan over Pd/C catalyst in the presence of molecular hydrogen [1]. The principal challenge of this stage is the fast deactivation of the catalyst under influence of rigorous reaction medium [2, 3].

The current work aims to elucidate the mechanism of Pd/C catalyst deactivation during concurrent hydrodebenzylation and acylation process in the presence of molecular H_2.

Pd/C catalyst samples were synthesized modifying the catalyst structure and composition of active component as well as varying the methods for active component deposition to provide a proper stabilization of active component. Stabilizing elements I, III, V groups of periodic table were introduced to the active sites during the process of either deposition or reduction of Pd^{2+}. Comparative study of the formation of active Pd component as well as characterization of catalyst samples before and after reaction recycles was carried out by XPS, HRTEM and EDX. It was shown that cyclic performing of 4,10-diformyl-2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitan synthesis results in a successive decrease in the concentration of palladium on the support surface with a simultaneous change in the ratio between oxidized and active forms of metallic palladium component. It was found that rapidly deactivated Pd/C catalysts contained mainly Pd^{2+}, the composition of an active phase and a distribution of Pd particle size changed during recycles while the introduction of an effective stabilizer maintains the high activity of Pd/C catalyst during several cycles preventing undesirable Pd sintering, leaching and oxidation.

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The Promoting Effect of Rare Earth Metals on Partial Oxidation of Methanol to Hydrogen over Ag and Cu Catalysts

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The main objective of this study is to design of catalysts have high catalytic performance in oxidation of methanol (POM) to hydrogen. Which based on noble metal Ag[1] and Cu[2] supported on multi-components rare earth metal oxides (viz., Ce, La, Dy, Gd etc.). The first catalyst series (Ag/RE-ZnO), used in this work is multiphase which contains Ag metal as hydrogen dissolving phase and the second conducting phase is nano-ZnO (35 nm) modified by 20 w/w % rare earth metal oxides. the second mutliphase catalysts series have studied (Cu/RE-ZnO), which contains Cu metal as hydrogen dissolving phase. The catalytic activity of the mentioned catalysts was investigated in POM at different temperatures.

In term of catalytic performance, the introduction of ceria was the most beneficial for production of hydrogen in the case of Ag/RE-ZnO catalysts, which exhibited hydrogen selectivity 90.8% with 95.2 % methanol conversion at 350°C. However the most positive effect in the performance of Cu/RE-ZnO catalysts was realized by gadolinium, resulting in selectivity 96.1% but with 50.4% methanol conversion at ca. 300°C. The observed drop in SH_2 over all catalyst under study above 350°C was attributed to decomposition of methanol to CO. Further investigation of the structure selectivity relationship are under way.

Acknowledgment

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PP-IV-2

Transition Metal Peroxo Complexes as Catalysts for Chemo- and Stereoselective Sulfides Oxidation

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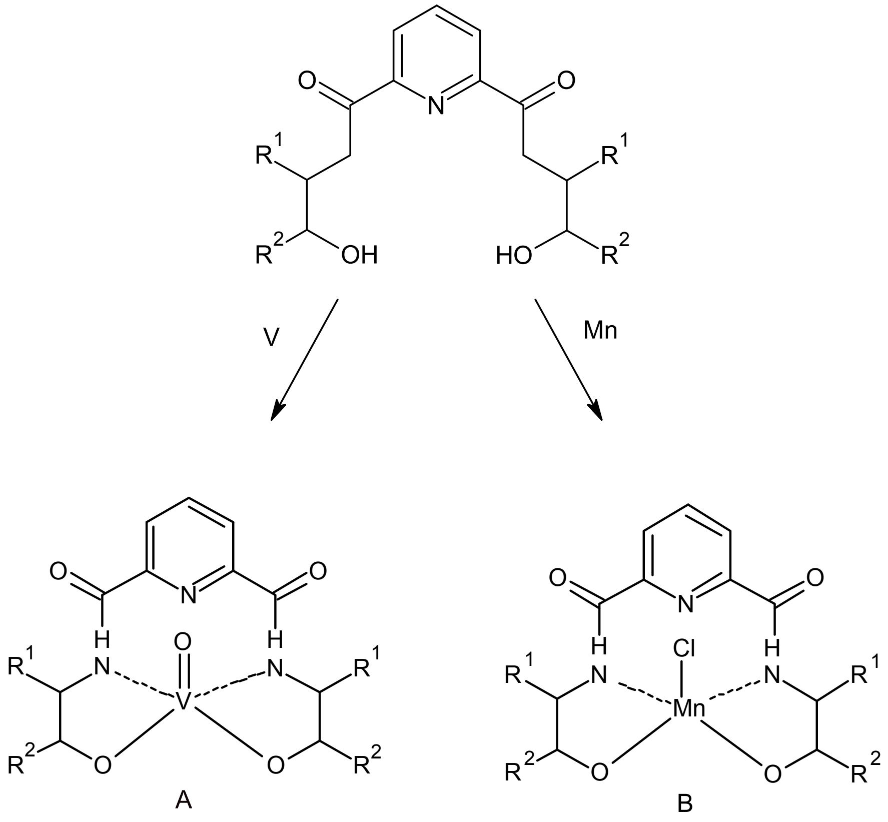
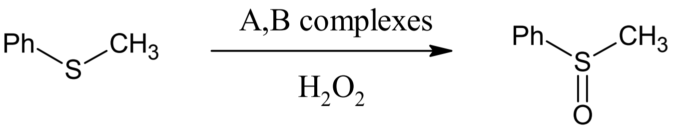
The synthesis V- and Mn- complexes with pyridincontaining ligands has been carried out from corresponding ligands and metal salts in water solutions according with following scheme:



Those complexes were applied at catalysts for chemo- and stereoselective oxidation of model sulfide to corresponding sulfoxides:



The structures of complexes and oxidation products were supported by NMR and mass-spectrometry methods.

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Mechanistic Aspects of Catalytic Hydrogen Production from Biomass Derived Formic Acid at about Ambient Temperature

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During last few years, it is observed a great interest to formic acid (FA) which can be used for hydrogen storage. FA is a by-product of biomass hydrolysis obtained in big concentration. Pd based catalysts are often considered as the best catalysts for hydrogen generation from FA [1]. The objectives of the present work were to further improve the activity of these catalysts by doping with alkali metal ions and to understand the reasons of the improved activity.

The rates of the reaction over a 1 wt.% Pd/C catalyst with mean particle size of 3.6 nm could be increased by 10-100 times by doping with K-ions taken in optimal concentration (10 wt.%) (Fig. 1a) [2]. The turnover frequency reached 1 s^{-1} at 353 K being comparable with those reported for homogeneous catalysts. Potassium was the best promoter than other alkali metals used (Cs, Na and Li) (Fig. 1b). The K-doped carbon support was inactive. The K-doped catalyst showed excellent hydrogen selectivity (<30 ppm CO) and stability at least during 22 h of operation at 343 K. The catalysts were characterized by CO chemisorption, XPS, TEM/EDS, XRD and BET surface area measurements. The results indicated that mobile highly dispersed K formate species can be an important intermediate providing improved hydrogen generation by decomposition on Pd active sites.

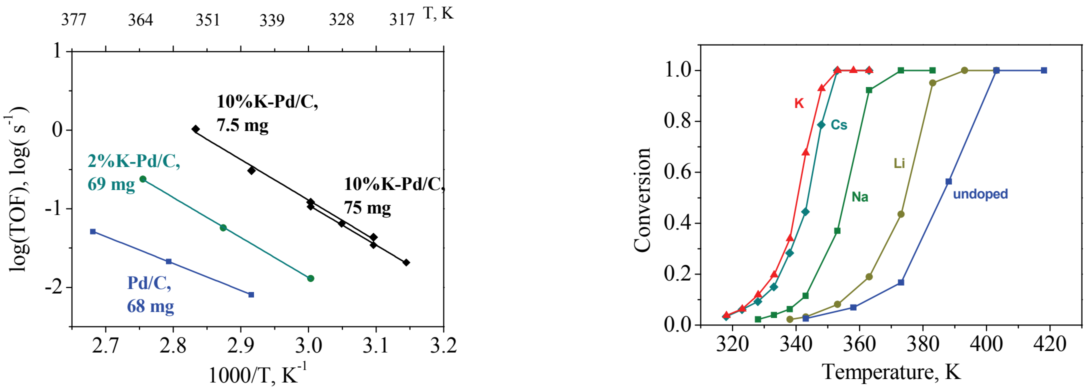

Fig. 1 a) Arrhenius plots for turnover frequency values, b) conversion - temperature dependence (alkali metal ions:Pd - 27:1 mole ratio, Pd weight – 0.68 mg, 2 vol.% FA/He, 51 ml min^{-1}).

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PP-IV-4

The Selectivity of Methyl Palmitate and Rapeseed Oil Hydroconversion on CoMoS/Al_2O_3 and NiMoS/Al_2O_3 Catalysts

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HDO is considered as important commercial rout for producing of distillate range bio-fuels from triglyceride-based feed-stocks such as vegetable oils, animal fats etc. The promising strategies to produce hydrocarbons with the required technical and environmental fuel standards could be the hydrodeoxygenation (HDO) of triglycerides alone or the co-hydrotreatment of triglycerides with petroleum fractions. In both cases the typical HDT catalysts, like CoMoS/γ-Al_2O_3 and NiMoS/γ-Al_2O_3, can be used. The HDO selectivity (trough the H_2O or CO/CO_2 removal) is a crucial factor for the process design and operation.

The aim of the present work is a comparison of selectivity of the methyl palmitate transformation as the model compound on the sulfided CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3 and the validation of the obtained results in the hydroconversion process of the rapeseed oil/SRGO blend.

The HDO of methyl palmitate were performed in a batch reactor at 300°C and hydrogen pressure 35 bars over CoMoS/γ-Al_2O_3 and NiMoS/γ-Al_2O_3 (0,14-0,25 mm particle size). The catalytic properties in HDO of the rapeseed oil/SRGO blend was evaluated in trikle-bed down-flow reactor at 340-360°C and 4,0 MPa of hydrogen using the full-size granule of catalysts (the trilobes with the l=3-5mm, d ~1,2 mm).

It was stated that methyl palmitate completely transformed into C_{15} and C_{16} hydrocarbons through the formation of oxygen- and sulfur-containing intermediate compounds, the tentative reaction scheme of methyl palmitate transformation was considered. It was shown that the main product of HDO of methyl palmitate obtained over CoMoS/γ-Al_2O_3 catalyst was hexadecane whereas pentadecane is preferably formed over NiMoS/γ-Al_2O_3 catalyst, pointing out to different reaction route of methyl palmitate conversion. The same dependency was obtained in the case of rapeseed oil hydroprocessing: CoMoS/γ-Al_2O_3 catalyst provides preferably the direct HDO route, when NiMoS/γ-Al_2O_3 catalyst support essentially the decarbonylation/decarboxylation transformation.

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

Steam Reforming of Bioethanol over $MnFe_2O_4$ Spinel

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The ethanol steam reforming (ESR) is a subject of undimishing interest as promising way of the hydrogen production from renewable feedstock:

$$C_2H_5OH + 3\ H_2O = 2\ CO_2 + 6\ H_2.$$

Recently, it was shown that $NiAl_2O_4$ spinel [1] reveals good performance in the ESR process. Here, we report a study of the ethanol steam reforming over $MnFe_2O_4$ spinel.

The reaction was carried out in a quartz flow reactor at atmospheric pressure, in the temperature range 300-700°C, initial reaction mixture 2.7 mol.% C_2H_5OH, 50 mol.% H_2O, N_2 (balance).

In the investigated conditions, we achieved the hydrogen yield of 5.5-5.7 mole of H_2 per mole of ethanol that is close to theoretical value for the ESR reaction. Moreover, the important distinctive peculiarity of catalytic action by $MnFe_2O_4$ is absence of CO as reaction product up to 650°C. These findings evidence that $MnFe_2O_4$ is promising catalyst for ethanol steam reforming. It was observed also that $MnFe_2O_4$ catalyzes formation of acetone with selectivity up to 55% at middle temperatures.

