Mechanisms of Catalytic Reactions VIII Volume II

"Mechanisms of Catalytic Reactions"

dedicated to the 70th anniversary
of Professor Kirill I. Zamaraev

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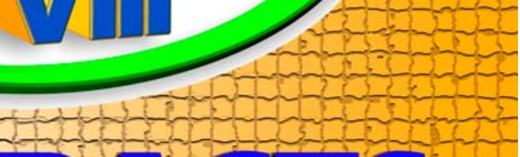
VIII

ABSTRACTS

Volume II



Novosibirsk
2009

Siberian Branch of Russian Academy of Sciences
Boreskov Institute of Catalysis

VIII International Conference

“Mechanisms of Catalytic Reactions”,

dedicated to the 70th anniversary of the birth
of Professor Kirill I. Zamaraev

June 29 - July 2, 2009
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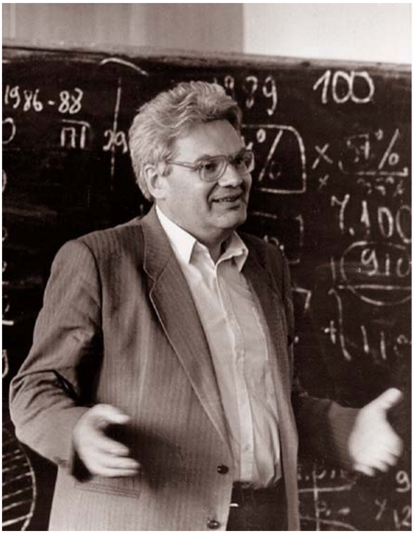
ABSTRACTS

Volume II

Novosibirsk-2009

Professor Kirill Ilyich ZAMARAEV

(1939-1996)



An extraordinary scientist, talented teacher and statesman, Professor Zamaraev was the Director of the Boreskov Institute of Catalysis (1984-1995), and the President of the International Union of Pure and Applied Chemistry (1994-1995).

Professor Kirill Ilyich Zamaraev was one of the pre-eminent physical chemists. His main field of interest was the application of new physicochemical techniques to the investigation of mechanisms of homogeneous and heterogeneous catalytic reactions. He was among the pioneers of NMR spectroscopic investigations of key catalytic intermediates and widely employed a range of physical methods such as solid state NMR, EXAFS and scanning tunneling microscopy.

Professor Zamaraev has made a considerable contribution to the establishment of relationships between fundamental and applied catalysis through his interest in the structure of active sites at the atomic and molecular level. He used his fundamental knowledge and capacity for innovative characterization for the search for new unconventional areas of catalysis.

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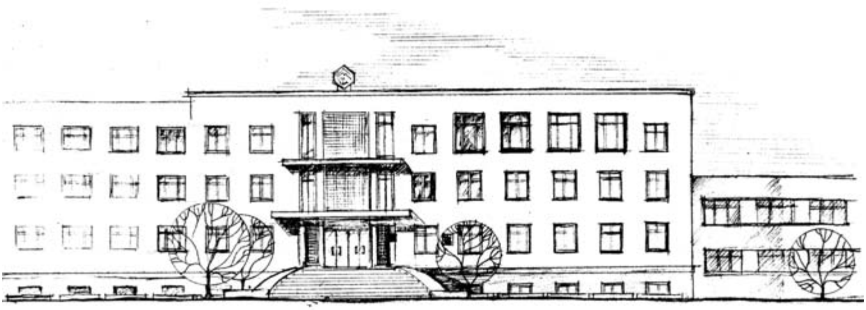

Study of Spectral and Catalytic Properties of Silver Dispensed on Oxide Supports

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Silver is widely used for partial oxidation of olefins [1] and represents promising catalyst for the low-temperature oxidation of CO, especially, in H_2 containing mixtures [2]. In spite of numerous investigations, the detail mechanism of substrate and oxygen activation on the supported Ag catalysts is still under debates. The main reason is the scarce knowledge on the surface characteristics of Ag species and multiformity of these species, whose variety proves in a strong dependence of the support, metal precursor, supporting conditions, etc.

In the present study, we prepared Ag catalysts with variation of (i) the nature and characteristics of the support, (ii) silver loading and type of the precursor, (iii) conditions of supporting and post-treatments. The samples were studied with chemisorption and UV-vis diffuse reflection (DR) spectroscopy, and tested in oxidation of CO and olefins (mainly with butadiene-1,3 as a substrate, that represents much less studied reaction in comparison with the ethylene epoxidation).

Catalytic properties are discussed in connection with spectral and adsorption characteristics of Ag samples. Properties of the samples have been shown to be strongly controlled by preparation technique. Proper adjustment of the whole of conditions (including red-ox treatments at high temperature) enables one to get especially dispersed Ag particles, to obtain samples with non-typical for metal particles DR spectra (band of plasmon resonance at ~14000 cm^{-1}), and to achieve high activity even for catalysts with low Ag loadings.

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PP-I-2

Synthesis and Characterization of Metal Containing Dendrimers and Their Catalytic Activities in Ethylene Polymerization

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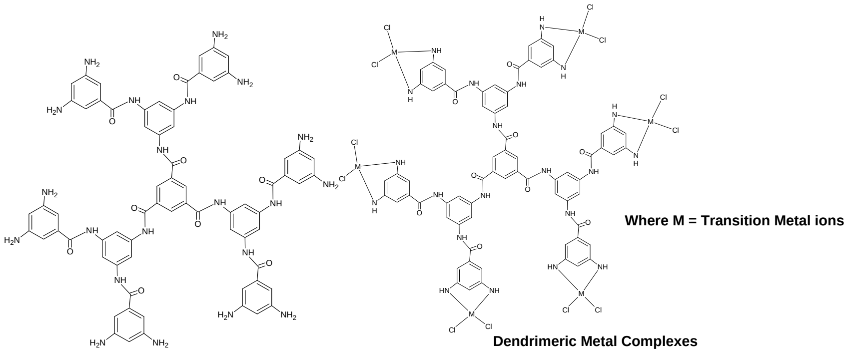
A novel, rapid, inexpensive, and highly efficient divergent approach for the synthesis of a 48-amine-terminated G3 polyamide dendrimers has been developed. Each generation dendrimers was successfully obtained by the condensation of the preceding generation dendrimers with the building block and the deprotection with hydrazine in one pot. All the dendrimers were easily purified by precipitation in alkaline water, and the purity was confirmed by NMR, MALDI-TOF mass spectra, and elemental analysis. The addition of MAO (methylaluminoxane) to these complexes generates catalytically active species for the homopolymerization of ethylene. The polymer products are high molecular weight (85–175 K). At temperatures of up to 60 °C both catalysts are a single site giving a mono-modal molecular weight distribution.



Catalytic Properties of Supported Transition Metals in the Reaction of Molecular Hydrogen Isotope Exchange

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The study concerns catalytic properties of supported transition metals in the reaction of molecular hydrogen isotope exchange: 2HD ↔ $H_2 + D_2$. This reaction is a model one and its investigation is of big interest not only for understanding catalytic processes with molecular hydrogen but also for its application in the industrial process of cryogenic distillation where it takes place between initial and final stages of deuterium concentrating.

The temperature and pressure dependencies of catalytic activity for a number of deposited transition metals (Ni, Pd, Ru, Rh, Pt) in the hydrogen isotope exchange reaction have been obtained. The influences of the following factors: metal nature, concentration of the metal deposited, type of the carrier, particle sizes of the active phase onto the catalytic activity have been revealed.

The quantitative model describing hydrogen isotope exchange reaction on the metal surface in a framework of transition state theory has been developed. The results of calculating catalytic activity according to the model are in reasonable agreement with experimental data.

Catalytic Dimethyl Ether Steam Reforming to Hydrogen Rich Gas

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Analysis of current literature shows that dimethyl ether (DME), which can be synthesized directly from synthesis gas, is expected to play an important role for the energy transportation. Therefore, hydrogen-rich gas produced by DME steam reforming (SR) seems to be attractive for fuel cells and other applications.

It is generally assumed that DME SR proceeds via consecutive two-step reaction mechanism. The first step is hydration of DME to methanol:
$(CH_3)_2O + H_2O = 2CH_3OH$
The second step is methanol SR to the hydrogen-rich gas:
$CH_3OH + H_2O = CO_2 + 3H_2$
Besides, during DME SR, the reverse water gas shift reaction may occur to produce carbon monoxide.

A design of active and selective catalysts for the DME SR requires knowledge on the properties of both Cu-containing catalysts for methanol SR and solid acids for the DME hydration to methanol.

The present work addresses the studies of DME SR to hydrogen rich gas on mechanically mixed catalysts. In particular, we demonstrate that:

- DME hydration to methanol catalyzed by numerous solid-acid catalysts and the catalysts’ activity strongly depend on the strength of the Brønsted acid sites;
- WO_3/ZrO_2 + $CuZnAlO_x$ to be an efficient for the DME SR. The catalyst provide almost 100 % conversion of DME to hydrogen-rich gas containing less than 1 vol.% of CO at 300 °C, GHSV = 10000 h^{-1}, and molar ratio $H_2O/DME = 3$.

PP-I-5

Ti-Doped Mesoporous Shell – Solid Core Silica Particles: Synthesis and Catalytic Properties in Selective Oxidation Reactions

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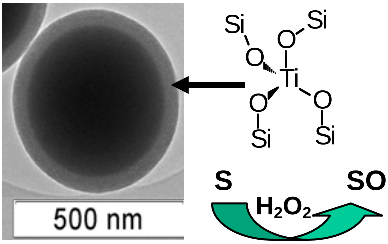
Hear we applied three nanotechnological approaches – on micro, nano and subnano levels – to synthesize for the first time near monodisperse spherical silica particles with a solid inert core covered by a well-organized titanium-silicate mesoporous shell, Ti-SCMS, as well as spherical submicron-size particles of Ti-MCM-41 and characterized the new materials by elemental analysis, N_2 adsorption, XRD, TEM, and DR-UV spectroscopy. The mesoporous Ti,Si-shell has a thickness of about 45 nm and incorporates isolated Ti centers predominately in tetrahedral coordination. Catalytic properties of Ti-SCMS and Ti-MCM-41 have been studied in selective oxidation of three representative bulky organic substrates, 2,3,6-trimethylphenol, methyl phenyl sulfide and caryophyllene, with aqueous H_2O_2 in MeCN medium. Ti-SCMS appeared to be more active and selective in the H_2O_2-based selective oxidation reactions compared to Ti-MCM-41, thus demonstrating an advantage of conducting a catalytic process in a thin mesoporous Ti,Si-shell.



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PP-I-6

The Investigation of Active Metal Species Forming in Pt(Pd)/SZ Isomerization Catalysts

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Sulfate promoted zirconia (SZ) is attractive isomerization catalyst due to its high activity at low temperature and its high selectivity to isomers. The addition of noble metals improves the activity and diminishes coking. In spite of large numbers of studies, the metal state as well as its function in alkane isomerization mechanism is still a matter of controversy.