Taking into account the literature as well as our data, we suppose as working hypothesis, the following simplified mechanism of the ESR reaction on $MnFe_2O_4$ (some steps are nonelementary):

$CH_3CH_2OH + 2\ O^* \leftrightarrow CH_3CHO + 2\ HO^*$; $CH_3CHO + HO^* \leftrightarrow H_2 + CH_3COO^*$;
$CH_3COO^* \leftrightarrow CH_3^* + CO_2$; $CH_3COO^* + {}^* \leftrightarrow CH_3CO^* + O^*$;
$CH_3CO^* + {}^* \leftrightarrow CH_3^* + CO^*$; $CH_3^* + HO^* \leftrightarrow CH_4 + O^* + {}^*$
$CH_3CO^* + CH_3^* \leftrightarrow CH_3COCH_3 + 2^*$; $CH_3^* + 4\ O^* \leftrightarrow CO^* + 3\ HO^* + {}^*$;
$O^* + CO^* \leftrightarrow CO_2 + 2^*$; $H_2O + {}^* \leftrightarrow O^* + H_2$; $2\ HO^* \leftrightarrow 2\ O^* + H_2$.

Active sites of the explored oxide catalyst include apparently ferrum ions which undergo reversible redox transformations $Fe^{3+} + e \leftrightarrow Fe^{2+}$ in the course of catalysis.

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PP-IV-6

Application of the Concept of Interlayer Dynamics for Design of Novel TMS-Based Catalysts for Synthesis of Mixed Alchohols

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In recent time much attention was attracted to alternative fuels such as alcohols. Conventional oxide catalysts used for alcohols synthesis are very sensitive to the presence of ultra-low sulphur amount in the feed sulphur. One of the ways to overcome this difficulty is to use systems based on widely used for hydrodesulphurization (HDS) transition metal sulphide (TMS) catalysts, modified for alcohol synthesis by addition of potassium. The aim of the present work is to investigate a structure of sulphide catalyst active sites in mixed alcohol synthesis (MAS). As a conceptual basis for this work the model of dynamic nature of the active sites of TMS catalysts was taken [1].

The results of investigation into the effect of carrier structure allowed us to assume that morphological characteristics and nature of the carriers essentially affect the catalytic activity. Information about a role of K in the catalytic activity was obtained by testing the samples with K content in the range 0-15 wt. %. With increasing of K content selectivity changes from HC to alcohols. Main part of the liquid products consists of C_1-C_4 alcohols (>85 wt. %), ethanol and propanol has concentrations more than methanol. Potassium concentration affects substantially HDS and HYD activities. In these reactions K represents itself a poison and primary poisons HYD active sites. Addition of K up to 10 wt. % reduces catalysts HDS activity in small extent, but reduces HYD activity. Poisoning of C-S hydrogenolysis sites occurs by increasing K concentration to 15 wt. %,. Basing on TEM data we suggested that K ions intercalates between two neighboring MoS_2 layers. Above 10 wt. % K “glues” MoS_2 slabs by basal planes growing layers number. Further increase of K content from 10 to 15 wt. % initiates growth of an average crystallite length via "sticking" by laterals.

Potassium affects active phase morphology and modifies the active sites of the TMS catalysts. It was shown that Co-promoted catalyst more selective to alcohols than unpromoted one. The observed Co promoting activity in MAS and HDS led us to conclusion about similarity in the nature of the active sites operating in both reactions.

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Effect of Medium on Hemin Oxidative Destruction by Hydrogen Peroxide

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Catalytic activity of hemin (FeIII-protoporphyrin IX, FePP) and its derivatives in hydrogen peroxide decomposition is often used in biomimetic catalase model systems. However, in contrast to heme holoenzymes, isolated hemin undergoes oxidative destruction in presence of hydrogen peroxide, leading to the formation of ferric species. In neutral or alkaline medium this process results in the formation of colloidal aggregates of ferric oxyhydroxides, which possess a large specific area, high sorption capacity and hence catalytic activity, particularly in hydrogen peroxide decomposition. In contrast to Fe-porphyrins, which show a relatively weak photoactivity as compared with d^0-d^{10} Me-porphyrins, the rate of H_2O_2 decomposition on ferric colloids increases significantly under irradiation due to their semiconducting properties. Thus there is a catalyst transformation during the reaction *in vitro* which significantly changes the shape of the kinetic curve.

The rate of both hemin oxidative destruction and H_2O_2 catalytic decomposition was shown to depend on the aggregation state of the pigment in solution [1]. The present study compares the rates of both processes in a medium with varying acidity and in micellar solutions of different surfactants in order to reveal the nature of intramolecular interactions, which govern the aggregation processes and influence the catalytic activity of FePP. The most effective hydrogen peroxide decomposition associated with rapid hemin destruction was obtained in alkaline solutions, corresponding to a dimeric state of the pigment with an absorption maximum at 386 nm. In acidic medium the rate of both processes is extremely slow, indicating the presence of oligomer aggregates with a narrow absorption band at 366-372 nm. The stability and catalytic activity of the monomeric form of FePP, expected to be predominant in micellar solutions and obtained in aqueous solutions near pH7 with an absorption maximum in the range of 392-402 nm, strongly depends on the surface charge of the surfactant micelles. Further studies should reveal the mechanism of FePP stabilization, resulting in a significant increase in catalytic activity of the protein-associated cofactor.

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PP-IV-8

Conversion of n-Paraffins Using Hybrid Catalysts Containing BEA Zeolite

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The FTS waxes, major components of which are long-chain normal paraffins are an environmentally clean source for transportation fuels alone or blended with petroleum-based products. It has been reported that catalysts containing zeolites (BEA, SAPO-11, ZSM-22) are effective for hydroisomerization and hydrocracking of hydrocarbons under mild conditions.

To improve the izomerization ability of hydrocracking catalyst, we used hybrid catalysts made by introducing BEA zeolite without metal promotion. The HBEA (Zeolyst; CP811E-150) extrudates were obtained using 20 wt.% of boehmite (Pural KR-1, Sasol GmBH) as a binding agent (catalyst HBEA-F)). A series of HC + HBEA-F(x) hybrid catalysts, x being the wt.% of HBEA-F zeolite, were prepared by physically mixing a conventional hydrocracking catalyst and a HBEA-F zeolite. HC catalyst activity was reduced by introducing of sodium (0.1 wt.%). The activity of the catalysts was tested in n-hexadecane hydroconversion in fixed-bed lab-scale microreactor operated at high pressure (260 to 360°C, 5 MPa, H_2:CH=350 Nm^3/m^3; WHSV=2 h^{-1}). A comparison of the product distributions over HC and HC + HBEA-F (30 wt. %) is shown in Figure 1. The results are presented for conversions of 77.5 wt.% for HC catalyst (360 ^{0}C) and 75.9 wt.% for HC + HBEA-F (30 wt. %) (300 ^{0}C).

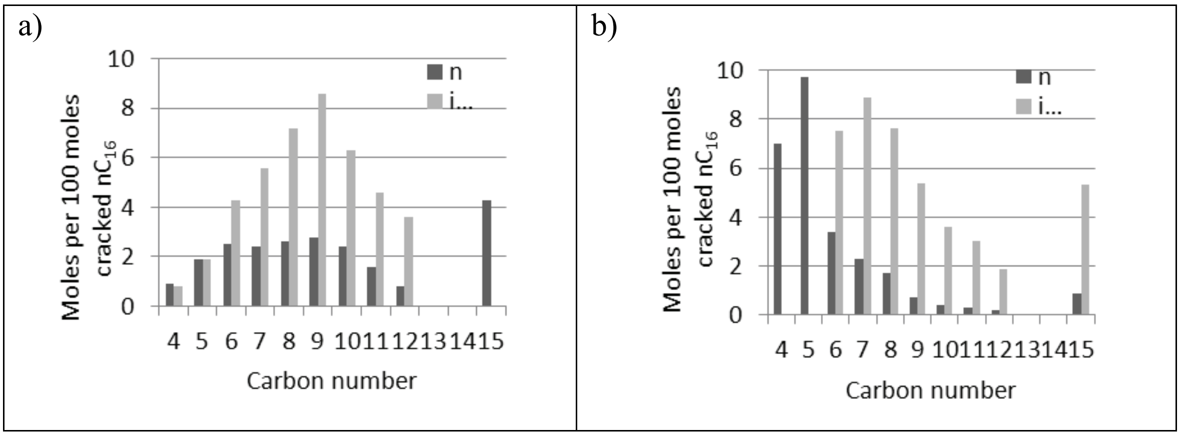

Fig. 1. Product distribution from n-C_{16} using a) HC and b) HC + HBEA-F (30 wt. %)

The results showed that a physical mixture of HC + HBEA-F (30 wt. %) yielded enhanced performance to i-C_{15} and i-C_{16}. Over hybrid catalyst no appropriate extent of hydrocracking could be achieved for C_7-C_9 paraffins.

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Hydrocracking and Hydroisomerization of *n*-Alkanes over Ni Catalysts

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Presently, the production of fuels and chemicals is based mostly on crude oil. However, because of economic, environmental, and technological factors, alternative energy resources e.g. biomass, become increasingly important. A promising application for biomass is syngas production and then Fischer–Tropsch (FT) synthesis to liquid fuels (BTL). FT technology, regardless of the feedstock (coal, gas or biomass) deliveries waxes as a by-product which can be a potential feedstock for bio-fuels production in the hydrocracking and hydroisomerization processes.

This work is focused on the activity of the Ni(4.5 wt.%) catalysts supported on AlSBA-15 (Si/Al=7) and $SiO_2Al_2O_3$ (Siral 30) in the the hydrocracking and hydroisomerization of long-chain *n*-paraffins i.e. n-C_{16} and n-C_{36}. Results of n-C_{36} hydroconversion show (table 1) that the yield of fules fractions and *n*-paraffins over both Ni catalysts is comparable but the yield of *i*-paraffins is slightly higher in the product mixture obtained on Ni/$SiO_2Al_2O_3$ than on Ni/AlSBA-15.

Table 1. Activity of Ni catalysts in hydroconversion of n-C_{36}, (autoclave, 360°C; 2,5h; 6MPa, 0,5g cat.)

Catalyst	C_6-C_9	C_{10}-C_{19}	$>C_{19}$	*n*-alkanes	*i*-alkanes	cycloalkanes	aromatics
Ni/$SiO_2Al_2O_3$	83.3	16.7	0	9.2	22.8	4.6	63.4
Ni/AlSBA-15	78.7	21.3	0	7.5	12.1	17.3	63.1

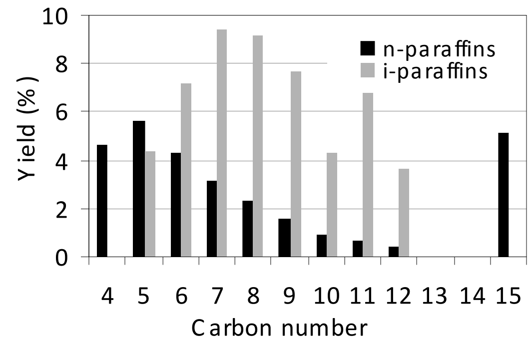

Fig. 1. Cracked products distribution obtained at 87 % of n-C_{16} conversion on Ni/AlSBA-15 (fixed bed reactor, 360°C; 3,5h^{-1}; 5MPa).

Fig. 1 presents carbon distribution of hydrocrackred and hydorisomerized products on Ni/AlSBA-15 obtained in conversion of n-C_{16}. Among the catalysts tested, Ni/AlSBA-15 shows the highest conversion of n-C_{16} and the highest yield of multibranched i-paraffins due to its weak acidity and mesopores.

Acknowledgements. This work was supported by the Polish Ministry of Science and Higher Education (Grant N R05 0088 10).

PP-IV-10

Novel Nanostructured Fe-, Co- Containing Materials as Heterogeneous Catalysts for the Decomposition of Heavy Oil Residue

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Nanomaterials catalysis has special interest, as nanostructured catalysts possess higher activity, and are capable to work at the mild temperatures. However substantial improvement of catalytic properties at transition to nanostructured systems is frequently accompanied by decrease in their chemical stability that demands detailed analysis of the numerous factors, including the nature and structure of the support materials. Heterogeneous catalysts are typical representatives of functional nanomaterials. Among the reported Fischer–Tropsch synthesis catalysts, iron and cobalt are used commercially at temperatures between 200 and 300°C, and at 10–60 bar pressure [1–3]. In this work our study is focused on increasing the activity of the nanostructured materials obtained in the reaction of fine-dispersed metallic Al with $C_2H_4Cl_2$ in the paraffin medium by modifying it in the mode of «in situ» with chlorides of Fe(III) and Co(II). Tested as catalysts samples of the solid products of these reactions before testing are treated at 400, 600 and 800°C under inert gas flowing. Electron magnetic resonance (EMR), X-ray fluorescence microscopy (XRFM) and thermal analysis (TG/DSC) are used to identify the nature of active sites of the catalyst systems, determine the active element distribution on the surface and near the surface levels. The formation of ferro-, superparamagnetic particles is established and as a function of treatment temperature of samples and concentration of transition ions are analyzed. The formation mechanism of carbon based nanostructured materials with the catalytically active bimetallic composition for the decomposition of heavy oil residue is discussed.

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Conversion of Aspen-Wood and Sucrose under the Action of Dissolved and Solid Acidic Catalysts

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The future success of biorefinary will require the new approaches to activation of lignocellulosic materials for further volarization and to design of a new generation of catalysts for the selective processing of cellulose and lignin.

Different methods of aspen wood pretreatment were compared. All studied methods change the overmolecular structure, chemical composition and reaction ability of wood. Treatments by steam at conditions of explosive autohydrolysis and catalytic oxidation by hydrogen peroxide make possible to separate the wood biomass on cellulose, low molecular mass lignin (LMML) and sugars from hemicelluloses.

Depending on the used method of wood biomass fractionation and type of further transformations of primary products the integrated processing of wood can be directed on the dominant production of liquid biofuels or chemicals. The studied integrated transformation of wood biomass to liquid biofuels includes the following steps: catalytic oxidation of wood by hydrogen peroxide to cellulose and LMML, acid-catalysed hydrolysis of cellulose to glucose, fermentation of glucose to bioethanol, thermal conversion of lignin to liquid hydrocarbons in ethanol medium under the pressure.

For promotion the key chemical reactions of integrated transformations of biomass the dissolved and solid acidic catalysts were used. The optimal conditions of alkaline thermal activation of different carbon-containing natural materials (fossil coal, lignocellulosics, cellulose and lignin) were selected which allow to produce porous carbons with surface area 1100–2890 m^2/g. After acidic treatments they were used as solid acidic catalysts for carbohydrates hydrolysis and lignin depolymerisation.

The dynamics of glucose and fructose formation at sucrose hydrolysis over mesoporous carbon catalyst Sibunit treated at 150 °C by $K_2Cr_2O_7$ + H_2SO_4 mixture was studied. The complete conversion of sucrose to glucose and fructose was observed at 80 °C. The activity of acid-treated Sibunit in sucrose hydrolysis at 80 °C is higher than that of catalyst Nafion NR 50 and close to activity of catalyst Amberlyst-15.

Catalytic Hydrolysis of Ammonia Borane with Iron and Nickel Oxides

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Ammonia borane (H_3BNH_3) is one of the perspective sources of hydrogen for feed power of portable fuel cells. As a result of full hydrolysis of 1 gramme of ammonia borane 2L hydrogen is formed. In conventinal conditions hydrolysis proceeds very slowly. Application of catalysts accelerates this process repeatedly. The best catalysts, as appears from references, are the catalysts on the basis of platinum and other precious metals. However their cost is high. In this connection works on search of more simple and less expensive materials all over the world are conducted. The aim of the given work is to study the possibility to use iron and nickel oxides as catalysts of hydrolysis reaction of ammonia borane.

FeO (OH), Fe_2O_3, NiO and double catalyst NiO-CuO/ZnO have been chosen as the objects of research. In experiments the weight of each oxide was 40mg. Ammonia borane of high degree of purification (99,8 % H_3BNH_3) was applied in the form of a water solution with the concentration 0,24wt. %. The process of hydrolysis was performed within the temperature range 20-80^{0}C.

The obtained data have shown that at temperatures below 50^{0}C the catalytic activity of the oxides tested is insignificant. Preliminary activation considerably raise the catalytic activity. So 30 ml of hydrogen can be obtained from ammonia borane in the presence of non-activated iron oxide at temperature of 80^{0}C for 495 sec, whereas after the activation required only 103 sec is for conducted the same volume of hydrogen. Approximately the same rate is noted at application NiO-CuO/ZnO (130 sec). FeO (OH) is intermediate: 295 sec. Nickel oxide shows the least catalytic activity (700 sec). In the present work the order of reaction of hydrolysis for the catalysts under investigation is defined, and the constants of rate and seeming activation energy are calculated.

On the basis of the conducted research it is possible to draw a conclusion that the oxides studied can serve as catalysts of reaction of hydrolysis of ammonia borane for the purpose of hydrogen production, the availability and cheapness of iron oxide make it rather attractive and perspective.

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Ion Exchange Resin Immobilized 12-Tungstophosphoric Acid as a Catalyst for the Oxidative Removal of Organosulfur Targeted at Clean Fuel

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The purpose of this paper was to investigate the desulfurization of the diesel oil, by immobilizing 12-tungstophosphoric acid (TPA) on several ion exchange resins, and further to screened the optimum resin (Amberlite-IRA900C). A solution of n-octane containing DBT was used as simulated diesel oil, H_2O_2 as oxidant, and acetonitrile (MeCN) as extractant. The best sulfur conversion efficiency was 95.8%. The optimum conditions were determined by adjusting the main factors that influenced the oxidative desulfurization (ODS) process, including O/S molar ratio, temperature, and catalyst dosage. The most favorable operating conditions were O/S = 28, T = 60 °C, the time of catalyst pre-contact with H_2O_2 for 8 min and the catalyst dosage of 0.222/0.500 (mmol g^{-1} dry resin). In the TPA/IRA900C-catalyzed oxidative desulfurization of the diesel oil (300 ppm sulfur), the sulfur content was reduced to 24.9 ppm. Moreover, the activity of the reused catalyst was almost the same as the fresh. Therefore, this immobilized catalyst TPA/IRA900C is promising for deep desulfurization by the ODS process.

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PP-IV-14

Radiative Decay of Freshly Catalyzed Peroxide in Crystallite Surface Fraction of Heavy Pyrolysis Tar

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Many recycled oil processing products, in particular, catalytic cracking and pyrolysis have intense luminescence. The use of complex physical, chemical and luminescence methods can determine not only the composition and structural characteristics of petroleum products, but also the elementary stages and mechanism of photo-oxidant processes. The last one proved to be particularly fruitful application of photothermoluminescence (TTF) and ESR in a wide range of temperatures, starting from temperature of liquid nitrogen (-196°C). There are TTF spikes in the petroleum hydrocarbon at temperatures above their freezing temperature caused by the collapse of peroxides. It was found that the latter include alkyl peroxides and endoperoxides of aromatic hydrocarbons and dioxetanes generated during low-temperature irradiated samples. The decay of these peroxides is that the presence of crystals in the system, this process occurs catalytically. As a catalysts formed freshly surface of the crystals [1], as a result of heating fractions. At the same time the width of the peaks in TTF significantly decreases and reaches 0.05 º C and below. These experiments give reason to believe that the number numerous fine-grained (over 120) of fine (TA) peaks TTF fractions of heavy pyrolysis resin (TSP) 200-300ºC are comparable with the number formed by heating the crystals. For higher-temperature fractions of TSP (300-350 and 350-400ºC) is also observed TS TTF, but the number of peaks is much smaller (4-5), and their width (from 2.5 to 12ºC) and the intensity is much greater. For higher-temperature fraction of TSP (>400ºC) crystals are not formed during the heating and decomposition of peroxides occurs only thermally. At the same time there are relatively broad maxima TTF (width more (exceeding) than 20ºC) at 101 and 182ºC. However, it should be noted that under certain conditions, TS TTF can be observed for a fraction of >400ºC. This requires heating the solution of this fraction after the photoirradiation. This is accompanied by evaporation of the solvent with the simultaneous formation of crystallites. This is accompanied by the appearance of multiple peaks in the TC. TS TTF at a fraction of >400ºC is also observed after rubbing it with well-luminescent crystals of aromatic compounds (anthracene, phenanthrene, etc.). Analysis of the results of experiments on TTF shows that the number of TC peaks occurring catalytically can be judged on the number of crystallites in the oil system.

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Comparative Study of Oxidative Coupling of Methane to Ethane and Ethylene over Na-W-Mn/SiO_2 and La-Sr/CaO Catalysts

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The direct conversion of methane to valuable products is the most attractive and economic route of natural gas valorization. The oxidative coupling of methane (OCM) is a challenging process of one-stage C_2 hydrocarbons (ethane, ethylene) production from CH_4 [1,2]. The present work is focused on the study of OCM reaction over two different catalytic systems - Na-W-Mn/SiO_2 and La-Sr/CaO in order to gain information about the role of various chemical components in the formation of active phase and reaction performance. The catalysts were prepared with variation of synthesis method and metals content, studied by the physicochemical methods and tested in the OCM reaction in a fixed-bed reactor with mass-spectrometric gas analysis. It was established that for Na-W-Mn/SiO_2 catalysts the synthesis method and type of SiO_2 have significant effect on the texture, while the Na/W ratio defines the phase composition. For La-Sr/CaO catalysts the synthesis method determines both the specific surface area (S_{BET}) and XRD phase composition: for example, the phases of CaO, La_2O_3 and SrO with $S_{BET} \sim 1$ m^2/g were identified in the sample prepared from the physical mixture of oxide precursors, while those of CaO, La_2O_3 and $SrCO_3$ with $S_{BET} \sim 10$ m^2/g - in the sample prepared by citrate sol-gel methods. The OCM kinetic data over Na-W-Mn/SiO_2 and La-Sr/CaO catalysts were compared and correlated with the results of DTA-TG, TPR, XPS and HRTEM analyses. As a result, the effects of Na-W-Mn/SiO_2 and La-Sr/CaO catalyst compositions on their physicochemical properties and activity in the OCM were elucidated.

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PP-IV-16

Hydroisomerization of Catalytic Cracking Gasoline over Bifunctional Catalyst

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The concept of oil-refining industry development envisages as primary goals an increase in extent of crude oil refining as well as a development of novel highly-efficient and ecologically clean processes and technologies. Combination of solutions of tasks on deepening oil refining and obtaining trade products meeting the requirements of modern standards is possible at the expense of development and usage of novel methods of refining «secondary» fractions of catalytic cracking, visbcreaking and coking processes [1, 2].

With the purpose of upgrading the quality of catalytic cracking gasolines their hydrotreatment was carried out in the presence of bifunctional catalyst. The studies were conducted at the flow type laboratory installation having stationary catalytic system Al-Co-Mo / Ni-Al-Si at the ratio 1:1 – 1:5 with the catalyst layer of the volume 200 ml under optimal conditions (temperature 360 ^{o}C, pressure 4 MPa, bulk velocity of feed-stock delivery 1.0 h^{-1} and volume ratio hydrogen : feed-stock 1500 l/l).

As a result of the performed researches it was established that upon complete hydrogenation of unsaturated hydrocarbons of normal and isostructure with an aid of hydrogenating layer (the ratio Al-Co-Mo / Ni-Al-Si = 1:1) not only the process of hydrocracking catalyst deactivation but also the process of formation of carbonium-ions (in their generation unsaturated hydrocarbons take part) becomes inhibited which is a accompanied by the process rate decrease. The octane number of the gasoline produced in the process of destructive hydroisomerization of catalytic cracking gasoline under these conditions makes 76 points against 82 points, obtained at the ration of the catalyst components 1:5. The content of aromatic hydrocarbons equals 28 % against 20 % wt whereas the yield of the isocomponent makes 41.8 % against 28.5 % wt. At the same time the produced gasoline has the octane number according to the motor method 82 points against 76 points.