In most cases the metal state was analyzed for finished catalyst prepared in specific conditions. In this paper the process of metal centers formation starting from the precursor supporting stage was investigated. It was shown by means of ESDR experiments how the platinum(IV) and palladium(II) chloride complex composition was changed as the interaction “precursor-support” was realized. Besides, the oxidation (drying and calcinations) and reduction stages at different temperatures were studied.

The investigation of surface metal complex reduction process was carried out by the means of TPR method. Some characteristics of Pt(Pd)/SO_4^{2-}-ZrO_2 catalysts (dispersity, electronic state of the Pt and Pd particles, and the sulfate decomposition products) were investigated by a complex of physicochemical methods such as pulse chemisorption, FTIRS, and XPS. The model reaction of benzene hydrogenation at low temperature (50-100 °C) was used as a test for metallic state.

It has been stated that the sulfate was decomposed and sulfur products poisoned the metal particles during catalysts reduction by hydrogen at T>300 °C. As a result, the hydrogenation capacity is highly inhibited and the same occurs with adsorption of H_2. According to XPS and FTIRS study the metallic particles in the poisoning samples were partly oxidized and covered by oxide and/or sulphide species.

Iron (III) – Catalyzed Ozonation of Glyoxal and Glyoxylic Acid in Aqueous Solution

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Catalytic ozonation is a promising alternative in water treatment for the removal of various organic pollutants. The use of homogeneous and heterogeneous catalysts based on transition metals contributes to increasing the efficiency and selectivity of the ozonation processes. One of the main problems is the degradation of short-chain carboxylic acids and aldehydes that are produced as refractory products during ozonation of phenols and other aromatic compounds.

In this work the iron(III) homogeneous catalyst has been used to improve the removal of glyoxal, glyoxylic, oxalic, and formic acids by ozonation. Ozonation was performed at room temperature in aqueous solutions acidified to pH 1.5 by adding H_2SO_4. A bubbling reactor was used. Ozone was obtained from air, $Fe_2(SO_4)_3 \bullet 9H_2O$ was used as a source of metallic ions.

It was found that iron in the form of Fe^{3+}-ions accelerate the oxidation of glyoxal, glyoxylic, and oxalic acids, but have no impact on the rate of the reaction of formic acid with ozone. It follows from the results obtained that catalyst is effective if the concentration of dissolved iron ions is comparable to that of the substrate to be oxidized. The largest catalytic effect was observed at the stoichiometric ratio (Fe^{3+}/substrate) $\geq 1/3$. Such a ratio obviously corresponds to the highest filling of the coordination sphere of the complex between metal ion and C_2-substrates which are bidentate ligands. The experimental evidence points to the fact that the addition of inactive towards ozone competing chelating ligands to a solution of glyoxal and glyoxylic acid undergoing ozonation suppresses the catalytic activity of iron ions.

The stoichiometric coefficients (ozone consumed/substrate oxidized) were determined. They are of about 1 for catalytic ozonation as well as for ozonation alone. It was showed that the decomposition of glyoxylic acid by ozone led to oxalic acid, no formic acid was detected in the products of catalytic ozonation.

The assumption was drawn from the results of this investigation that in acidic medium at $pH < 2$ catalytic ozonation of glyoxal, glyoxylic, and oxalic acids may proceed without change in the oxidation state of Fe^{3+} ions and without the participation of free radicals. As a role of metal we consider that it activates substrate through formation of iron-substrate complexes – chelates, in which substrate has lower red-ox potential and might be easier oxidized by molecular ozone.

On Mechanism of Asymmetric Induction in Reactions of Alkene Carbo- and Cycloalumination Catalysed with Chiral Zr π-Complexes

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The work is devoted to a mechanistic study on alkene enantioselective carbo- and cycloalumination by AlR_3 (R = Me, Et), catalyzed with chiral Zr π-complexes $L_1L_2ZrCl_2$ (L_1 = Cp, L_2 =Cp^* (1-neomenthylindenil-4,5,6,7-tetrahydroindenyl) [1] $L_1 = L_2 = Ind^*$ (1-neomenthylindenyl) [2]). It was shown that chemo- and enantioselectivity of the reactions significantly depends on sterical (symmetry group, size of substituted π-ligand) and electronic features of the catalysts, together with solvent and OAC type.

We carried out experimental (DNMR) and theoretical (DFT) investigation on the processes of R-Cl redistribution in systems $L_1L_2ZrCl_2$-AlR_3 (R = Me, Et) and the intermediate structures as well. It was established that conformational behavior of substituted π-ligands in the intermediate Zr,Al-complexes, which depends on the solvent and OACs type, controls the asymmetric induction in the processes of alkene carbo-and cycloalumination. Moreover, the encounter synthesis of the intermediates $CpCp^*ZrRCl$ in the reaction of $CpCp^*ZrCl_2$ with LiR (R = Et, ^{i}Bu) provided the first results on the synthesis of complexes with chiral center on Zr (diastereomeric ratio = 10:1 by NMR).

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PP-I-8

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Kinetics and Mechanism of Oxidative Dehydrogenation of Isobutyl Alcohol over Zeolite Catalyst CuPdNaY

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In the present paper, it has been investigated the kinetic laws of oxidative dehydrogenation(OD) of isobutyl alcohol for the determination of mechanism of this reaction over modified zeolite catalyst CuPdNaY, containing 2,0%Cu^{2+} and 0,1%Pd^{2+}.The modified catalyst was prepared by the method of ion exchange and heating at 600°C.

Kinetic experiments were carried out in a flow apparatus at atmospheric pressure, in temperature range 280-380°C, space velocity 1000-4000h^{-1} and partial pressures of reagents $P_{alcohol}$=0,11-0,37atm and P_{O2}=0,12-0,23atm, and with catalyst of 0,23-0,63 mm in size in the kinetic field.

Isobutyric aldehyde and small amount by products: carbon-dioxide (CO_2), methylacrolyn, and isobutylene were obtained by the reaction of OD of isobutyl alcohol. It has been established that the conversion of alcohol and the yield of CO_2 with increasing of $P_{alcohol}$ at P_{O2}=const. decrease, but with increasing of P_{O2} at $P_{alcohol}$=const it has been observed the increasing of this parameters.

Dependence of the yield of isobutyric aldehyde from $P_{alcohol}$ and P_{O2} has extreme character and the highest yield of isobutyric aldehyde, 66,8% was obtained at T=360°C, $P_{alcohol}$=0,28atm and P_{O2}=0,15atm.

The mechanism of reaction has been suggested and the kinetic model has been developed on the basis of experimental data. It has been determined kinetic parameters of the model. The relative errors of experimental and theoretical data are 5,0-7,0%.

PP-I-10

Structure of Active Component of Al-Mn Catalyst

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Calcination of $MnO_x/\gamma\text{-}Al_2O_3$ in air at 900-1000 °C causes a sharp increase of the activity in reaction of deep oxidation of hydrocarbons [1]. It has been found previously, [2] that catalyst is the system consisting of $\alpha\text{-}Al_2O_3$ and cubic spinel $Mn_{1.5}Al_{1.5}O_4$ at 950 °C. Under the cooling spinel decomposes to nanocrystalline particles of $\beta\text{-}Mn_3O_4$. In this work formation and transformations of $Mn_{1.5}Al_{1.5}O_4$ were investigated under different conditions.

Original sample (Mn:Al = 1) contains mixture of oxides. Formation of corundum $\alpha\text{-}Al_2O_3$, $\alpha\text{-}Mn_2O_3$, and manganese-alumina cubic spinel were observed, when sample was heated up to 950 °C in air. It was found that manganese-alumina cubic spinel $Mn_{1.5}Al_{1.5}O_4$ was formed under vacuum conditions at 1200 °C. The spinel kept cubic structure and composition during slow heating and cooling in vacuum. During slow heating in air up to 800 °C decomposition of spinel $Mn_{1.5}Al_{1.5}O_4$ and formation of nanocrystalline $Mn_{2.8}Al_{0.2}O_4$ tetragonal phase and cubic spinel $Mn_yAl_{2+x}O_4$ were observed, sample reduced its initial structure and composition at 950 °C. On the other hand, during slow cooling in air spinel $Mn_{1.5}Al_{1.5}O_4$ decomposed to nanocrystalline $Mn_{2.8}Al_{0.2}O_4$ phase and cubic spinel $Mn_yAl_{2+x}O_4$.

This work was supported by the integration project SB RAS №36 and the grant under the program "Development of scientific potential of the higher school" №2.1.1/729.

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PP-I-11

Oxidizing Ability of Catalysts for Clearing Exhaust Gases During Optimization of Structural Characteristics

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The aim of this work – catalytic activity study of Pd-Rh/Al_2O_3 catalysts processed at various temperature modes and revealing of a technological optimum of heat treatment. Experiments on the kinetics of methane oxidation were performed in the flow-circulation reactor with a parallel study of textural characteristics of the samples (specific surface, dispersion of active metals on the catalyst carrier, the porosity).

It has been established that oxidizing ability of the new catalyst towards methane varies in a wide range that is related to changes of its crystal structure, textural characteristics as a result of optimization of a thermal treatment mode. Optimization increases catalytic reactivity on the average by 30 %. Artificially aged samples showed a rather unusual picture when higher conversion ability is registered at samples passed rigid ageing – 1100 °C, in comparison with the samples aged at 900 °C.

Research of dynamics of temperature and concentration of methane in the reactor has allowed us to reveal naturally repeating process of «run» the catalytic activity of the sample at the phase transition and the formation of oxide structures in a certain temperature range.

The mechanisms influencing oxidizing activity of investigated samples are discussed.

PP-I-12

Study of Thermocatalytic Conversions of Cu-Modified Plant Polymers

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Main regularities of the thermocatalytic transformations of cellulose and lignin polymers modified by copper acetate as well as the structure and properties of the carbon materials produced were studied by methods of IRS, DTA, XRD, BET and the functional analysis. It was established that the interaction of $Cu(OAc)_2$ with the oxygen-containing groups of lignin and cellulose leads to the formation of copper carboxylates, phenolates, and other compounds as well as to changing the permolecular structure and plant polymer reaction ability at thermochemical transformations. The catalytic action of the copper becomes apparent in decreasing the temperature of polymer degradation process and in the variation of the chars structure obtained. The differences observed in the thermal conversions of Cu-modified and non-modified polymers are connected with the influence of copper on the composition of the polymer functional groups both at the preparation stage and during the process of thermal degradation.

The peculiarities of thermochemical transformations of modified polymers greatly depend on the concentration of Cu-catalyst and on the heating speed value. Active carbons (AC) obtained by the high-speed steam activation of the lignin with 2 wt.% of Cu differ from AC from non-modified lignin by the higher yield, microporosity, and by different permolecular structure (the more large interlayer distance, the smaller stack sizes and number of the layers, the lower degree of stack ordering).

Obtained results show that the use of copper implantation to plant polymers allows regulating the rate of depolymerization, gasification, and condensation which are responsible for the yield and structure of AC produced by thermocatalytic transformations of plant polymers.

Peculiarities of the Mechanism of Cross-Aldol Condensation of Acetaldehyde with Formaldehyde in the Presence of Amino Acids and Their Derivatives

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Recently views on the classical acid-base catalysis are undergoing significant changes. It is extremely important study on the development of new catalysts with specific features that allow to increase the yields of products and selectively of the reaction, compared to traditional systems. The most promising approach is the usage of bifunctional catalysts containing both base and acid groups, which may be regarded as a simplified model of enzymes [1]. Previously, we found that in liquid phase cross-aldol condensation of formaldehyde and acetaldehyde in the presence of amine salts it is possible to achieve a higher yields and selectivities compared to the reactions catalyzed by individual acids, bases, or pure amines [2].

In present work we investigated cross-aldol condensation of formaldehyde with acetaldehyde in the presence of amino acids and their derivatives. The following amino acids were used (linear and cyclic α- and ε-amino acids). The main product of the reaction is acrolein, a large number of by-products of acetaldehyde homocondensation – 2-butenal and higher polienals with linear and branched structures were also observed.

To establish the contribution to the catalytic process of each of the functional groups we performed the protection of carboxyl groups using esterification reaction to obtain ester derivatives, for the protection of amino group using N-benzoylation of aminoacids to obtain bensoil-substituted derivatives.

It was found that the most selective formation of acroleine was observed when using bensoil-substituted derivatives. Also, a solvent and temperature have significant impact on the selectivity of the reaction and the conversion of reagents. In the report we discuss comparison with acid- and base-catalysis and explain peculiarities of the mechanisms in the presence of bifunctional catalysts.

This work was supported by RFBR Grant (07-03-12238) and Grant of RF President (1809.2007.3).

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Mechanism of Competitive Codimerization of Activated Olefins with Norbornadiene

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Interaction norbornadiene (NBD) with activated olefins, containing electron withdrawing group in the presence of complexes of Ni(0) leads to products of [2 +2 +2]-codimerimerisation and cyclic homodimers of NBD [1, 2]. Previous reaction mechanism involves formation of two types of transient intermediates - gomoligand norbornadienes complexes of nickel and heteroligand complexes containing molecules NBD and olefins. Basic education and by-products according to the kinetic runs on parallel routes. In this paper, conducted a study on simultaneous codimerisation of NBD wi th different pairs of olefins. These data confirmed the hypothesis that a key set of codimerisation of NBD from olefins is monoolefin complex. Stereoselectivity in each group of products has remained unchanged as compared to individual reactions. At the same time scodimerisation branch of the mechanism responsible education heteroligand complexes nickel atom divides and gives rise to two parallel branches of education products codimerisation. The observed ratio of the reaction products, as well as the relevant speeds of education confirm this hypothesis. The data obtained are very interesting to compare the reactivity of olefins in the catalytic Diels-Alder reactions. We obtain a model to predict the product competitive codimerisation on the basis of constant velocity of individual stages in the individual reactions. In the report represented the mechanism of competition codimerisation of activated olefines with NBD show his difference from the normal reaction. This work was supported by RFBR (grants 08-03-00743) and grant the President of Russia MK-1809.2007.3.

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PP-I-15

High-Molecular Compounds in the Heavy Oil Cracking Process Catalyzed by Microspheres from Coal Ash

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The increasing part of heavy oil in the world's crude oil production has caused the need for research and development of new technologies in oil-refining industry [1]. High content of S,N-atoms and high-molecular compounds, such as resins and asphaltenes, is the main obstacle for usage of catalysts in heavy oil processing.

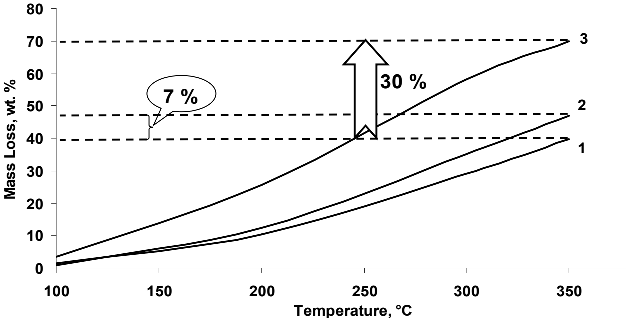

Figure 1. Curves of mass loss of initial heavy oil and oil after cracking at 450 °C. 1 – initial heavy oil; 2 – thermal cracking; 3 – cracking with 10 wt.% of microspheres.

In this study, microspheres from coal ash are used as catalyst of cracking. The major chemical substances in microspheres are Fe_2O_3 and FeO, as well as SiO_2 and Al_2O_3. It was shown that cracking of heavy oil with 10 wt.% of microspheres at 450 °C has higher yield of light fractions (IBP-350 °C) comparing with the yield of thermal cracking process (Figure 1) occurring with high molecular compounds during the process. In Table 1 basic structural parameters are presented. Average molecules of resins and asphaltenes in catalyzed cracking products have significantly lower weight, greater aromaticity (for asphaltenes), less aliphatic chains and structural blocks.

The influence of microspheres on the resins and asphaltenes contents and structural characteristic in feed and product oil have been investigated. The results of substantial composition analysis of feed and products of catalytic cracking at 450 °C have shown that the yield of hydrocarbons increases by 5 wt.%. The yield of asphaltenes in products decreased from 3.5 to 1.7 wt.% in catalytic cracking. The change in substantial composition is the result of greater destruction of resins and asphaltenes in conditions of catalytic cracking.

Structural analysis [2] of resin and asphaltene average molecules in feed and product oils were used for estimation of these compounds conversion. The analysis allows understanding the chemical transformations.

Table 1. Average structural parameters of resins and asphaltenes in feed and product oil.

Parameter	Resins		Asphaltenes	
	Feed	Product	Feed	Product
Molecular weight, a.m.u.	1290	500	2365	1020
Number of atoms: C total	96.7	33.5	172.1	73.5
C aliphatic	45.4	14.6	70.9	15.0
C α-position	13.6	3.9	20.8	8.4
C γ-position	4.4	3.6	11.9	2.9
H	123.3	50.1	241.2	78.7
N	0.8	0.5	2.0	0.7
S	0.1	0.04	0.2	0.1
O	3.7	2.4	1.4	2.9
Ring composition: K total	17.7	4.5	24.2	13.8
K aromatic	10.8	2.0	13.4	9.5
K naphthenic	6.9	2.5	10.8	4.3
Distribution of C, %: *f*-aromatic	25.5	25.6	33.0	55.8
f-naphthenic	27.5	30.7	25.8	23.8
f-aliphatic	47.0	43.7	41.2	20.5
Number of structural blocks (m_a)	2.2	1.3	3.9	2.7

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Mechanism of Phenol Oxidation over Pt-Nanoparticles Impregnated in Matrix of Hypercrosslinked Polystyrene

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Catalytic wet air oxidation (CWAO) is one of the significant methods for wastewater treatment containing high concentration of highly toxic compounds [1]. A great challenge for solving problem of phenol compound waste water treatment is to design a highly selective catalyst comprising of an active site with the correct ensemble of metal atoms and other active components [2]. The mechanisms of the fine chemistry reactions catalyzed by metals stabilized nanodispersions are in focus of modern research.

Polymer based Pt containing hypercrosslinked polystyrene was used for the investigation of the phenol catalytic wet air oxidation mechanisms. The kinetic peculiarities of the processes CWAO of phenol were studied, substrate ratio and activation energies were determined. The mathematical models of the reactions were developed and the hypotheses were put forward. The kinetics investigation and the data of physical and chemical analyses of catalytic systems show the possibility of the interaction of the catalyst active component with solvent, support, modifier, and substrate. According to investigation data the oxidation reactions run through a polyligand reaction complex. The substrate activation proceeds via the electron density transfer from the catalyst active component.

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PP-I-17

A New Method for Reclaiming Waste Rubbers and Tires with Nitrous Oxide

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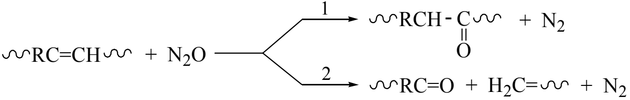
A new method for converting waste tire-rubber into useful polymeric materials has been developed [1, 2]. It was shown that the treatment of a waste rubber in organic solvent with nitrous oxide, N_2O, at 180-230 °C under 3-6 Mpa pressure results in the formation of plastic product. Under these conditions the so-called carboxidation reaction proceeds. This non-catalytic reaction includes two routes:



The major route (1) leads to selective conversion of C=C bonds in vulcanized rubber into C=O groups formed in the polymer backbone. The minor route (2) leads to cleavage of C=C bonds and fragmentation of a polymer chains and rubber vulcanization network. The N_2O reacts solely with the C=C bonds, being inert toward all other bonds (C-C, C-H, C=O, etc.). A fragmentation degree of the vulcanization network and, accordingly, resulting viscosity of reclaimed material depend on the type of parent vulcanized rubber and conversion of C=C bonds.

The method is applicable for reclaiming various vulcanized rubbers containing C=C bonds (polybutadiene, polyisoprene, natural rubber, etc.). It allows reclaiming tire crumb and large tire pieces, providing an easy separation of steel cord and textile fiber from the reclaimed rubber. The resulting plastic products can be revulcanized over the remaining C=C bonds. They could be used for replacement of virgin rubbers in compounded rubbers and potentially as additives to asphalt, bitumen, etc.

The work was supported by RFBR grant no. 08-03-12071-ofi.

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Preparation of Compounded Rubbers Using Waste Rubbers Reclaimed with N_2O

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Recently, a new method for reclaiming waste tire-rubbers has been developed at the Boreskov Institute of Catalysis [1, 2]. The method consists in the treatment of a waste rubber with nitrous oxide, N_2O, at 180-230 °C under 3-6 Mpa pressure (the so-called carboxidation). It results in the destruction of vulcanization network with formation of plastic polymeric products containing polar C=O groups.

The present work considers a possibility of using N_2O-reclamed rubber (N_2O-RR) for full replacement of virgin rubber in compounded rubber. For such replacement we used N_2O-RR sample and, for comparison, two commercial samples of reclaimed rubber produced by conventional thermo-mechanical method. N_2O-RR sample was prepared via carboxidation of tire crumb (150 g) with N_2O (2 mol) at 230 °C for 1 h. It contains 0.3 wt.% of oxygen in the form of C=O groups.

The results obtained show that full replacement of virgin rubber for N_2O-reclaimed rubber enhances the strength characteristics of vulcanizate as compared to commercial samples of reclaimed rubber. With N_2O-reclaimed rubber, the conditional rupture strength increases from 6.3-6.6 to 8 MPa, rupture tensile strain increases from 227-245 to 285%, hardness increases from 60 to 64 relative units, and simultaneously the rate of rubber ageing decreases. The study demonstrates that the products of waste rubber carboxidation can be revulcanized over the remaining C=C bonds and could be used repeatedly for preparing compounded rubbers.