Thus, it is expedient to carry out the destructive hydroisomerization of the catalytic cracking gasoline fraction at the ratio of the catalyst components Al-Co-Mo / Ni-Al-Si = 1:5. In this case unsaturated hydrocarbons of normal structure contained in the fraction are hydroisomerized and cracked whereas aromatic hydrocarbons are practically not hydrogenated that contributes to improvement of quality and elevation of octane number of the produced gasoline by 3 points (according to motor method) as compared with the initial gasoline.

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PP-IV-17

Control of Metal Dispersion, Chemical Composition, Porous Structure and Thickness of Mesoporous PtSn/TiO_2 and PdZn/TiO_2 Coatings for Microcapillary Reactor

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Bimetallic catalysts are widely used in the fine chemical industry, e.g. for selective hydrogenation of acetylene alcohols and selective hydrogenation of α,β-unsaturated aldehydes. These processes are of particular interest because hydrogenation products are intermediates in the synthesis of vitamins and fragrant substances. In stirred tank reactor the reaction rate is often limited by interphase mass transfer. To overcome this problem, multi-phase reactions can be performed in microcapillaries with a catalytic coating deposited on the interior surface. In order to offer a good host matrix for embedding active component, the preparation of titania coating with large surface area, controlled thickness and pore size should be required [1]. A (poly-)metallic nanostructured catalyst, with its capacity to specifically activate a selected functionality, can render a chemical reaction more efficient, faster and more selective, and thus, lower the raw material costs and/or increase the productivity. The non-selective deposition by conventional methods (such as impregnation with aqueous solutions and deposition-precipitation) leads to the formation of mono-and bimetallic particles with different compositions. In this sense, the preparation of bimetallic nanoparticles and clusters is envisaged as a suitable alternative to conventional methods since both composition and particle size can be controlled. Prior to incorporation, the synthesis parameters should be optimized to obtain bimetallic clusters and nanoparticles with a predefined and narrow size distribution and required chemical composition [2]. The correlation between physical-chemical properties of Pt-Sn/TiO_2 catalysts vs. their activity in selective hydrogenation of citral has been established [3].

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H_2S Purification from Biogas to Feed MCFC by Partial Oxidation on the V_2O_5-CeO_2 Catalyst

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Biogas can be used for energy production in non conventional systems as the molten carbonate fuel cells (MCFC). The utilization of the biogas as fuel for MCFC presents different problems concerning the poisoning of the anode, of the electrolyte, and the deactivation of oxidation sites by sulphur based compounds (H_2S, COS) that are always presents in biogas. Because the MCFC have a poor tolerance to these compounds, it's necessary to reduce the H_2S concentration at values about 1-5 ppm [1].

Direct selective oxidation of H_2S to sulphur at low temperature appears to be the greatest promise for the removal from biogas to feed to MCFC.

In the previous works vanadium-based catalysts supported on the metal oxides (CeO_2, $CuFe_2O_4$, TiO_2) were investigated in the range of temperature of 50-250°C.

A high activity at T=250°C in terms of H_2S, O_2 conversions and a low SO_2 selectivity (14%) were obtained on the V_2O_5/CeO_2 catalyst. Further investigations were performed to order to minimize the SO_2 selectivity by varying the H_2S feed concentration (250-1000 ppm), the gas hourly space velocity (15,000-45,000 h^{-1}) and the feed molar ratio (O_2/H_2S=0.4-0.5). A good result in terms of selectivity to SO_2 was observed with a sub-stoichiometric feed ratio (O_2/H_2S = 0.4) for which the SO_2 selectivity obtained was of 4%.

After found the optimal sample, additional tests will be performed to individuate the main kinetic parameters, and try to obtain preliminary indications concerning the main steps of reaction mechanism, and the basic kinetics parameters in order to determine the reaction rate expression. Preliminary investigations on the kinetic parameters showed the reaction mechanism is based on the Langmuir Hinshelwood model with an apparent reaction order for O_2 of 1 and of 1 for H_2S.

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PP-IV-19

Methane Auto-Thermal Reforming in a Compact Thermal Integrated ATR Reformer: Monolithic Catalysts Performances

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Up to now, hydrogen and fuel cells combination is the most viable answer to the antithetic problems of energy growing demand and environmental pollution reduction: in this contest, hydrogen results as the most promising solution. In order to realize distributed H_2 production, very compact and small size production plants are required: to this goal, hydrocarbons auto-thermal reforming reaction assures a self-sustaining process and high reactor compactness, resulting as the best method for distributed H_2 production to couple to a fuel cell system. In spite of the increasing interest in renewable sources, due to the low costs, the widespread existing delivery pipelines, fossil fuels still remain the best choice in a transition period towards hydrogen based economy.

In this work the auto-thermal reforming of methane (as natural gas surrogate) was analyzed. Structured commercial monolithic catalysts performances in methane processing were studied: the different catalyst geometry covers a fundamental role in the process performances. The activity tests were conducted in a compact catalytic reactor thermally integrated. Through a heat exchange system, integrated in the reactor, water and air stream are preheated by exploiting the heat from exhaust stream, so allowing to feed reactants at room temperature as well as cooling product stream at a temperature suitable for further purification stages (WGS, PROX). In order to achieve a very comprehensive process analysis, temperatures and composition are monitored in 6 point along the catalytic bed. The influence of catalytic system geometry as well as thermal conductivity in the process performances was also analyzed. Preliminary tests showed high thermal system efficiency, with a good hydrocarbon conversion at different operating conditions. The low start-up times makes the system extremely versatile, and suitable for batch operations. In one hand the monolith catalyst allows a flatter temperature along the catalytic bed, so reducing hot spot phenomena and improving reaction performances in the thermodynamic point of view. On the other hand, the continuous reaction stream mixing realized by the foams catalysts (as well as by a special configuration of monolith catalyst) assure a products composition very close to the thermodynamic equilibrium, and allows higher gas space velocity.

Effect of Cu-Catalyst Based Permeable Contactor Membrane on the Products Distribution in the Fatty Acids Triglycerides Hydrogenation

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Hydrogenation of fatty acids triglycerides solves the problem of efficient processing of renewable raw materials to produce components of diesel fuel (hydrocarbons with a boiling point of 200-350°C) and a number of valuable chemicals for pharmaceutics and cosmetics.

The aim of this study was to compare the catalytic behavior of copper-containing catalysts in the hydrogenation reaction of stearic acid triglyceride in two types of reactors: (1) a stirred reactor with a conventional pellet catalyst and (2) reactor equipped with a permeable membrane contactor (PCM). Also it has been shown the influence of the nature of Cu-containing catalyst composition inside PCM on the hydrogenation behavior.

A new way of the catalyst's layer design (PCM) leads to the changes in the ratio of the reaction products. Along with diesel range hydrocarbons, the formation of a comparable amount of ester, made up of acids and alcohols produced from triglyceride was observed. The products distribution changing for different catalyst layer organizations suggests that it determines the direction of triglyceride hydrogenolysis, namely the place of bond opening in the ester group (Fig. 1). In the case of the granular catalyst bond opened mainly at position 2. The use of PCM leads to bond opening primarily at a position 1.

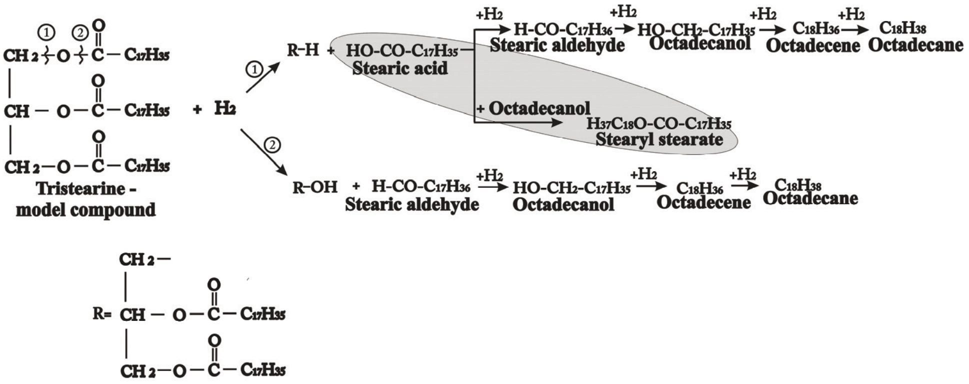

Figure 1. The scheme of consecutive and parallel reactions in the stearic acid triglyceride hydrogenation.

Changes in the ratio of the rates of hydrogenation successive stages, and thus in the ratio of final products was observed for different catalysts compositions in the PCM.

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PP-IV-21

Mechanistic Study of Reaction Pathways in Butyl Lactate to Propylene Glycol Hydrogenolysis over Cu/SiO$_2$

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A catalytic method starting from lactic acid obtained by fermentation of crude biomass is promising way of 1,2-propanediol synthesis instead of conventional petroleum-based per-oxidation process. However it is well known that catalytic hydrogenation of carboxylic acid to corresponding alcohols is a very difficult process, which requires high hydrogen pressure and temperature. For example, the hydrogenation of lactic acid to propylene glycol over Ru-containing catalyst was carried out at 145 bar and 423 K to reach noticeable conversion of lactic acid and selectivity to propylene glycol [1]. Using copper-containing catalysts permits to reduce hydrogen pressure up to 1 bar, but consecutive dehydration-hydrogenation reaction path occurs under such conditions leading to formation of undesirable propanoic acid [2]. Possible way to avoid dehydration and thereby to increase selectivity is preliminary esterification of lactic acid. The goal of the present work is to study kinetic peculiarities of butyl lactate hydrogenolysis in fixed-bed reactor over Cu/SiO$_2$ catalyst in order to develop high selective process of propylene glycol synthesis.

Hydrogenolysis of butyl lactate was carried out over 45.5wt% Cu/SiO$_2$ at P_{H_2} 1 bar in the temperature range from 403 to 493 K. It was observed that increase of temperature leads to increase of substrate conversion as overall reaction rate grows while selectivity to propylene glycol decreases due to increase of hydroxyacetone formation. Propanoic acid formation was not detected during hydrogenolysis. Effect of residence time on composition of reaction mixture was studied. It was found, that concentration of butyl lactate is decreased and concentrations of main products are increased with increasing residence time. It is noteworthy, that ratio between propylene glycol and hydroxyacetone was independent on residence time and substrate conversion. The data obtained allow assuming that formation of propylene glycol and hydroxyacetone is equilibrated thermodynamically and therefore this equilibrium can be shifted to desired product by slight increase of hydrogen pressure [3].

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H_2-Least Approaches for Deoxygenation of Phenolic Compounds

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Deoxygenation of phenolic compounds has become major concern for upgrading pyrolysis bio-oils due to (i) a large consumption of H_2 for hydrotreating approaches [1,2] and (ii) severe catalyst deactivation [3]. Unlike carbonyl compounds found in the pyrolysis bio-oils, oxygen in phenolics cannot be readily removed via decarbonylation and decarboxylation. The resonance structure strengthen C-O bond of the phenolics and direct hydrogenolysis cannot be simply achieved over renowned catalysts [4,5]. To avoid excessive H_2 intake, new approaches involve weakening of C-O bonds without ring saturation. This can be achieved either by (i) partial hydrogenation-dehydration or (ii) coupling-hydrogenolysis approaches. In the first case, phenolics can be partially tautomerized [6] over oxophilic catalysts [7]. The keto-form intermediates can be subsequently hydrogenated and oxygen can then be removed by dehydration of the alcohol formed. For the latter approaches, phenolics can also be coupled to larger oxygenate species over bifunctional catalysts [8]. Together with H-transfer, active metal readily promotes hydrogenolysis of larger precursors since cleavage of the C-O bridging in the bulky isolated rings can be easily facilitated, as compared to that in the single ring aromatics. However, coke deposit is largely regulated by coupling/hydrogenolysis rate in this case.

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On the Role of Mass-Transfer Processes in the Overall Kinetics of the Three-Phase Glucose Oxidation into Gluconic Acid over Pd, Au and PdAu Catalysts

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The biomass of green plants contains *ca.* 75% carbohydrates which are the main source of the renewables employed for the production of bio-based products. One of these products is gluconic acid which is widely used in industry. Nanosized supported Au, Pd, and PdAu catalysts are known to be the best catalysts for the glucose oxidation. However, efficiency of heterogeneous catalytic processes in multiphase medium depends not only on an intrinsic catalytic activity but also on mass-transfer phenomena.

The aim of this work is a study of the mass-transfer impact on the apparent reaction rate of the glucose oxidation process over the Au, Pd and PdAu catalysts supported on C and Al_2O_3. The catalysts with the different active components and their morphology, hydrophobicity were chosen in order to evaluate the influence of these factors on the overall kinetics.

The rates of the gas-liquid and liquid-solid oxygen transfer were calculated and compared with the apparent reaction rate of the glucose oxidation. For estimation of the effectiveness factor of the catalyst grain the Weisz modulus was calculated. The influence of the mass transfer of oxygen on the overall kinetics was analyzed under different regimes of the process.

The catalysts on alumina demonstrated the higher catalytic activity than the samples on carbon at the same dispersity of the supported metals at high Glu:Au molar ratios. High effectiveness of the catalysts (>95%) was found for the Au/Al_2O_3 with a uniform distribution of Au in support grains as well as for the Pd/C catalysts with an egg-shell distribution of the noble metal. The effectiveness factor of Au/C grains was estimated to be 60-70% which implies pore-diffusion limitation of reaction due to uneven distribution of Au nanoparticles in the grains of catalysts.

At low Glu:Au molar ratios (large amount of catalysts), when the oxidation process is limited by the oxygen gas-liquid transfer, the apparent rate of the glucose oxidation over the carbon-supported catalysts is higher than over the alumina-supported ones. This phenomenon can be explained by a high adhesion between oxygen and hydrophobic carbon facilitating the gas-liquid-solid oxygen transfer.

Combined Methods for Mono-, Di- and Triglycerides Determination: A Biodisel Production over CaO Catalyst

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Biodiesel has been considered as a promising responce to environmental, economic, and political problems concerning fossil fuels. Its advantages are: renewability, bio-degradability, low cost, and environmental suitability. Biodisel is a mixture of fatty acids methyl esters (FAME) obtained in a catalyzed reaction of transesterification of methanol and vegetable oils or animal fats. Commercial sunflower oil was used as the raw material for biodiesel synthesis. GC-MS analysis determined the oil fatty acid profile: palmitic acid (9.20%), linoleic acid (61.20%), oleic acid (19.30%) and stearic acid (6.44%). Transesterification reaction was carried out with methanol-to-oil molar ratio = 1:6 using 1% CaO as catalyst, at 65°C and 1 atm, for 5h with time increments of 1h. The obtained FAME were analyzed using GC-MS (Hewlett-Packard series 6890N), equipped with MS detector and a capillary column DB-5. The related GC FAME peaks were detected as follows: methyl palmitate, methyl linoleate, methyl oleate, and methyl stearate, based on the corresponding retention indexes. The estimated average biodisel yield was 90.9%.

As supplemental method, reversed-phase high-performance liquid chromatography (RP-HPLC) was used for determination of total TGs, diacylgycerols (DGs), monoacylglycerols (MGs) and FAME. The method was used for analysis of early aliquots, composed of unreacted mixture of TGs, DGs and MGs, and quantitation of residual TGs in the final product. Non-aqueous mobile phase composed of 30% acetone + 70% acetonitrile (v/v), and C18 column without linear gradient, and UV detection at 220 nm were used.

A simple combination of adequate GC and/or HPLC methods has been modified and adapted to be used as an analytical tool for the full charactrization of FAME and residual transesterification reaction intermediates (total TGs, DGs and MGs). Such combined methods excluded additional need for use of derivatization techniques for particular compounds analysis.

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PP-V-1

Electrocatalytic Oxidation of Glycine at a Nano-Structured Ni Chelidamic Acid and Bimetallic Au-Pt Inorganic-Organic Hybrid Nanocomposite onto Glassy Carbon Modified Electrode

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Amino acids are essential building blocks of biological molecules and play key roles in many neuro-chemical response mechanisms, such as memory, appetite control and pain transmission [1]. The disruption of amino acid regulation has been linked to many disorders such as Huntington, Alzheimer and Parkinson diseases [2]. In this research a novel nickel complex was used as electrocatalyst for electrooxidation of glycine. A nano-structured nickel cheliamic acid was electrodeposited on a bimetallic Au-Pt inorganic-organic hybrid nanocomposite modified electrode. The electrode possesses a three-dimensional (3D) porous network nanoarchitecture, in which the bimetallic Au-Pt NPs serving as metal nanoparticle based microelectrode ensembles are distributed in the matrix of interlaced 3,3′,5,5′-tetramethylbenzidine (TMB) organic nanofibers (NFs). The hydrodynamic amperometry at rotating modified electrode at constant potential versus reference electrode was used for detection of glycine. Under optimized conditions the calibration plots are linear in the concentration range 1µM- 0.75mM and detection limit was found to be 0.3µM.

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PP-V-2

Oxygen Exchange and Degradation of LSM—YSZ Cathode Materials

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Composite $(1–x)\cdot$LSM—$x\cdot$YSZ based materials are successfully used as cathode materials in Solid Oxide Fuel Cells. The interphase exchange rate and the apparent oxygen diffusion coefficient were measured by the isotope exchange method with gas phase analysis for $x = 0$—1; T = 600—850°C; $Po_2 = 10^{-3}$—$10^{-1.5}$ atm and for $x = 0.6$ at T = 800°C, $Po_2 = 10^{-2}$ atm during 1000 hours. The electrical resistivity of the samples was measured by a dc 4-probe method at the same temperature and oxygen partial pressure during 1000 hours. The microstructure of the samples was studied by SEM on a JSM 5900LV with INCA Energy spectrometer after 0, 40, 500 and 1000 hours of the exposure time. Electrical conductivity was found to increase in time during exposure at 800°C and $Po_2 = 10^{-2}$ atm, whereas both the oxygen interphase exchange rate and the diffusion coefficient decrease at the same conditions, see Figure 1 Microstructure analysis allows to determine the microstructure changes with the composite phase ratio and the specific triple-phase boundary length dependence on time to predict the polarization resistivity behaviour measured by EIS method. The mechanism of the oxygen exchange and degradation of LSM—YSZ is discussed.

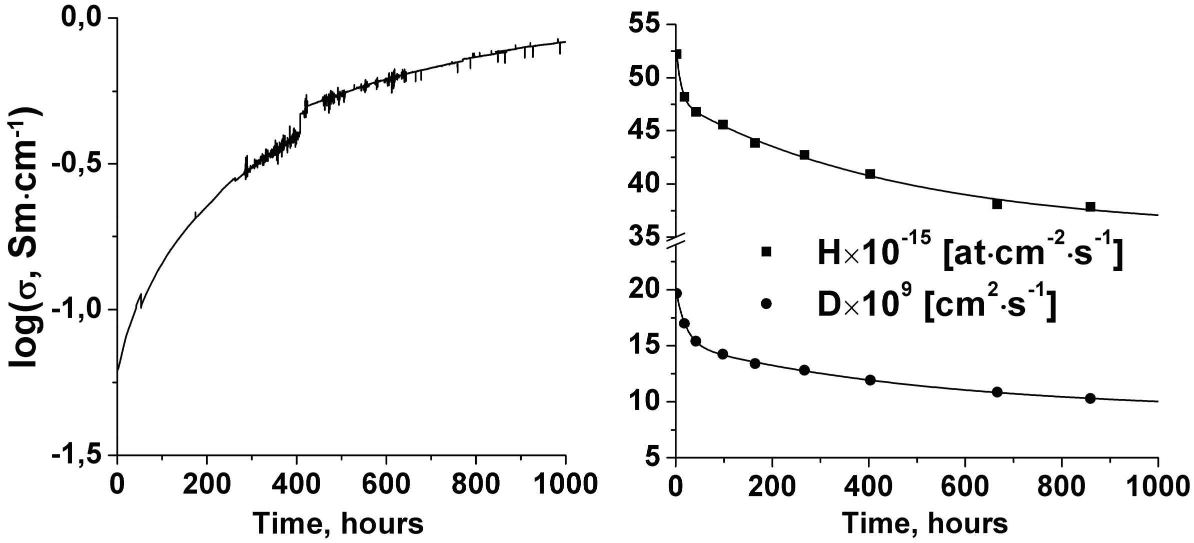

Fig. 1. Conductivity (σ), interphase exchange rate (H) and oxygen diffusion coefficient (D) time dependences for LSM—YSZ at 800°C, $Po_2 = 10^{-2}$ atm.

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PP-V-3

Dioxo-Mo(VI) - Complexes Anchored on Titania as Catalysts in Photo-Oxidative Decomposition of Some Aromatic Organochlorine Compounds by Dioxygen

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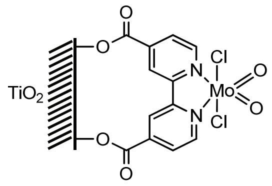

Recently synthesized and fully characterized dioxo-Mo(VI)-dihalo[4,4'-dicarboxylato-2,2'-bypiridine] complexes anchored on the surface of titania with different characteristic parameters (specific area, porosity, size of grains) have been tested in the photochemical oxidative decomposition of aromatic organochlorine hydrocarbons such as 1-chloro-4-ethylbenzene and 4,4'-dichloro-diphenylmethane. These oxidation processes under UV-irradiation or visible light may be considered as model reactions for the degradation of persistent organic compounds (pesticides and other organochlorine POP's). Studies have been carried out using a photochemistry installation and elaborating a special protocol of reaction allowing the separation of the period of reaction between the anchored complex and the substrate under UV-irradiation ($\lambda = 254$ nm) in the absence of O_2, from the period of regeneration reaction between the anchored complex and O_2 in the dark. The oxidative decomposition occurs mainly by an oxo-atom transfer to the benzylic carbon of chlorinated aromatic hydrocarbon. In the case of 1-chloro-4-ethylbenzene, the intermediate is 4'-chloroacetophenone that undergoes further decomposition to chlorobenzene, forming also small amounts of oxygen-containing organochlorine compounds, CO_2 and H_2O. Supporting evidence was obtained by submitting 4'-chloroacetophenone to the same reaction conditions and observing the formation of chlorobenzene as a main product of its decomposition. The ratio of [final product]/ [Mo-complex] increases during the reaction up to 350–400%, which provides evidence of a catalytic process. It has been suggested that oxo and oxo-peroxo-Mo(VI) moieties are active centers of the reaction.

The overall catalytic mechanism can be summarized as follows:

1. $L\text{-}(Cl)_2Mo^{VI}O_2 + CH_3CH_2C_6H_4Cl \rightarrow L\text{-}(Cl)_2Mo^{IV}O + CH_3C(OH)C_6H_4Cl$
2. $L\text{-}(Cl)_2Mo^{VI}O_2 + CH_3C(OH)C_6H_4Cl \rightarrow L\text{-}(Cl)_2Mo^{IV}O + CH_3C(O)C_6H_4Cl + H_2O$
3. $L\text{-}(Cl)_2Mo^{IV}O + O_2 \rightarrow L\text{-}(Cl)2(O\text{-}O)\,Mo^{VI}O$ (in the dark)
4. $L\text{-}(Cl)2(O\text{-}O)\,Mo^{VI}O + CH_3CH_2C_6H_4Cl \rightarrow L\text{-}(Cl)_2Mo^{IV}O + CH_3C(O)C_6H_4Cl + H_2O$

$\llcorner\!\rightarrow C_6H_5Cl$

where L is [4,4'-dicarboxylato-2,2'-bypiridine]/TiO_2.