The work was supported by RFBR grant no. 08-03-12071-ofi.

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[1] Dubkov, K.A. et al. Patent application RU 2007142266, 15.11.2007.
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PP-I-19

Features of the Mechanism of Reaction Cycloaddition of Activated Olefins to Norbornadiene

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Cycloaddition reactions involving norbornadiene (NBD) and activated olefins provide a variety of carbocyclic compounds [1, 2]. Problems of isomerism in the reactions involving NBD are of paramount importance. In the present work we investigated the cycloaddition reaction of a wide range of activated olefins to norbornadienu in the presence of bis(η^3-allyl)nickel. As dienofila were selected substrates representing different organic compounds: esters of acrylic acid (methyl-, ethyl-, n-butyl-, tert-butyl-, 2-methyladamantil-), acroleine, methylacroleine, methylvinylketone and acrilonitril, 2-metilakrilonitril, furanone. It was found that formed during the reaction [2 +2 +2]-cycle adducts of NBD and olefins and gomodimers of NBD. The ratio of dimers NBD is constant and does not depend on the olefins. Introduction to the reaction the phosphorous ligands allowed to rule out formation of dimers of NBD. The kinetic studies allow detecting the order of reactions of reagents and the role being dimerisation of NBD in the total education cycle adducts. We also conducted research on the competitive cycloaddition to NBD different pairs of olefins. The kinetics of the process was studied in detail. The combination of experimental data and dependencies offered consistent mechanism of cycloaddition of different substrates for NBD. The work is carried out a detailed comparison of the mechanisms cycloaddition of activated olefins with NBD and its catalytic gomodimerisation, discusses the common traits and characteristics of each of the mechanisms. Work is executed at financial support of the Russian Federal Property Fund (grant 08-03-00743) and the grant of the President of Russian Federation MK-1809.2007.3.

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PP-I-20

Catalytic Nanosystems for Hydro-Upgrading of Fuel Oil Fractions

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According to modern ideas, the highly dispersed MoS_2 particles with Co or Ni atoms localized on their lateral faces are an active phase of Co(Ni)-Mo-sulfide hydrofining catalysts [1]. At the same time, the active potential of applied catalytic systems is practically exhausted. New composites based on nanostructured carrier and Co(Ni)-Mo(W)-S active component may prove promising.

The purpose of the present wok is to study the nanosized electroexplosive and gas-phase aluminum oxides, the nanofiber sorbent based on aluminum oxides or hydroxides, and W, Mo, Ni, and Co nanopowders in pyrocarbon coating or without it.

The high capacity of catalytic systems for hydrodesulfurization and hydrogenation has been demonstrated in the process of hydro-upgrading of middle distillate oil fractions. A symbatic change in sulphur content and optical density values for hydrogenisates obtained at wavelength $\lambda = 348$ nm has been revealed, which permits to select the optimal composition of nanocatalysts via the method of mathematical modeling.

The study has been performed with financial support from the Presidium of SB RAS (grant No. 27-50).

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PP-I-21

Kinetics of the Reduction of Copper Cations from Mixed Oxide Catalysts

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Cu-containing catalysts are used in many industrial processes. The main stage of their activation is thermal treatment in hydrogen-contiaining gas stream. This treatment is accompanied by the reduction of Cu^{2+} to form Cu^0 particles. In literature, two mechanisms of copper reduction are proposed. The first is characteristic for many oxides, incl. individual oxides CuO and Cu_2O, and is accompanied by the elimination of O^{2-} to form H_2O. Another mechanism supposes oxidation of H_2 to $2H^+$, which are absorbed by the oxide structure and substitute for Cu^{2+}. The latter mechanism was earlier shown to realize for the reduction of $CuCr_2O_4$.

Here we present the kinetic study of the reduction in hydrogen of individual copper oxides CuO and Cu_2O, as well as a series of Cu-containing catalysts: copper hydrosilicate $(Cu,H)_2Si_2O_5(OH)_4 \cdot nH_2O$, solid solutions of Cu^{2+} in MgO and in ZnO, and copper chromite $CuCr_2O_4$. The state-of-the-art approaches are applied for determination of kinetic parameters from DSC/TGA kinetic curves.

Certain similarity is found between the kinetics of Cu^{2+} reduction from individual oxides, copper hydrosilicate and from Cu-Zn, Cu-Mg mixed oxide, if those were exposed to air before the measurements. Effective activation energy values are close to each other and vary in the range from 42 to 65 kJ/mol. Copper chromite reduction kinetic curves are very different and E_{act} is much higher: 90-120 kJ/mol.

Reduction of Cu-Zn mixed oxide, which was thermally treated in Ar at 350 °C just before the measurements in hydrogen flow, differs a lot from that of the sample exposed to air. E_{act} = 120-130 kJ/mol, which accords with the data of the physical methods and allows conclusion on absorption of hydrogen in the oxide structure during the reduction.

Reduction of Cu-Mg mixed oxide treated in Ar just before the measurements proceeds with unexpectedly low E_{act} of 19 kJ/mol.

PP-I-22

Development of Catalysts of Propene Epoxidation Process

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Propylenoxide (PO) is intermediate chemical product demand for which is constantly increased. It is used as a feedstock for production of a wide range of goods (polyurethane, propylene glycols, etc) applicable to manufacturing of industrial and consumer goods.

Now in Russia PO is obtained only by two ways: chlorohydrin method and oxidation by peroxide (Halcon process). The main disadvantages of PO production using these technologies are PO high price because of formation of diversified byproducts and difficulty of its separation and refining, and also usage of not ecologically friendly reagents. Therefore last years research is directed essentially at development of technology of PO production process with direct propene oxidation.

The aim of the present study is investigation of PO production process with direct propene oxidation by atmospheric oxygen; obtaining series of catalyst samples containing as an active components Au, Ag, Pd; as promoters – metals of I and II groups deposited on titanium oxide and synthetic titanosilicates.

Samples of obtained catalysts were studied by XRD, IR, EPR, and TPR analysis.

Gas-phase reaction was carried out in a steel tube fixed-bed reactor under variable conditions (temperature range from 70 to 130 °C and pressure interval from 1 to 3 bar).

Interesting results were obtained when optimizing pores structure; it was observed increasing activity and PO selectivity. A mechanism of the reaction was suggested.

Subsequent research will be directed at improvement of physical-mechanical and strength properties of catalysts and also at stabilization of the active phase on its surface.

PP-I-22

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Mechanistic Study on Zr Catalyzed Alkene Carboalumination by Trialkylalanes

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The reaction of alkene carboalumination by AlR_3 (R = Me, Et) catalyzed with L_2ZrCl_2 (L = Cp, CpMe, $CpMe_5$, Ind, Flu) has been studied. It was shown that the process chemoselectivity depends on the nature of organoaluminium compound, Zr π-ligand environment, type of solvent and reaction conditions (reagents ratio, temperature). It was shown that in the case of $AlMe_3$ hydro-, carboalumination products and alkene dimers are formed. The catalytic reaction of $AlEt_3$ with olefins yields aluminacyclopentanes together with hydro-, carboalumination products, and dimers. Application of $(CpMe_5)_2ZrCl_2$ as a catalyst in the reaction of alkenes with $AlMe_3$ in CH_2Cl_2 at 15-20 °C provides the best conditions for the carboalumination pathway. The carboalumination products – 1-dialkylalumina-2-alkylhexanes $R_2AlCH_2CH(R)Bu$ (R = Me, Et) were characterized by the means of NMR spectroscopy (^1H, ^{13}C, ^{27}Al) for the first time.

Investigation of L_2ZrCl_2 interaction with AlR_3 using dynamic NMR spectroscopy together with DFT calculations shows formation of Zr,Al- intermediates $[L_2ZrRCl \cdot AlR_3]$ (L = Cp, CpMe, $CpMe_5$; R = Me, Et), which carbometallate olefins. Further, we carried out theoretical modeling of the process of alkenes coordination on “neutral” complex $[L_2ZrRCl \cdot AlR_3]$ excluding the preliminary stage of complex dissociation to cation $[L_2ZrR^+]$. The probable reaction mechanism is proposed.

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PP-I-24

Peculiarities of H/D Exchange of Molecular Hydrogen with Brønsted Acid Sites of Zn- and Ga-Modified Zeolite BEA

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Kinetics of hydrogen H/D exchange between Brønsted acid sites of pure acid-form and Zn or Ga- modified zeolites beta (BEA) and deuterated hydrogen (D_2) has been studied by ^{1}H MAS NMR spectroscopy *in situ* within the temperature range of 340-550 K. Profound increase of the rate of the H/D exchange has been found for Zn and Ga–modified zeolites as compared to that for pure acid-form zeolites. For metal-modified zeolite samples different by metal loading, the rate constants are higher for the zeolite with higher metal loading. Meanwhile, the rate of exchange for Zn-modified zeolites is one order of magnitude higher compared to the rate for Ga-modified zeolites, provided that the exchange for most active Zn-modified zeolite occurs 3 order of magnitude faster as compared to pure acid-form zeolite BEA. Promoting effect of metal on the rate of H/D exchange was rationalized by preliminary dissociative adsorption of molecular hydrogen on metal oxide species or metal cations. Dissociatively adsorbed hydrogen is further involved in the exchange with the acid OH groups located in vicinity of metal species. The role of different metal species in the possible mechanisms of the exchange with involvement of zeolite Brønsted acid sites and metal species is discussed.

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Joint Butane and Hexane Aromatization on Pt/Al_2O_3 Catalysts

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Using of the system approach in the development of new naphtha reforming catalysts has allowed to find the possibility of joint C_3-C_4 and C_{6+} hydrocarbon aromatization with the increase of motor fuels high-octane component yield (Beforming process) [1-2].

The purpose of the presented work is studying of chemical composition of Pt/Al_2O_3 catalysts on kinetic parameters of the reaction of butane and hexane mixture joint aromatization.

Catalyst samples with different contents of platinum, different strength and amount of Lewis acid sites (L_z) were synthesized. The obtained experimental data, kinetic parameters of the reaction and IR-spectroscopy data have allowed defining the most optimum platinum contents, amount, L_z strength, as well as their L_z/Pt ratio.

A possible construction of catalyst active sites and a scheme of carrying out of the reaction of joint butane and hexane aromatization have been offered. According to this scheme C-H bond of butane activation is carried out on L_z-centers with formation of positively charged carbenium ion. Hexane activation is rather well carried out on Pt-centers with formation of negatively charged carbenium ion. Presence of carbenium ions with different charge in the immediate proximity leads to formation of united C_{10} intermediate complex. The following conversions of C_{10} intermediate complex cause obtaining of products with greater thermodynamic formation probability (toluene, xylene).