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Efficient Photocatalytic Decomposition of Nitric Oxide over TiO_2-Based Nanotubes Catalyst

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TiO_2-based nanotubes were prepared by microwave-assisted hydrothermal procedure, with TiO_2 powder immersed in relatively concentrated (5 M) NaOH solution and treated hydrothermally under microwave irradiation at 220°C for 30 min. The high resolution transmittance microscopy revealed a multi-layered open-ended nanotube morphology, with several hundred nanometers in length, 3 - 5 nm of inner diameter and 8 - 10 nm of outer diameter. The XRD profile exhibited the typical diffraction peaks of titania nanutube as obtained from conventional hydrothermal method [1]. Nearly 300 m^2/g of BET surface area and 1.42 cm^3/g of pore volume were obtained by nitrogen adsorption isotherm at 77 K. The adsorption capacity and the mechanism of photocatalytic decomposition of nitric oxide (NO) were investigated by *in-situ* EPR spectroscopic studies and the resulted products were analyzed by a quadropole mass residual gas analyzer as in our previous study [2]. The results indicated that the catalyst activity for photodecomposition of NO was highly dependent on its pre-treatment. The hydrogen-reduced catalyst exhibited high catalytic activity for NO decomposition under UV (300 nm) irradiation. The conversion of NO reached nearly 100% in 15 min under UV irradiation with 82% of N_2 selectivity. The present study indicated that the titania nanotubes would be a potentially efficient photocatalysts for NO reduction that leads to a direct conversion of NO into N_2, with no need of a reducing agent such as NH_3 used in the selective catalytic reduction (SCR) of NO that usually causes secondary pollution.

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PP-V-5

Photocatalytic Synthesis of Bioactive Fused Pyrazolopyrimides and their Derivatives

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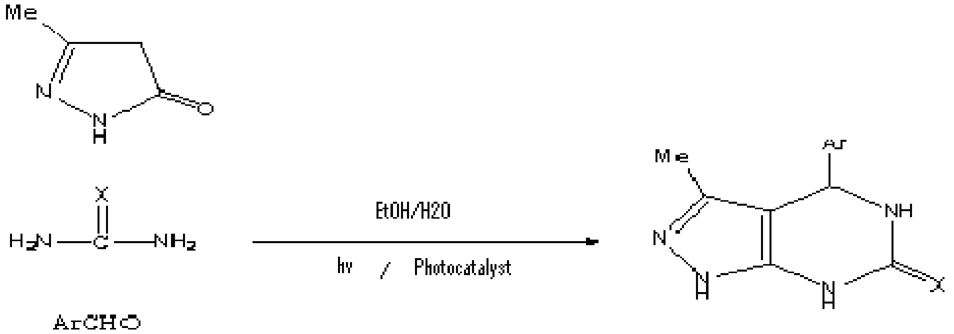
The application of heterogeneous photocatalysis to “selective organic transformations” has been studied. The photocatalytic synthesis of pyrazolopyrimidine derivatives has been investigated. This study examined some of the factors and influences involved in the applications of the photocatalytic techniques for the synthesis of some of pyrazolopyrimides and their derivatives. The photocatalytic reactions were carried out in aqueous medium instead of organic solvent, so, the photocatalytic processes would be environmentally friendly with low cost techniques. In addition, the preparation of efficient photocatalysts to be used in the photocatalytic reactions has been studied. The lab-prepared photocatalysts were characterized using different techniques such as: Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) etc.

Key words: Photocatalysis, fused pyrazoles, pyrazolopyrimidines, bioactivity



1

Ar ; (Ph), (p-ClC6H4) ,(P-NMe2C6H4) ,(P-NO2C6H4),(2,5-MeO2C6H3), (O-ClC6H4), (O-BrC6H4)

X ; S or O .

Supercritical Fluids as Solvents for Enzyme Catalyzed Reactions

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A "green" revolution as a part of necessary sustainable development, use also high pressure as a tool. The main impetus for this conversion is on one way driven by a concern to the environment to reduce the usage of solvents and energy and on the other hand high pressure is a tool to design and produce the products with completely new characteristics.

Supercritical fluids and dense gasses are a unique class of non-aqueous media with many features (due to their physico-chemical properties) that make their use as a solvent for biocatalysis and separation particularly desirable. The advantages of supercritical fluids as solvents fall into four general categories of benefits: environmental, process, chemical and health/safety. Other attractive features of supercritical fluids as solvents for biocatalytic processes include their high diffusivities, low toxicity and environmental impact; ease downstream processing and recyclability. Lipases have been used as versatile and very efficient biocatalysts for a wide variety of chemical reactions such as esterifications, transesterification, interesterification and ester hydrolysis. Because of their high activity and selectivity they have a great potential for the use as biocatalysts in industrial applications. Lipases are endowed with exceptional substrate specificity. They can be employed in the production of pharmaceuticals, cosmetics, foods, medical diagnostics and other organic synthetic materials. Application of high pressure lipase esterification technology is currently mainly restricted to those operations where the cost of the product is high, but the enzyme cost is relatively low in relation; i.e. this technology is applicable to high value fine chemicals. Lipases may also be attractive in processes that involve thermolabile substrates/products or that may entail a number of side reactions and in processes where high enantio- and/or regio-selectivity is required. Another opportunity for applications is in aroma and flavours industries, such as foods or dairy perfumes; the production of various ingredients by natural processes assumes great significance in this field. Using enzymes in high-pressure batch system may cause changes in biocatalysts activity due to pressurization/depressurization influence. Continuous reactors for SCFs have the advantage over batch reactors that they do not require depressurization to feed in the reactions or to recover the products.

An overview of fundamental data, design of the processes, application of various types of rectors, economics of the processes will be presented.

PP-V-7

New Photocatalysts Based on Cadmium and Zinc Sulfides for Hydrogen Evolution from Aqueous Na_2S–Na_2SO_3 Solutions under Visible Light

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The rapid depletion of oil resources necessitates extensive mastering of alternative energy and raw material sources for the chemical industry. Serious attention is presently given to use of hydrogen as a fuel. An advantage of hydrogen is its high heating value. Furthermore, the product of its combustion is water, an environmentally friendly substance. The photocatalytic decomposition of water to hydrogen and oxygen using solar energy is one of the most promising methods of hydrogen production.

Cadmium sulfide was the first photocatalyst to be employed in hydrogen production by irradiation of its aqueous suspensions with visible light using sulfide ions as electron donors. Cadmium sulfide is characterized by a band gap of 2.4 eV, and the positions of its valence and conduction bands are suitable for the photocatalytic decomposition of water. However, the sulfide ion is readily oxidized to sulfate by the photogenerated holes, with Cd^{2+} ions escaping into the solution. Use of sulfides as electron donors diminishes the photocorrosion of the catalyst. A possible way of enhancing the photocatalytic activity of cadmium sulfide is to develop composite materials based on CdS and broader band semiconductors, for example, ZnS. Zinc and cadmium sulfides have similar crystal structures, so they fairly readily form $Cd_{1-x}Zn_xS$ solid solutions.

Efficient hydrogen evolution on the sulfide photocatalysts $Cd_{1-x}Zn_xS$ is attainable without adding noble metals, which makes it possible to decrease the cost of the materials.

In the present work, we propose a two-step method for preparation of cadmium–zinc mixed sulfides with a large specific surface area and developed porous structure.

The activity of the synthesized materials was estimated in the photocatalytic hydrogen evolution from aqueous solutions of sodium sulfide and sodium sulfite ($\lambda > 420$ nm), that the highest activity was shown by $Cd_{0.3}Zn_{0.7}S$, whose band gap is Eg = 2.71 eV. We studied the influence of the catalyst concentration, pH, and the initial substrate concentration on the rate of photocatalytic hydrogen evolution. At optimal process parameters, the quantum efficiency of photocatalytic hydrogen evolution was up to 12.9%, which is a large value for a process occurring under irradiation with visible light on a catalyst containing no noble metal.

Production of Highly Active Doped Titania Photocatalysts by Aqueous Sol-Gel Processing - Synthesis and Characterization of the Xerogels

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Environmental pollution has become a critical issue for modern society and numerous studies involving semiconductor-mediated heterogeneous photocatalysis have been carried out to develop materials for the purification of air and water under natural or artificial-light illumination [1]. In our research, an environmentally-friendly aqueous sol-gel process was developed to produce anatase photocatalysts doped with Fe^{3+} in order to be able to activate the photocatalysts with visible light. The physicochemical properties of the xerogels were characterized by ICP-AES, XRD, UV-Vis spectroscopy and N_2 adsorption-desorption. The photocatalytic activity of the pure and doped photocatalysts was evaluated by monitoring the degradation of *p*-nitrophenol under visible light using a home-made installation [2].

The results showed that the dopant was successfully incorporated into the TiO_2 photocatalysts with a high precision and reproducibility. XRD measurements established that all photocatalysts are constituted of TiO_2-anatase after drying at room temperature and it was also found that the optical properties, especially the value of the band-gap E_g, of the catalysts decreased when increasing the dopant content in the TiO_2 matrix. The textural properties of the photocatalyst were measured and it has been observed that the materials are purely microporous and presents a high specific surface area, S_{BET}, which slowly decreases when increasing the dopant content. The photocatalytic activity measured under visible light for Pure-TiO_2 produced by this aqueous sol-gel process was remarkably high for a non-calcined material. In the case of doped TiO_2, the evolution of the activity with the dopant content has been studied and an optimal dopant content value has been determined.

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PP-V-9

Electrocatalytic Detection of Arsenic at Silver-Doped Zeolite-Carbon Nanostructured-Epoxy Composite Electrodes

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A study of two substrates namely carbon nanotubes and carbon nanofibers for silver zeolite-carbon nanostructured-epoxy composite electrodes envisaging arsenic(III) electrodetection via anodic stripping voltammetry/amperometry is reported. Morphological characterization of both composite electrodes was carried out by scanning electron microscopy, and a good dispersion of both carbon filler and silver-doped zeolite within the epoxy matrix was revealed. Mechanistic aspects for arsenic deposition and stripping have been investigated on both electrodes using cyclic voltammetry technique. Both composite electrodes allowed to detect an arsenic signal using anodic stripping with a deposition potential of -0.4 V/SCE for 120 seconds at the potential value of about +0.2 V/SCE. The results of arsenic detection sensitivity using cyclic voltammetry in relation with the electrocatalytic activity of carbon nanotubes towards arsenic deposition and stripping led to the selection of silver zeolite-carbon nanotubes composite electrode for further detection studies. Differential-pulsed voltammetry, chronoamperometry and multiple-pulsed amperometry techniques were applied for arsenic detection via anodic stripping. In comparison with other results reported [1, 2], better electroanalytical performance in relation with the sensitivity and the lowest limit of detection for arsenic detection were achieved in this study. Also, a recovery degree of 98% was found for arsenic electrodetection using differential-pulsed voltammetry for spiked water samples.

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Electrocatalysis in Ionic Liquid Using Organic Mediators

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In this work we used one of the special properties of ionic liquids - high electroconductivity and wide polarization potential value interval [1]. We investigated electrocatalytic thiol oxidation by different electromediators in the ionic liquid without supplemental electrolyte application. Aromatic amines (tri-p-tholylamine, tri-p-bromphenyl-amine, 2,2`,4,4`-tetramethoxiphenylamine, N,N,N`,N`-tetramethyl-1,4-phenylenediamine, phenoxazine) were used as electromediators. Aromatic amines were brought in minimum amount and allowed to minimize power inputs in 0.5-0.8V [2]. Consequent electrolysis led to dibutyldisulfide formation thereupon dibutylsulfide (1,7V) as products of one-electron oxidation, fragmentation and dimerization of thiols. Product identification was performed by cyclic voltammetry, IR-spectroscopy and gas chromatography.

The study was financially supported by RFBR (12-03-00513a), grant of the President of RF (MK-923.2012.3), federal special-purpose programme "Scientific and pedagogical personnel of innovative Russia" 2009-2013 (ГК № 16.740.11.0594).