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PP-I-26

Physical and Chemical Characteristics of Ruthenium-Containing Catalysts for Clearing Exhaust Gases

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The aim of this work – production of a new catalytic system with ammonium chloride complexes of ruthenium for neutralization of car emission.

Ruthenium-containing catalysts were synthesized using autoclave thermolysis of ruthenium complex compounds. For functionality estimation, catalytic activity of samples was tested in the flow-circulating reactor with an estimation of conversion CH_4, CO, O_2, NO, textural characteristics (a specific surface, dispersion of metals on the catalyst carrier, linear dimensions of metals) at initial samples and subjected to artificial ageing. The effectiveness of the synthesized ruthenium catalysts was estimated in comparison with industrial Pd:Rh/Al_2O_3 samples. The results of tests on catalytic activity are shown in Table 1.

Table 1. Temperature of 80% conversion CO, NO and conversion (%) CH_4 in the flow-circulating reactor on Ru:Pd and Pd:Rh catalysts.

CO		NO		CH_4	
Ru:Pd	Pd:Rh	Ru:Pd	Pd:Rh	Ru:Pd	Pd:Rh
182	218	199	236	39.7	35.5

Thus, the Ru-containing sample realizes the oxidation-reduction properties at lower temperatures and is of lower cost.

Mechanisms of conversion of compared systems are considered.

SSITKA Study of Ethylene Epoxidation and Methanol Partial Oxidation on Nano-Dispersed Silver Catalysts

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SSITKA studies were carried out on nano-dispersed silver powders prepared via metal evaporation with powerful electron beam in various gas media [1]. It was found that, unlike methanol oxidation, catalytic properties of silver nano-powders in ethylene epoxidation are strongly influenced by the conditions of their preparation: samples evaporated in argon (Ag(Ar)) are much more selective than the others (Ag(N_2), Ag(He)). Increased selectivity of Ag(Ar) sample was proposed to be associated with oxide-like species observed on Ag particle surface [2].

It was shown that both methanol oxidation towards formaldehyde (250-400 °C) and ethylene epoxidation (200-350 °C) proceeds at comparable temperatures on nano-dispersed silver powders allowing us to suggest that similar (or the same) adsorbed oxygen species participate in both reactions.

Correlation between preparation conditions, concentrations of different oxygen species (including sub-surface one) and catalytic performance of nano-powders was revealed based on SSITKA study of the dynamics of labeled oxygen transfer to the reaction products. The schemes of the reaction mechanisms were proposed, and reaction rate coefficients of key steps were estimated.

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PP-I-28

Mechanism of Catalytic Dehydration of Methanol to Formaldehyde Initiated by Hydrogen Peroxide

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The initialization effect in the main process of obtaining formaldehyde using hydrogen peroxide in the direct dehydration of methanol to formaldehyde has been revealed.

A hypothesis of the reaction mechanism has been forwarded suggesting the conjugation of methanol dehydration with the activation of hydrogen peroxide accompanied by the formation of $HO_2^{\bullet}$ radicals.

The kinetic pattern of the conjugated dehydration of methanol has been studied. Based on this, a kinetic model of the reaction was suggested and kinetic parameters were calculated for two samples. It was shown that irrespective of increased activity, the sample modified with Zinc did not possess much working stability. It was discovered that when other substances like ethane and ethylene were used as initiators, the surface of the quartz catalyst was suddenly coked. On the SiO_2(K-1) sample, the temperature of the dehydration process at 45-50% formaldehyde formation in the presence of hydrogen peroxide (1% in the solution of the methanol feed) decreased by 50-60 °C and the reaction carried out at 820-830 °C.

The kinetic difference in the mechanisms under different temperature ranges is connected with the domination of the route leading to the formation of carbon monoxide and methane at lower temperatures and the increase in contribution of the main conversion to formaldehyde at moderate and high temperatures. The second difference in the mechanisms common to the three temperature ranges has to do basically with the formation of methane by different routes.

Introducing hydrogen peroxide into the system initiates the process by inductive interaction of the chain reaction of hydro peroxide disintegration by conjugates with the main reaction of formaldehyde formation. This type of conjugation is possible at moderate and high temperatures, since thermodynamic constraints do not allow the real disintegration of hydrogen peroxide into radicals at temperatures below

800 °C. The following reaction cycle of a conjugated initiated reaction is proposed:

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O$$
$$HO_2^{\bullet} + H_2 \rightarrow H_2O + OH^{\bullet}$$

$$H_2O_2 + H_2 \rightarrow 2H_2O$$

Generally two attacking particles take part in the reaction initialization migrating in homogenous-heterogeneous chain process between the catalyst surface and reaction volume – $OH^{\bullet}$ $HO_2^{\bullet}$. At the same time, ensuring chemical conjugation and self regeneration property of the contacting surface.

PP-I-29

The Role of Catalysis in Selectivity and Sensitivity of Metaloxide Semiconducting Gas Sensors

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The role of catalytic processes in the change of electric conductivity of semiconducting metal oxides under their exposure to various gas media (CO, CH_4, C_2H_5OH, CH_2O, O_3, NO_2) has been studied. The electric conductivity change was interpreted as a sensor response.

The experimental data that indicate the possibility to increase a threshold sensitivity of selective sensing layers by introducing active oxides and adjusting operating temperature were considered. The study was mainly focused on solving the problem of selective detection of separate gases in gas mixtures.

Selective determination of CO in the presence of CH_4 [1] and C_2H_5OH in the presence of hydrocarbons [2, 3] was reached by employing oxides with different activity in partial oxidation reactions. Distinctions in mechanism of O_3 and NO_2 detection in air by In_2O_3, In_2O_3–MoO_3, and In_2O_3–Fe_2O_3 film sensors were revealed [4, 5].

Mechanisms of selective detection of some gases were discussed, in particular, CO, NO_2 by NiO–SnO_2 film and ceramic sensors; C_2H_5OH by SnO_2–MoO_3 and SnO_2–Fe_2O_3 ceramic sensors, and by In_2O_3–Fe_2O_3 film sensors; NO_2 by In_2O_3–γ-Fe_2O_3 and In_2O_3–MoO_3 film sensors.

The above oxide systems have been prepared by inorganic sol-gel approach that provides obtaining the catalytically active nano-sized hetero-structures with electro-physical features required for gas sensors.

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The Influence of Structure and Surface State of CeO_2–ZrO_2–La_2O_3 Complex Oxide System on Its Catalytic Properties

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The influence of structural features of CeO_2–ZrO_2–La_2O_3 system and electronic state of metals (Ce, Zr, La, Pt, Ru) on catalytic activity of CeO_2–ZrO_2–La_2O_3/Pt(Ru) (1.5 wt.%) composites has been studied.

The catalytic activity of the composites in selective CH_4 oxidation to syngas, and their thermal stability have been estimated [1]. The effect of La_2O_3 concentration (CeO_2:ZrO_2 = 1:1) on the properties and structure of the material has been studied. It was shown that the mechanism of La_2O_3 influence differs at its low (1-10%) and high (30%) content. The first mechanism is connected with the change of oxygen vacancy concentration and activation of Zr^{IV} due to the formation of $La_2Zr_2O_7$ phase. Another one arises from the isolation of La_2O_3 oxide and blocking the Ce(Zr)O_2 active surface.

The CeO_2–ZrO_2–La_2O_3 composites were obtained by sol-gel approach employing inorganic metal precursors [2]. The samples were found to be structurized and inhomogeneous at nano-scale level. In particular, phases based on Ce–Zr–O and La–Zr–O were distinguished. Annealing the composite results in complex interaction of $La_2Zr_2O_7$ and $Zr_{0.4}Ce_{0.6}O_2$ phases with the deposited Pt^{IV} and Ru^{IV} metals. The indicated interaction leads to the change of electronic state of all the metals, thus determining catalytic properties of the CeO_2–ZrO_2–La_2O_3/Pt and CeO_2–ZrO_2–La_2O_3/Ru composites.

The work has been supported by the ISTC (Project No 3234).

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PP-I-31

Selective Hydrogenation of Crotonaldehyde over Ir/Ga_2O_3 Catalysts in a Liquid Phase

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α,β-Unsaturated alcohols are very important group of compounds, widely used in a chemical industry. Desired products of hydrogenation – unsaturated alcohols found an application as semi products in synthesis of drugs, fragrance agents and other „fine chemicals" [1, 2].

In our previous studies we proved the high catalytic efficiency of galia supported noble metal catalysts, first of all Pt/Ga_2O_3 and Ir/Ga_2O_3 in the reaction of hydrogenation of crotonaldehyde in a gas phase [3, 4].

In this work, catalytic hydrogenation of crotonaldehyde over iridium supported on α-Ga_2O_3 and β-Ga_2O_3 in a liquid phase, has been studied. Effect of iridium loading (5, 2, 1 wt.%) has been examined. The reaction was carried out in the static reactor, reaction products were analyzed by gas chromatography. Catalysts were characterized by BET, TPR, XRD, and SEM methods. The highest selectivity to crotolalcohol (89% and 88%) showed 5% Ir/α-Ga_2O_3 and 5% Ir/β-Ga_2O_3 catalysts respectively.

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The Modification of Rhodium Catalysts by Tin in Dehydrogenation of Light Alkane Mixture in Reducing Environment

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The dehydrogenation of light alkane mixture was carried out in flowing mode at constant control of contact gas composition. The process was conducted in following modes: a) in the absence of hydrogen; b) in the presence of hydrogen; c) in the presence of water's vapour; d) in the presence of both hydrogen and water's vapour. At first two cases the process goes in balance conditions. Inserting water's vapour in systems leads to unbalance conditions at the expense of combining homogeneously adsorbed dissipative structures.

The modification of base Rh/Kl (natural klinoptilolit) catalyst with compounds of tin and potassium leads to increasing of its catalytic activity during the dehydrogenation of light alkanes and to rising of its selection by propylene. The maximum output of olefins is achieved in the presence of water's vapour, and its quantity on $Rh/SnO/K_2O/HKl$, where content of olefins is 30-32%, is much higher than its content on Rh/SnO/HKl or on base Rh/HKl.

Beside active metal in content of catalyst there are natural zeolits, which proceed reaction of acid-base type. The active centres by their power and quantity are decisive for these processes. The power and quantity of active centres on $Rh/SnO/K_2O/NCl$ were determined by method of ammonium' thermo-programmed desorption (TPD). So, the quantity of middle powerful centres on $Rh/SnO/K_2O/HKl$ is falling 3-4 times comparing with Rh/HKl, and concentration of powerful centres almost fall twice, whereas at these conditions the quantity of faint centres on $Rh/SnO/K_2O/HKl$ are increasing.

It's evident that the number of active centres is decreasing because of covered metal. This process is getting intensive when it's carried out at unbalance conditions. Finally it was found that dehydrogenation is increasing as tin's content increases as well.

PP-I-33

Methanol Conversion to Hydrocarbons

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Today commercial interest in conversion of methanol-to-olefins (MTO) is again increasing. There are already some commercial technologies for the production of hydrocarbons from methanol [1].

The conversion of methanol over ZSM-5 catalysts proceeds via the sequence of steps: methanol → DME → olefins → aromatics and paraffins. According to mechanism of methanol-to-hydrocarbons (MTH) process, gaseous olefins are primary products which quickly turn to other hydrocarbons. One of the ways to brake secondary transformations of light olefins is the decrease of Lewis acid site concentration. As the silica modulus increase, the strength of acid sites decreases because of a decrease in the content of Al^{3+} in the zeolite framework. Thus high SiO_2/Al_2O_3 ratios (low concentration of strong acid sites) have resulted in raising light alkene selectivity.

High-silica ZSM-5-type zeolites with SiO_2/Al_2O_3 = 60-500 were synthesized using hexamethylenediamine as a template. The concentration of acid centers was studied by the temperature programmed desorption of ammonia (TPDA). Total acidity was found to decrease from 481 to 203 μmol/g for the samples with SiO_2/Al_2O_3 ratio 60 and 500 respectively. Catalytic properties of the zeolites were studied in MTO process (T = 390 °C, ambient pressure). The samples show high catalytic activity and stability in MTO process. Low concentration of Lewis acid sites allows the highly selective production of light olefins from methanol (the increase of the SiO_2/Al_2O_3 ratio from 60 to 500 gives rise selectivity light olefins from 3.78 to 29.78%, respectively). Superhigh-silica ZSM-5-type zeolites show prolonged lifetime in MTO process (unto 1000 h).

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Selective Transformations of Ethane over VMoNbO Catalysts. Structure of the Active Phase

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Nonstoichiometric molybdenum oxides with tunnel structure substituted by Group IV and V metals has become the great deal of scientific attention in the last time due to their catalytic activity in the selective oxidation of alkanes C_2-C_3. For instance, triple V-Mo-Nb oxide, which in crystalline state has the Mo_5O_{14}-like structure, acts as an active phase in ethane selective (amm)oxidation [1-3].

In the scope of present work, we have performed a systematical study of VMoNbO catalysts including synthesis of VMoNbO compounds with different V/Nb ratio in the Mo_5O_{14}-like structure.

The catalysts were synthesized according to procedure described in [2] with thermal treatment in air at 400-650 °C. The complex of physical and chemical methods (EXAFS, HREM, XRD, and Differential Dissolution) was applied for structure characterization of catalysts.

According to obtained data, in triple $(Mo, Nb, V)_5O_{14}$ oxides V/Nb ratio varies in the range 0-1. Catalytic tests of studied samples in oxidative transformations of ethane (ammoxidation to acetonitril, dehydrogenation to ethylene and oxidation to acetic acid) revealed the most effective compositions $V_{0.3\text{-}0.43}Mo_1Nb_{0.24\text{-}0.4}$, calcinated in air at 400 °C with utmost V/Nb ratio ≈ 1.

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PP-I-35

The Role of Platinum Ionic Forms in Catalysis of Low-Temperature n-Hexane Isomerisation

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The influence of the platinum charge in Pt-X/Al_2O_3 (X = Cl, Br, F) and Pt/SO_4/ZrO_2 catalysts on activity and selectivity of n-hexane isomerisation was studied. It is shown that temperature areas of these classes of catalysts (high-, middle-, and low-temperature isomerisation) correlates with the platinum charge. This correlation is defined by the presence of electron-deficient platinum in catalysts and its ability to accumulate adsorbed hydrogen in raised quantities. The quantity of adsorbed hydrogen is in a range from 2.5 to 3.0 H/Pt_S on most active catalysts. By DRIFTS and H-D change methods it is shown that adsorption of hydrogen on ionic platinum proceeds with formation of hydride ions at temperatures about 150 ÷ 200 °C (Figure 1).

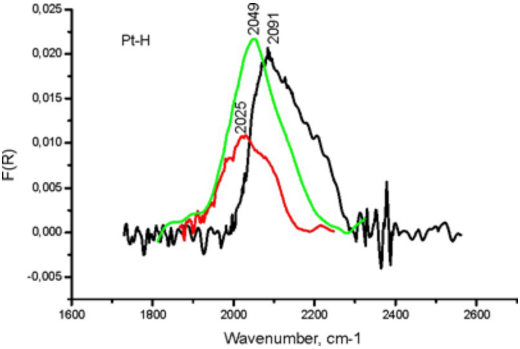

Figure 1. IR spectra of platinum hydrides for Pt-Cl/Al_2O_3, Pt/SO_4/ZrO_2, and mixture of Pt/Al_2O_3 with SO_4/ZrO_2 catalysts.

It is assumed that a role of platinum state in Pt/SO_4/ZrO_2 catalysts of C_5-C_6 alkane isomerisation can be explained by participation of ionic platinum in dissociative adsorption of hydrogen and following interaction of hydride ion with intermediates (isomeric carbocations forming on Lewis acid sites). It promotes increase of total velocity of isomerisation reaction, raises the selectivity and the yield of isomerisation products and reduces catalyst deactivation processes.

The Mechanism of the Reaction of Ozone with Lignin and its Model Compounds Catalyzed by Mn^{II} Ions

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A usage of catalytic processes for the treatment of renewable sources of raw materials is absolutely meet the requirements of sustainable green chemistry. There is a lack of data about the catalytic reaction of ozone with cellulose, which is the main component of biomass. In the reaction of ozone with different organic substances one can use transition metal ions and their complexes with organic and inorganic ligands as homogeneous catalysts as well as metal oxides and metals applied on solid support as heterogeneous catalyst.

Kinetics and mechanism of oxidation of lignin and its model compounds by ozone in the presence of Mn^{II} ions are investigated. Lignin is a polyfunctional polymer composed of phenyl propane units (PPU). Guayacol and veratrol are used as lignin model compounds. Maleic and oxalic acids are investigated as products of the destruction of aromatic ring of lignin model compounds.

It is found that the rate of the reaction of lignin with ozone rises at the initial stages in the presence of Mn^{II} ions. A hypothetical scheme of catalytic conversion of phenol fragments of lignin under the action of ozone and Mn^{II} ions is proposed on the basis of the experimental and literature data. In accordance with the scheme at the first stages Mn^{II} is oxidized by ozone up to Mn^{III}, which is stabilized by products of lignin oxidation by ozone forming chelate complexes. The Mn^{III} complexes act as a low weight mediator that attack phenol structures of lignin forming unstable phenoxy radical. Moreover, catalytic action of Mn^{II} ions is stated for the oxidation of the intermediate products of ozonation of lignin such as saturated carboxylic acids, ketones, and aldehydes which are stable to ozone as itself. Therefore, catalytic ozonation of oxalic acid is interrogated. Chelate complexes of Mn^{III} are found to play the main role, due to intramolecular electron transfer they can decay to CO_2 and radical.

The efficacy of usage of oxidation system Mn^{II}/O_3 to destruct lignin and its oxidation products is shown. Obtained data may be useful for creation environmental friendly technologies for obtaining pulp and paper and waste water treatment.

PP-I-37

Gas Sorption and Electrocatalysis on Polymer Sorbents

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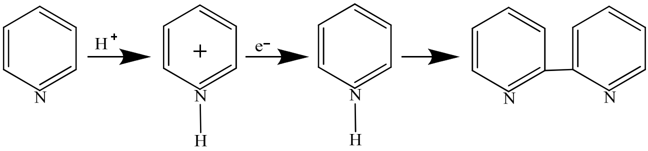
Solid polymer electrolytes – organized layers of organic molecules with the given thickness and structure. Distinction of these materials from their inorganic analogs is structural heterogeneity. It is in dipole-dipole interaction of functioning groups and formation of separate clusters containing sorbent water. There is substance chemisorption with CPCH (complex from charge transfer) formation, the base of catalysis process of gas absorption on polymer sorbent.

The experiment was conducted on the chromotograph «Crystal-2000M» with flame ionized detector, sorbent capillary column – 10% nitrilothreenitrilpropan, fr. 0.14-0.25 mm. Temperature changes from 90 to 190 °C. Ion diffusion and migration coefficients, ion mobility, ion conductivity by gas sorption (piridin, toluol), energy activation and migration were calculated as a result of researches.

Superficial group CN and molecules of solvents are adsorption centers. The calculation of physic-chemical sorption characteristics depends on the volume of gas sorption. With V = 1 ml and V = 0.5 ml of examined gas so-colled «matrix effect» is formed. With V = 2 ml, two-measured condensation π,π complex proton active complex is formed. Energy of migrations of proton complex is negative. This fact is explained by formation of hydrogen bonds. The length bond is 0.06 nm. The length bond between protons and two-measured gas molecule is 0.33÷0.46 nm in dependence on temperature of polymer sorbent. The partial charge on proton is 0.04÷0.08 depending on sorbent temperature.

Catalysis mechanism by two measured condensation pyridine can be presented by scheme:



Protonisation stage is limited stage. Speed process as determined from the equation (2):

$$j = k \cdot c_{H^+} \cdot exp(-\frac{\alpha FE}{RT}) \tag{2}$$

where j – speed process expressed in electrounits (A); α – transfer coefficient; R – gas constant; F – faraday's number; k – speed constant of straight process (protonizig); T – temperature; E – boundary potential (absorbed phase); C_{H^+} – ion concentration. Magnetic band χ depends on temperature of polymer sorbent, χ (T_c 120 °C, δ ~ 0.07; pyridine) ~ $-1.04 \cdot 10^{-15}$; χ (T_c 90 °C, δ ~ 0.06; toluene) ~ $-1.96 \cdot 10^{-15}$.

PP-I-38

The Activity of $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ Catalysts in Hydrodesulfurization of Alkyldibenzothiophenes: The Solvent Influence

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The main problem arising during the ultra low sulfur diesel production is the removing of refractory S-containing molecules: alkyl substituted dibenzothiophenes (DBT). They can react via direct desulfurization (DDS) or trough hydrogenation (HYD) followed by desulfurization. To get information about the reaction pathway in the presence of different catalysts and to elucidate the influence of the N-containing molecules and aromatics, the model mixtures are commonly applied.

The aim of the present work is to study the influence of the solvent on the activity of $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts in the HDS of the DBT, 4-MDBT and 4,6-DMDBT. To provide this study, the hexadecane and desulfurized gas oil (DSGO) were used as solvents.

The catalysts were prepared by impregnation of alumina with a solution containing bimetallic Co(Ni)Mo complexes followed by sulfidation with H_2S/H_2 mixture. Reactions were carried out in the batch reactor at 340 °C and 3.5 MPa H_2. HDS kinetic constants were calculated assuming pseudo-first order kinetics referred to DBT's concentration.

It was stated, that the both catalysts provide a lower activity, when the DSGO was used as a solvent instead of hexadecane. The inhibition can be explained by the presence of aromatics in DSGO. $NiMo/Al_2O_3$ catalyst revealed higher activity when the hexadecane was used as a solvent, while the activity of $CoMo/Al_2O_3$ catalysts was higher in the case of DSGO. Therefore, we concluded that $NiMo/Al_2O_3$ catalyst is subjected the greater inhibition of aromatics than $CoMo/Al_2O_3$.