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PP-V-11

Photocatalytic Degradation and Mineralization of Methylene Blue Dye onto Ag-Modified Natural Zeolite Catalyst

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Dyes are characterized by complex aromatic molecular structures, which offer physicochemical, thermal and optical stability. They may also be carcinogenic, mutagenic and highly toxic to human beings [1,2] and need to be removed from industrial wastewaters. This has always been a major problem because can not be easily treated by conventional methods, *i.e.,* coagulation, chemical flocculation or by biological procedures [3,4]. Also, conventional oxidation treatment encounters difficulty to oxidize dyestuffs and complex structure of organic compounds. In this study, the photodegradation and the mineralization of a Methylene Blue (MB) cationic dye from aqueous solution was investigated, in the presence of hydrogen peroxide, using an Ag-modified natural zeolite catalyst (Z-Ag_{red}). The catalyst was synthesized by a chemical activation prior to the ion exchange and followed by a silver reduction with sodium boron hydride. The photocatalytic performance of Z-Ag_{red} catalyst was proved by photocatalysis application without and in the presence of hydrogen peroxide for the decolorisation, degradation and mineralization of MB dye containing wastewater under visible irradiation. The effect of H_2O_2 dose on the MB degradation and mineralization efficiencies by photocatalysis on Z-Ag_{red} highlighted that in the applied working conditions (initial MB concentration of 50 $mg \cdot L^{-1}$, 1 $g \cdot L^{-1}$ catalyst dose at pH 9), 20 mM H_2O_2 was sufficient to reach a high degradation efficiency and to achieve an effective mineralization. The kinetic study revealed that the photodegradation rate follows pseudo first order kinetics. The photocatalytic rate of MB significantly increased in the presence of hydrogen peroxide. The good results regarding the photocatalytic degradation and mineralization of MB dye using Z-Ag_{red} catalyst claim it as a potential for the real photocatalysis application in MB-containing wastewater under solar light.

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Study of Free Charge Carrier Distribution on the Surface of Titania-Based Photocatalysts

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Application of TiO_2-based photocatalysts for decomposition of volatile organic compounds (VOC) in air and water has attracted much attention. However, a photocatalytic efficiency of such materials should be enhanced for their wide application. Energy-band structure of effective photocatalyst could provide transfer of valence electron to exited state and prevent the electron-hole recombination. The presence of strongly defected amorphous phase could be attributed to a large number of defects, which are a trap for charge carriers. Fujihara has shown that amorphous phase of octahedron complexes TiO_6^{8-} participates in transfer of charge from Ti^{3+} to O^- [1]. This provides a decrease of electron-hole recombination. Unfortunately, the amorphous phase is very unstable and should be stabilized. The most promissing method of amorphous phase stabilization is distribution of TiO_2 over suitable support, for instance, SiO_2 aerogel [2].

In the present work, the distribution and type of free charge carrier generated on the surface of samples was investigated. Two series of TiO_2/SiO_2 and TiO_2/Al_2O_3 photocatalysts were prepared by heterogeneous deposition [2]. TTIP (98 %), TEOS (99 %) and γ-Al_2O_3 were selected as precursors of titania, silica and aluminia, respectively. The content of active component was varied from 3 to 15 % wt. Physical-chemical properties and structures of the catalysts prepared were studied using XRD, FTIR and UV-Vis spectroscopy. The model reactions of photochemical deposition of cationic Ag^+ and Pb^{2+} were used for identification of a character of the free charge carrier distribution on the photocatalyst surface according to [3]. The activity of photocatalysts was investigated in photooxidation of methylene blue dye under the static conditions.

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PP-V-13

Mathematical Modelling of Photocatalytic Degradation of Methylene Blue under Visible Irradiation

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Methylene blue (MB) is the most widely employed basic dye, which finds enormous applications in dyeing and printing industry. Large volumes of coloured wastewater are thus produced and, for this reason, various treatment methods, based on physical, chemical, and biological unit operations have being investigated, however the development of a cost effective removal technology still eludes the scientific community [1-2]. In this context, photocatalysis appears as one of the most viable solutions that can be exploited advantageously for the complete mineralization of various dye pollutants present in liquid media. It is well known that the main photocatalyst used, TiO_2, absorbs only a little fraction of the solar spectrum emission because of the value of its band-gap energy (3.0-3.3 eV). Thus, the anion-doped TiO_2 has attracted considerable attention due to its reported activity under the visible light. Among all, the N-doped TiO_2 seems to be the most promising visible absorbing photocatalyst. In this work, the N-doping TiO_2, obtained by direct nitration during the hydrolysis of titanium tetraisopropoxide with ammonia aqueous solutions [3], was used to evaluate the photodegradation of MB in aqueous solutions, chosen as model dye-contaminated wastewater. Photocatalytic tests were carried out in a pyrex photoreactor and irradiated with visible light emitted by WHITE LED surrounding the photoreactor, with a tuneable incident light intensity among 8 and 32 mW/cm^2. The effects of many operating conditions on MB removal, such as initial MB concentration, the dosage of catalyst amount and light intensity were evaluated by both UV-Vis spectrophotometry and TOC analyses as function of time of irradiation. The experimental results were used to develop a mathematical model based on Langmuir-Hinshelwood kinetics [4] that results to well describe the behaviour of the system in different experimental conditions.

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Catalytic Decomposition of Hydroperoxides in the Interface between Low Density Polyethylene Film and ZnO Thin Coating

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Some metal-oxide semiconducting transparent thin films are able to protect polymers from photodegradation caused by ultraviolet (UV) radiations [1, 2]. As early was described, zinc oxide thin (20÷150 nm) coatings were deposited by us in various conditions via radio frequency magnetron sputtering on low density polyethylene (LDPE) films in order to obtain effective photoprotector for polymer [3]. It was found that the presence of these coatings strongly reduced the rate of LDPE photo-oxidation, because, firstly zinc oxide absorbs UV radiations up to 380 nm, and, secondly, oxygen permeability of the ZnO/LDPE assemblies decreases when the thickness of coating increases from 0 to 50 nm. Meanwhile, the signs of photocatalytic activity of ZnO at the interface of coating/polymer were detected both by some other authors [2] and by us [4].

The aim of this study is to gain a better understanding of physic-chemical interactions occurring in the interfacial region between ZnO and LDPE surfaces.

The coated LDPE samples were irradiated in artificial conditions (λ>250 nm, T=60 ^{o}C), and concentration of oxidate was measured by FTIR spectroscopy each 12 hours. In order to show the photocatalytic effect of ZnO, a neutral glass plate with the same UV transparency characteristics and the same impermeability for oxygen was also deposited on LDPE film before irradiation. Experimental data shows that ZnO layer and the glass layer have protected LDPE in different ways. Under ZnO protection, the accumulation rate of hydroxylated products (3410 cm^{-1}) and hydroperoxides (3552 cm^{-1}) was lower, but the accumulation rate of carboxylated products' (isolated carboxylic acids 1767cm^{-1}, esters 1737 cm^{-1}, ketones 1724 cm^{-1}, associated carboxylic acids 1714 cm^{-1}) was insignificant greater in comparison with sample protected by glass plate. Most probably, the cause of these differences is the dissociative adsorption of peroxides on ZnO surface and their catalytic decomposition.

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Fuel Cells Powered by HPAs: FlowCath® Technology

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Heteropolyacids (HPAc) have attracted much interest as catalysts that can be exploited for PEM fuel cell application due to their distinctive redox and catalytic properties. Catalysis by HPAc is a well established field of study with a developed understanding of the mechanisms of HPAc catalytic activity on molecular level. This has resulted in the optimisation of novel and existing industrial processes. HPAc based catalyst's activity can be explained by its reversible ability to be reduced and reoxidised repeatedly [1]. Thus HPAc catalysis has the potential to offer substantial economic and environmental returns with the capability of satisfying global demand for efficient usage of energy and resources. ACAL Energy Ltd has developed proprietary technology that utilizes an HPAc based redox cathode approach for PEM-type fuel cells that avoids the drawbacks of using precious metal catalysts and resolves a significant number of the durability issues associated with current PEM cells. In addition, it affords substantial cost reduction opportunities and simplification of the fuel cell system processes.

The basis of the technology is that an aqueous solution-based redox approach is used for the cathode, instead of an oxygen gas MEA-type cathode. The cell consists of an anode flow field, electrode assembly and membrane which are very similar to the current anode and membrane. No membrane electrode assembly is employed on the cathode side; the membrane is in contact with the aqueous solution, called the catholyte solution. The solution contains a dissolved redox species – the mediator – which carries out the redox processes; the solution passes through a porous electrode at the cathode where the mediator is reduced. The solution is circulated to a regenerator where oxygen from air is brought into contact with the solution. A soluble catalyst reacts with the oxygen and protons to oxidize the mediator and form water. As a result, the technology is applicable to the fuels commonly used in PEM-type systems, hydrogen and liquid fuels such as methanol.

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Section of the young scientists

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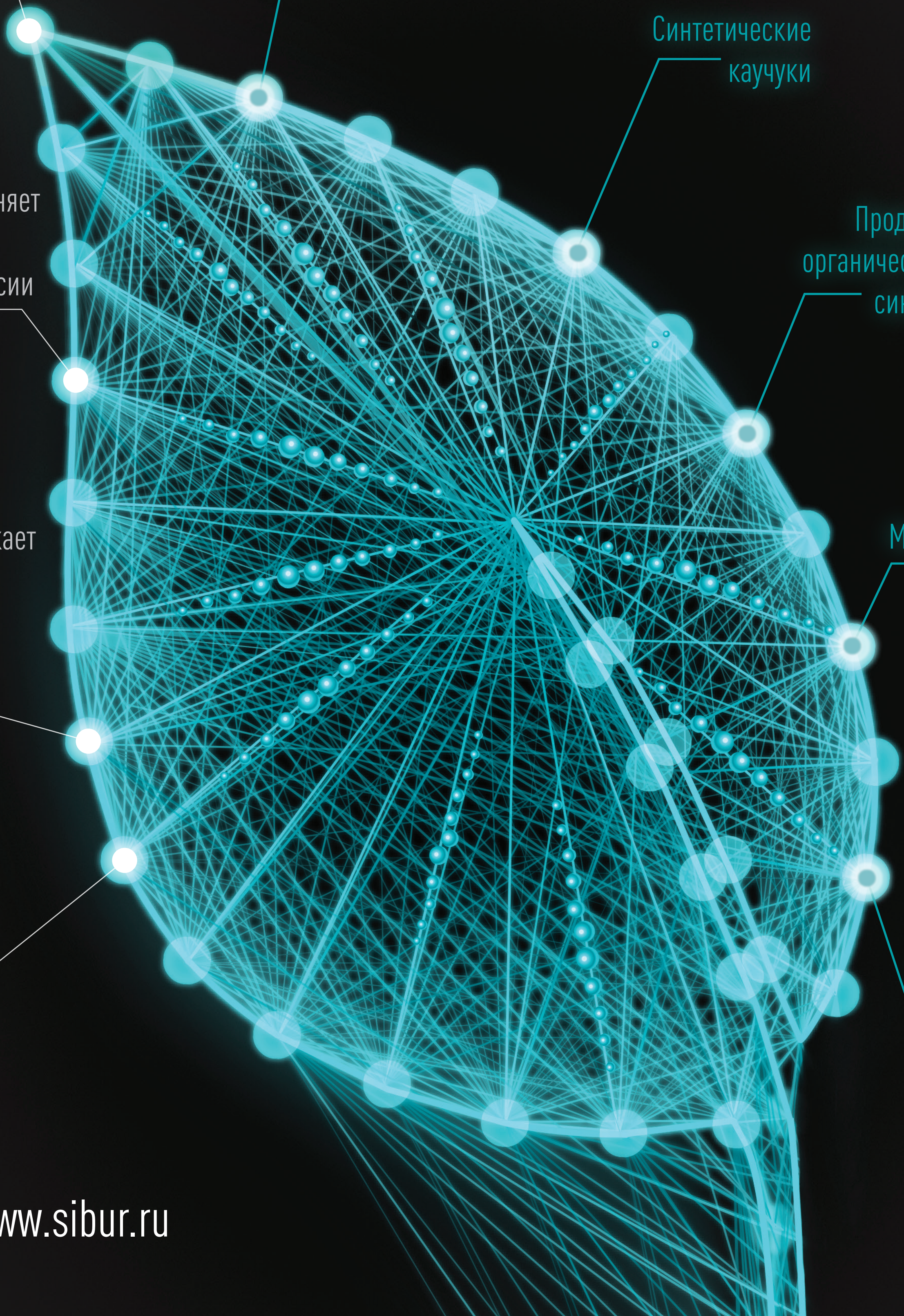


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ООО “Реолгрейд сервис” (г.Новосибирск) – аналитическое и лабораторное оборудование

ООО "Реолгрейд сервис" - авторизированный дистрибьютор компании "Agilent Tehnologies", США.