Thus, the solvent used affects strongly the activity of the catalysts in the HDS of the DBT's. This aspect should be taken into account when the activity of different catalysts or the influence of inhibitors on the reaction pathways is studied using the model mixtures.

Cracking of Paraffin for Synthesis the Long Chain α-Olefins and New Catalysts on the Basis of System Hetero-Poly-Acid-Zeolite

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Hetero-poly-acids (HPA) have the stronger acid centres, than many zeolites. Series of catalysts on the basis of HPA W_{12} and Mo_{12} rows obtained on the basis of phosphoric acid and the modified natural zeolite consisting generally of clinoptylolite have been prepared. Cracking has been made in flow system at atmospheric pressure and an interval of temperatures from 400 to 500 °C in a mode reaction – regeneration.

On catalysts PW_{12}-HPA/NCl and PMo_{12}-HPA/NCl the hyperactivity is observed at cracking of paraffin in comparison with pure modified zeolite NCl. The yield of olefins in one pass reaches 46%, that is close to the theory. After regeneration catalysts restore initial activity.

With application of method of IRS and use of low-temperature adsorption of CO it is shown that after modifying by acid of natural zeolite of type NCl by HPA, there are formed the centres on a zeolite surface, which are several times stronger, than the acid centres on NCl or the usual proton centres. By methods of electronic microscopy (PEM) of the high permission and x-ray PES it is identified, that such centres are nano-parts of HPA with the sizes 1-2 nanometres, which are distributed in regular intervals and hardly bonded with a surface of clynoptilolite. Uniform distribution of HPA and its interaction in a zeolite surface leads to growth of a surface of catalysts to 247 m^2/g whereas surface NCl does not exceed 22 m^2/g. Obviously, the result of interaction is more active acid centres, which show hyperactivity at cracking of paraffin.

At thermal cracking of paraffin in the flowing environment at atmospheric pressure and temperatures 550-650 °C there have been found new radical forming additives (water, alcohols), which considerably raise the yield of exit long chain α-olefins.

PP-I-40

Creation of Selective Catalysts for Benzene's Hydrogenation in Presence of Other Aromatic Compounds

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It's necessary to create new effective catalysts for benzene hydrogenation in order to settle this actual world problem. The Rhodium is the most active metal of Platinum group for benzene hydrogenation. We are proposing series of catalysts on different layers with rhodium on their surface: sibunit, birchen activated coal (BAC), pit activated coal (PAC), and traditional layers SiO_2, γ-Al_2O_3&MgO. Content of rhodium is 1-3%, ready catalysts were modified by ammonium molybdate.

Maximal activity is observed on rhodium laid on BAC. Furthermore, the rate of reaction is twice higher, than on other layers. By rate of hydrogenation layers are settled in next order: BAC(400) > SiO_2(150) > sibunit(100) = PAC(100) > γ-Al_2O_3(18) > MgO(3). The hydrogenation is proceeding at ambient temperature and hydrogen pressure of 40 atm, after the reaction the benzene is not detected in products. Initial concentration of benzene was 2-3% in solution. The highest rate is recorded in water, then in alcohol and hydrocarbons. Obviously, the growth of medium's polarity stimulates active participating in process of different forms as rhodium as other elements, which are taking active part in processes of adsorption and catalysis.

As it can be seen by X-ray PES information, there are more charged forms of rhodium on sibunit, than on BAC. The connection's energy of Rh^{+3} charged forms is 311.2 eV, for Rh^0 is 307 eV. Based on this, we can suppose that the charged forms of rhodium are between Rh^0 and Rh^{+3}. BAC has more ionized Rhodium and sibunit has more metallic Rhodium.

The modification of prepared catalysts by ammonium molybdate permits selective hydrogenation of benzene on PAC in the presence of other aromatic compounds, such as toluene, xylene, and kumene. The rate of benzene hydrogenation is noticeably higher, than the rate of other aromatic compound hydrogenation.

The Investigation of Direct Methane Conversion over Mo- and W/HZSM-5 Zeolite

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Catalytic methane conversion (CMC) into a valuable petrochemical raw material is of considerable interest as an interesting method for natural gas use.

The studied catalysts were prepared by mechanical mixing of HZSM-5 zeolite with silica modulus SiO_2/Al_2O_3 of 40 and nanosized Mo and W powders produced by wire electroexplosion in argon medium. It is known that the reaction involves two main stages: methane activation and cyclization [1]. The final products of CMC are benzene, naphthalene, and toluene. The highest value of methane conversion of 11.5% is achieved on 4.0% Mo/HZSM-5 catalyst after 20 min of reaction (Figure 1). After that, it was observed slow decrease of methane conversion. It has been shown that the zeolites containing Mo and W nanopowders simultaneously exhibit a higher activity and stability in methane conversion as compared with the catalysts modified one of the metals. The Mo-W/HZSM-5 zeolite has an activity of 6.5% after 420 min of CMC.

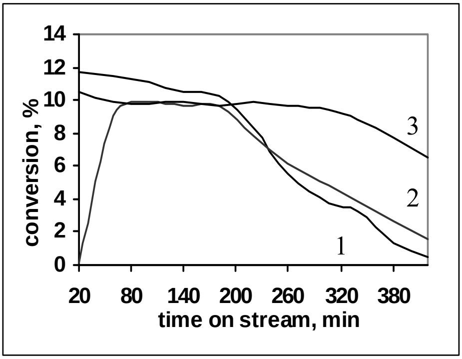

Figure 1. The dependence of methane conversion over ZSM-5 modified 4,0 % Mo (1), 8,0 % W (2) and 2,0 % Mo-4,0 % W (3) on time of reaction.

References:

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PP-I-42

The Active Species of Polymerization Catalysts Based on Titanium and Zirconium bis(Phenoxyimine) Complexes

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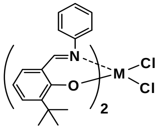
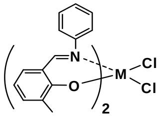
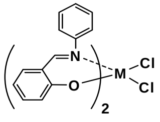
The intermediates of highly active homogeneous catalysts for olefin polymerization formed upon activation of titanium and zirconium bis(phenoxyimine) complexes with methylaluminoxane (MAO) have been studied by ^{1}H NMR and ^{13} C NMR spectroscopy. The catalysts based on $(L^R)_2MCl_2$, where M = Ti or Zr, L = N-(3-R-salicylidene)aniline (R = H, Me and ^{t}Bu), were investigated.



M-^{t}Bu



M-Me



M-H

The activation of complex **Ti-^{t}Bu** with MAO results in the formation of the outer-sphere ion pair $[(L^{tBu})_2TiMe(S)]^+[Me\text{-}MAO]^-$ (S = solvent), which is the highly active ethylene polymerization catalyst (55 kg PE/mol Ti bar min, polymerization at 40 °C for 10 min, MAO/Ti = 1000). For zirconium based analog, activation of **Zr-^{t}Bu** with MAO results in the formation of the ion pair $[(L^{tBu})_2Zr(\mu\text{-}Me)_2AlMe_2]^+[Me\text{-}MAO]^-$. The latter system is even more active towards polymerization of ethylene (250 kg PE/mol Zr bar min). Thus, both $[(L^{t\text{-}Bu})_2TiMe(S)]^+[Me\text{-}MAO]^-$ and $[(L^{t\text{-}Bu})_2Zr(\mu\text{-}Me)_2AlMe_2]^+$ $[Me\text{-}MAO]^-$ can be precursors of the polymerization active species. The lower polymerization activity of titanium and zirconium phenoxy-imine catalysts with the smaller substituent R is caused by the formation of the intermediates $[(L^R)_2\mathbf{M}(\mu\text{-}Me)_2AlMe_2]^+[Me\text{-}MAO]^-$ or $[(L^R)_2\mathbf{M}Me^{+\cdots}Me\text{-}MAO^-]$ which are less active than the corresponding intermediates in the catalytic systems containing bulkier substituent R.

In agreement with this conclusion, the activation of **Ti-H** with MAO leads to formation of the heterobinuclear ion pair

$[(L^{H})_2Ti(\mu\text{-}Me)_2AlMe_2]^{+}[Me\text{-}MAO]^{-}$, which is inert towards ethylene polymerization. The interaction of **Ti-Me** with MAO results in the complicated mixture of the ion pairs of the type $[(L^{Me})_2Ti(\mu\text{-}Me)_2AlMe_2]^{+}[Me\text{-}MAO]^{-}$ and $[(L^{Me})_2TiMe^{+\cdots}Me\text{-}MAO^{-}]$, showing low activity at ethylene polymerization (5 kg PE/mol Ti bar min). The activation of **Zr-Me** with MAO leads to tight ion pairs $[(L^{Me})_2\mathbf{Zr}Me^{+\cdots}Me\text{-}MAO^{-}]$, which are less active than the outer sphere ion pairs $[(L^{tBu})_2Zr(\mu\text{-}Me)_2AlMe_2]^{+}[Me\text{-}MAO]^{-}$.

PP-I-43

Microwave-Assisted Click Chemistry: Synthesis of mono- and bis-1,2,3-Triazoles Acyclonucleoside Analogues of ACV via a Copper(I)-Catalyzed Cycloaddition

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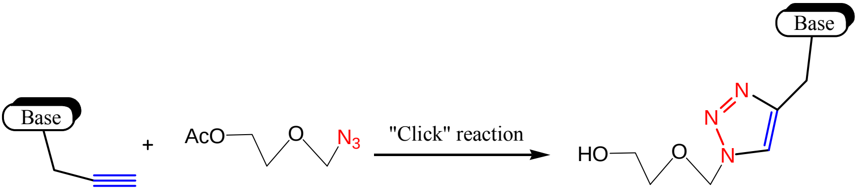
Triazole heterocycles are found to be potent antimicrobial, antiviral, and anti-proliferative agents. The pharmaceutical importance of triazoles has prompted the design and synthesis of various triazolonucleosides. Ribavirin was the first synthetic triazole nucleoside analogue found to show anti- viral activity against many viruses, is the only small-molecular-weight drug available so far for treating viral infections caused by hepatitis C virus (HCV). In addition, recent studies have disclosed a series of 1,2,3-bistriazoles as potent HIV-1 protease inhibitors for the inhibition of viral replication.

Since the discovery of acyclovir [9-(2-hydroxy-ethoxy)methyl)guanine (Zovirax)] as the highly selective antiviral drug for the treatment of herpes simplex (HSV) virus infections and Varicella-Zosterl, several acyclonucleosides was synthesized and tested. In view of the biological importance of 1,2,3-triazoles and Acyclovir, it was of considerable interest to develop novel compounds incorporating both the ring system. In connection to our previous studies on the synthesis of acyclonucleosides, we report here a regioselective synthesis of 1,2,3-triazoles and bis-1,2,3-triazoles acyclonucleosides analogues of ACV in which the heterocyclic base is linked to a pseudo-sugar via a methylene-1,2,3-triazole group.