Компания “Реолгрейд сервис” осуществляет:

- комплексное оснащение лабораторий различного профиля аналитическим и вспомогательным оборудованием;
- поставки и запуск оборудования зарубежных производителей, не имеющих представительства в Российской Федерации;
- гарантийное и послегарантийное обслуживание поставляемого оборудования.

Спектр поставляемого оборудования:

Agilent Technologies

Широкий спектр самого современного оборудования для молекулярной спектроскопии и хроматографического анализа крупнейшего производителя Agilent Technologies:

- Атомно-абсорбционные спектрометры;
- Оптико-эмиссионные спектрометры;
- ИК-Фурье микроскопы/ИК-Фурье спектрометры;
- Портативные ИК-Фурье анализаторы;
- УФ-Вид спектрофотометры;
- Спектрофлуориметры;
- Газовые, жидкостные и гель проникающие хроматографы;
- Расходные материалы для газовой и жидкостной хроматографии;

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Общелабораторное оборудование Daihan Scientific.

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СПЕКТРАЛЬНОЕ И ХРОМАТОГРАФИЧЕСКОЕ ОБОРУДОВАНИЕ Agilent Technologies:

Атомно-абсорбционные спектрометры

Атомно-абсорбционные спектрометры (ААС) Agilent отличаются производительностью, удобством в эксплуатации и высочайшей надежностью. Они широко применяются как для сложных аналитических задач, так и для поточного анализа в лабораториях. Топовые модели линейки ААС ***Agilent 240FS/280FS*** - самые быстродействующие и высокопроизводительные ААС с пламенным атомизатором в мире. ***Agilent Duo*** - уникальный, единственный в мире приборный комплекс, позволяющий проводить истинно параллельный анализ методами пламенной и электротермической атомизации.

Оптико-эмиссионные спектрометры

Оптические эмиссионные спектрометры с индуктивно-связанной плазмой (ИСП-ОЭС) ***серии 710*** фирмы Agilent обладают превосходными характеристиками. Они предназначены для лабораторий поточного анализа со средним пробопотоком. ИСП-ОЭС ***серий 720 и 730*** фирмы Agilent отличаются превосходными рабочими параметрами, быстродействием и адаптабельностью. В соответствии с аналитическими задачами возможен выбор оптимизированной осевой (710/720/730) или радиальной (715/725/735) конфигурации.

ИК-Фурье микроскопы/ИК-Фурье спектрометры

Совершенный оптический дизайн ИК-микроскопов, в сочетании с высокой светосилой спектрометров Agilent, образуют непревзойденную по возможностям и чувствительности комбинацию. ***Cary 640 FTIR*** – доступный по цене ИК-Фурье спектрометр с улучшенными характеристиками, выпускаемый с двух версиях: для работы в ближней и средней ИК области. Серия ИК-спектрометров ***Agilent Cary 660/670/680*** FTIR изготовлена на базе интерферометра Майкельсона с динамической юстировкой и может перекрывать широкий спектральный диапазон при наличии соответствующих источников, светоделителей и детекторов.

Портативные ИК-Фурье анализаторы

Портативные ИК-фурье анализаторы ***4100 Exoscan*** и ***4200 Flexscan*** обладают высокой производительностью, устойчивостью к внешним воздействиям и могут использоваться в полевых условиях при анализе материалов, поверхностей, молекулярном анализе камней, минералов, грунтов и твердых веществ. Интерфейс на основе диффузионного отражения не требует предварительной подготовки образца. Для анализаторов доступна геофизическая базы данных коэффициентов диффузионного отражения, что позволяет проводить быструю идентификацию состава образца.

УФ-Вид спектрофотометры

Линейка УФ-ВИД спектрофотометров включает в себя приборы различных классов. ***Cary 60*** - уникальный по своим техническим характеристикам прибор для самого широкого круга спектрофотометрических задач от рутинного анализа до уникальных специфических анализов. Спектрофотометры ***Cary100/300*** с двухлучевой схемой предназначены для рутинной лабораторной работы. Спектрофотометр ***Cary 5000*** с инновационной технологией PbSmart, позволяющей расширить спектральный диапазон в ближнюю ИК область до 3300 нм.

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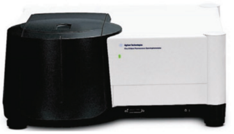
ООО “Реолгрейд Сервис” (г.Новосибирск) – аналитическое и лабораторное оборудование

Спектрофлуориметры

Cary Eclipse - спектрофлюориметр с двумя сверхбыстрыми сканирующими монохроматорами, построенный на основе пульсирующей ксеноновой лампы и оптики Шварцшильда. Cary Eclipse обеспечивает работу в режимах измерения флюоресценции, фосфоресценции, хеми- и биолюминесценции. Сочетание мощности светового импульса лампы с оптикой Шварцшильда обеспечивает максимальную чувствительность прибора, повышает светоотдачу более чем в 100 раз и создает световую иммунность к комнатному освещению при открытом кюветном отделении.



Хроматографическое оборудование

Серия хроматографов ***Agilent 1200*** имеет модульную конструкцию, позволяющую формировать конфигурации, наиболее подходящие по требованиям прикладных задач любой сложности. Жидкостные хроматографы Agilent – это превосходные завершенные системы, рассчитанные на самую высокую производительность с одновременным улучшением качества хроматографических результатов. В списке оборудования представлены линейка высокоэффективных газовых хроматографов от микро- до потоковых промышленных хроматографов.

Расходные материалы для Хроматографии

В компании “Реолгрейд сервис” представлены расходные материалы для газовой и жидкостной хроматографии.

Это капиллярные колонки для газовой хроматографии, колонки для жидкостной хроматографии для аналитического или препаративного применения, предколонки, держатели предколонок, фитинти, сорбенты, стандарты, тестовые смеси, шприцы для ввода проб, виалы и прочие товары.

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Конфокальный рамановский микроскоп Renishaw inVia – инструмент, позволяющий решать широкий круг аналитических задач. Renishaw inVia обеспечивает высокую скорость сканирования и получение рамановских и фотолюминесцентных спектров в диапазоне от 10 до 10000 см$^{-1}$. Конфокальный режим позволяет снимать спектры с объектов, находящихся в толще матрицы, без их разрушения. Комбинация прибора с атомно-силовым или электронным сканирующим микроскопом, позволяет проводить спектрохимическое картирование образца с высочайшим пространственным разрешением.

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В ассортименте компании “Реолгрейд сервис” представлено общелабораторное оборудование фирмы Daihan Scientific, Корея. Перечень оборудования включает в себя: автоклавы, бани водяные и термостаты, бани масляные, ванны ультразвуковые, вортексы и шейкеры, гомогенизаторы, дистилляторы, бидистилляторы, инкубаторы, климатические камеры, лопастные и магнитные мешалки, печи муфельные, плитки, термостаты и криотермостаты циркуляционные, шкафы сушильные.

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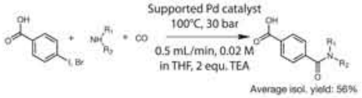

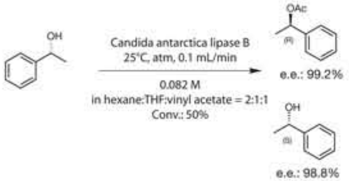

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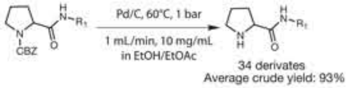

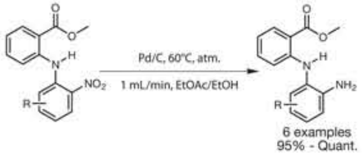

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Масштабирование

- Оценка катализатора для процессов переработки тяжелых нефтяных фракций
- Оценка промышленного катализатора в реальных условиях техпроцесса
- Селективное гидрирование
- Гидрокрекинг
- GTL - реакции
- Риформинг
- Гидродесульфуризация
- Реакция окиси углерода с водой
- Гидродеароматизация
- Селективное окисление
- Синтез Фишера-Тропша
- Изомеризация

ПРОМЫШЛЕННЫЕ ПРОЦЕССЫ

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Thermo Scientific TPDRO 1100

Высокоточный автоматизированный прибор для исследования каталитической активности

Thermo
SCIENTIFIC

Позволяет исследовать процессы ВОССТАНОВЛЕНИЯ, ОКИСЛЕНИЯ, ДЕСОРБЦИИ И ХЕМОСОРБЦИИ газов, проходящих через слой катализатора при различных температурах.

Фундаментальные свойства катализаторов (площадь поверхности металла, дисперсность металла, количество активных центров и энергия активации) могут быть максимально быстро и точно определены на приборах TPDRO производства Thermo Scientific. Данные устройства используют метод динамического потока, выполняя программируемый анализ температуры для таких процессов, как восстановление, окисление, десорбция или изотермическая хемосорбция. Многозадачность, точность и высокая производительность – это наиболее яркие особенности TPDRO 1100.

- TPDRO может быть легко и быстро сконфигурирован для выполнения большого числа экспериментов: химической десорбции чистых реакционных газов, их смесей и паров органических соединений, для исследования поверхностной активности и реакционной способности катализаторов; использования аммония и диоксида углерода (или аналогичных газов) для определения основности или кислотности поверхности; применения стандартной модели BET для определения общей площади поверхности катализатора. Осуществление данных методик стало возможным, благодаря созданию специальной многозадачной программы, с несколькими базами данных, которая позволяет управлять прибором, регистрировать результаты и формировать отчеты.

- Высокочувствительный 4-нитевой TCD-детектор позволяет TPDRO обнаруживать даже очень незначительное количество газа и получать невероятно точные результаты. Кроме того, к TCD может быть последовательно подсоединен масс-спектрометр для более полного и качественного анализа проходящего газа.

- Исследование катализаторов часто занимает много времени, главным образом, из-за стадии подготовки образцов для анализа. Перед экспериментом необходимо провести процедуру активации катализатора. TPDRO изящно решает эту задачу, используя особый реактор собственной разработки. Два катализатора могут тестироваться одновременно, один, находясь в модуле подготовки образцов, а второй, в аналитическом цикле. TPDRO позволит сэкономить Ваше время и значительно увеличить Вашу производительность! Кроме того, с одним и тем же катализатором может быть проведено неограниченное число аналитических циклов в автоматическом режиме, при этом, экспериментальные данные будут последовательно записаны на вашем компьютере.

КАТАЛИТИЧЕСКАЯ АКТИВНОСТЬ

- Удельная поверхность подложки катализатора
- Процент распределения металла по подложке
- Концентрация кислотных/основных активных центров
- Энергия активации десорбции
- Окислительно-восстановительные свойства

Эксклюзивный представитель в России

CZL
лабораторное оборудование

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Промэнерголаб – российская компания, специализирующаяся на комплексном оснащении научно-исследовательских институтов и предприятий широким спектром аналитического и лабораторного оборудования, в том числе и промышленными и лабораторными реакторами.

Реакторные системы южнокорейской компании **Reaction Engineering** хорошо зарекомендовали себя на российском рынке, благодаря простоте эксплуатации, гибкости и высокой надежности.

Reaction Engineering изготавливает системы как проточного, так и периодического типа, которые способны работать в широком диапазоне давлений и температур.

CZL

лабораторное оборудование

Проточный каталитический реактор

система для проведения непрерывных каталитических процессов

Основные характеристики

Вместимость реактора	5 мл – 2 л (в стандартном исполнении)
Расчетное давление	до 400 бар
Расчетная температура	до 800 °C
Материал изготовления	Нержавеющая сталь 316SS, Hastelloy C-276
Количество зон нагрева	5 зон
Подача газа	0.05 – 3 л/мин
Подача жидкости	0.02 – 100 л/мин

Реактор периодического типа

с эффективным перемешиванием

Основные характеристики

Вместимость реактора	100 мл – 10 л (в стандартном исполнении)
Расчетное давление	до 400 бар
Расчетная температура	до 600 °C
Материал изготовления	Нержавеющая сталь 316SS, Hastelloy C-276
Мощность электрического нагревателя	0.5 кВт – 10 кВт
Скорость перемешивания	0 – 3500 об/мин

REACTION ENGINEERING, INC.

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ABSTRACTS

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