In summary, we report a short and efficient synthesis of 1,2,3-triazole and bis-1,2,3-triazoles acyclonucleoside analogues of ACV using the Cu(I)-catalyzed alkyne-azide cycloaddition reaction under microwave irradiation. These products are under investigation for their biological activities.



PP-I-44

Mechanism Features of Dimethyl Ether Conversion to Light Olefins

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The development problem of light olefin obtaining methods from the natural gas via syn-gas and factory building for this aim in Russia, which has one third of world gas resources, is important today. The process of syn-gas to light olefin conversion is usually realized via methanol on microporous zeolites SAPO-34 type and permits to produce ethene and propene with yield about 75-80%. However, this process accompanies with high quantity of heat. In the IPS RAS developed method of $C_2^{=}$-$C_3^{=}$ olefin obtaining from dimethyl ether (DME), which is an intermediate in methanol to olefins (MTO) process on zeolite catalysts. This method has a number of advantages as compared with MTO method. More favorable thermodynamics allows carrying out DME synthesis under lower pressure, than methanol synthesis and reaching higher syn-gas conversion per pass. It results in reducing of energy and capital costs. An advantage of this method is reducing of heat effect on DME to olefins (DTO) stage. To control DTO selectivity, it is necessary to know the reaction mechanism. However, the DTO mechanism on zeolite catalysts is not adequately explored. DTO occurs with participation surface-bonded methoxy group by carbon-ionic or methane-formaldehyde mechanism which have close values of activation energy. In investigation of methanol and DME adsorption on HZSM-5 by IR-spectroscopy [1] their adsorption results in surface methoxylation at 250 °C were shown. The most of scientists suggest that ethene formation from DME proceeds via methylethyl ether or via ethanol.

Negligible amounts of light olefins and ethanol were found in DME and methanol conversion products at 220-240 °C. Methylethyl ether was not found. Ethanol can form in the reaction conditions by isomerization of DME or homologation of methanol. It was experimentally shown, that the rate of methanol to ethanol homologation is slower than DME to ethanol isomerization in the reaction conditions.

To increase light olefin selectivity the zeolite catalyst contained La and Zr and modified by transition metals of VIII group was developed. Such catalyst permits to produce $C_2^=$-$C_4^=$ olefins with 88% yield at ~100% DME conversion and ~ 80% $C_2^=$-$C_3^=$ olefin yield.

Catalyst developed in the IPS RAS permitted for the first time to carry out the synthesis of light olefins from pure DME with high yields like commercial MTO processes (UOP, Norsk Hydro, Lurgi) at lower temperature by using of more long-lived catalyst. Methanol substitution on pure DME enables to convert natural gas more productively.

References:

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PP-I-45

Metallic Nanoparticle Formation on Silicon Nitride Surface

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Silicon nitride owing advantageous properties, like rather high thermal conductivity, high hardness and strength, has perspective applications as the support of metallic catalysts for deep and selective oxidation of organic compounds. The aim of present work is to reveal the factor influence of the active surface formation of the metallic particles deposited on silicon nitride on the catalytic properties (Ag catalysts for the ethylene glycol oxidation into glyoxal and palladium catalysts for deep oxidation of methane). It is established that stability and activity of metal catalysts deposited on silicon nitride depend on the structure-phase (ratio $\alpha-\beta-$ phases) and the morphology of the silicon nitride powder used and also on preparation condition of the catalysts. It is shown that properties of such systems strongly depend on both the nature of precursor solutions and the character of their interaction with carriers. It was shown that hydrophobic and hydrophilic environment of precursor can strongly influence on catalytic properties. It was shown that studied systems have different structures and adsorption properties of metallic nanoparticles, which influence on the form of reagent adsorption, catalytic properties, and mechanism of surface reactions. Revealing correlations between the catalytic properties of catalysts, the chemical nature of active center precursors, and the conditions of the preparation of palladium and silver systems deposited on was found.

Not Additive Effects at Thermal Degradation of Natural and Synthetic Polymer Mixtures in the Presence of Haematite Catalyst

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Thermal conversions of cellulose, lignin, high density polyethylene (HDPE), and their mixtures in the presence of mechanically treated haematite catalyst were studied. The chemical composition of obtained liquid fractions was investigated by FTIR, NMR, GC-MS, high performance TLC combined with densitometry techniques. Heavy liquids were preliminary separated into different fractions by open LC and TLC methods.

Hydropyrolysis process gives the higher degree of mixture conversion and of increased yield of light liquids as compare to pyrolysis in argon. Observed in some cases non-additive effects indicate that the interaction between wood and plastic derived products takes place during mixture thermal treatment. The more pronounced synergistic effects were detected for hydropyrolysis process. Iron catalyst promotes the formation of liquid hydrocarbons and influence on their composition.

The composition of heavy liquids of co-pyrolysis significantly depends on biomass/plastic ratio. The addition of plastic to wood biomass increases the concentration of saturates and light aromatics with synchronous decreasing by a few times the content of polar compounds.

According to GC-MS data, the light liquids of biomass/plastic hydropyrolysis contain mainly normal paraffines C_7-C_{13} (about 75%), alkylbenzenes, and alkylfuranes compounds.

Alkanes approximately range from C_{13} to C_{30} with the maximum of the distribution centered approximately in C_{22}. These data are coherent with the formation of free radicals from the corresponding copolymer under the thermal degradation process. An important percentage of n-hexane eluted fractions might come from the polymer bond-breaking.

PP-I-47

Synthesis of Allobetulin, Betulin Diacetate, and Betulinic Acid by Catalytic Conversions of Betulin

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Biologically active triterpene compounds obtained by chemical transformations of betulin have prospects to use for the new drug design. Catalytic conversions of betulin to allobetulin, betulin diacetate, betulinic acid were investigated in order to improve the methods of their synthesis.

It was found that acidic catalyst H_3PO_4 promotes the reaction of betulin isomerization to allobetulin in butanol or isobutanol medium. At optimum reaction conditions the yield of allobetulin reaches 94 wt.%. The isomerization of betulin to allobetulin proceeds also in the acetic acid medium under the action of sulfuric acid catalyst. But in the presence of H_3PO_4 catalyst the rate of betulin acetylation exceeds the rate of its isomerization in acetic acid solution. This results in the formation of betulin diacetate with yield to 95 wt.%.

The known two-stage synthesis of betulinic acid includes the oxidation of betulin to betulonic acid and its following hydrogenation to betulinic acid by sodium borane in the two-phase system water-organic solvent.

In order to intensify the reaction of hydrogenation of keto-group of betulonic acid, the phase-transfer catalysts (FTC) were used. The nature of FTC and organic solvent, concentration of betulonic acid, $NaBO_4$, and catalyst were varied. The most effective catalysts are tetrabutylammonium bromide and tetrabenzylammonium chloride dissolved in the system benzol-water. These FTC promote the reduction of keto-group of betulonic acid at 25 °C. They make possible to obtain betulinic acid with the yield 98.5-99.3 wt.% and to reduce by 2 time the consumption of sodium borane.

PP-I-48

The Effects of Specific Features of the Defect Structure on the Bonding and Mobility/Reactivity of Oxygen in Ceria-Based Nanomaterials

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Oxygen bonding strength and reactivity in the catalysts control the rates and direction of the processes in oxidation catalysis. It is well-known that fluorites based upon ceria are promising catalysts for various oxidation processes due to their high oxygen mobility. Specific features of their defect structure and microstructure, especially for nanomaterials, strongly depend upon the type and concentration of promoters and affect the state of supported Pt [1].

In the given work the energy features and effective diffusion parameters of the surface and bulk oxygen in Ce-Zr(Sm)-O solid solutions with fluorite structure including Pt supporting ones (as estimated by TPD O_2 data and by reduction by CO and CH_4) are discussed on the basis of model defect structure of those nanomaterials (distortion of Ce environment, interstitial oxygen and trimer clusters $Me_{Ce}' VO^{\bullet\bullet} Me_{Ce}'$) and state of Pt species.

The enthalpy of the removal of oxygen from the lattice of pure ceria in contrast to the energy barrier of its lattice migration is rather high and could be reduced by formation of defects and/or distortions in cerium environment. It have been shown that the amounts of weakly bound surface oxygen depends on the type and amounts of promoter and grows with increasing the distortions in Ce environment. The removal of weakly bound oxygen and formation of anion vacancies facilitate subsequent migration of oxygen from subsurface layers. The amounts of desorbed O_2 at higher temperatures depend on the structural features of solid solutions. The specific character of activation of reductant (CO, CH_4) can control the values of effective diffusion parameters in the fluorites along with features of defect structure and states of Pt.

References:

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PP-I-49

Effect of Al^{3+} Cations on the Acid and Catalytic Properties of Sulfated Zirconia

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The effects of Al^{3+} cations with the concentrations varied in a wide range on the acid and catalytic properties of the sulfated zirconia based catalysts were monitored. The IR spectra including the spectra of adsorbed CO were used to characterize the acidity.

The introduction of the Al^{3+} cations was shown to result in an increase in the strength and number of Lewis acid centers. The IR spectra of CO adsorbed on sulfated zirconia with 1.5% Al^{3+} exhibited a sharp peak at 2211-2213cm^{-1} indicating the presence of very strong Lewis centers. The total number of the moderate and very strong centers (νCO 2196-2213 cm^{-1}) passed via maximum at 5-10% Al^{3+} concentration. The highest number of Bronsted acid centers with approximately equal strength exhibited at the Al^{3+} concentration of 1.5-5,0 %.

The n-butane isomerization over Al^{3+} promoted sulfated zirconia in a flow tubular reactor effectively occurred at the temperature of 145-175 °C. The extremal dependence of isomerization activity upon the Al^{3+} content was found.

The comparison of the catalytic activity with the acidity revealed that the most active catalysts had the enhanced concentrations of both Bronsted and Lewis centers, the concentration of the latter being 2-4 times more than Bronsted centers. However no correlation was found between the number and strength of Lewis centers. The linear correlation between the isomerization rate and the total number of moderate and strong Bronsted centers was established. The statistical treatment using the Fisher criterion at the significance level of $\alpha = 0.95$ showed the correlation to describe adequately the experimental data.

Mechanism of CO Methanation over Supported Nickel Catalysts

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The reaction of methanation is used to remove CO from feeding gases in many industrial processes, such as, coal gasification, ammonia synthesis and hydrogen production. Although there are many publications on CO methanation over nickel catalysts, there is no opinion on mechanism of this reaction. We used stationary and unstationary (response method) kinetic data as well as isotope and adsorption-desorption ones to study the mechanism of CO methanation over nickel catalysts. Early the optimal compositions of nickel catalysts were determined [1, 2] and the following catalysts were used for the investigation: 37.5%(wt.) $NiO/\gamma\text{-}Al_2O_3$ (I), 37,5% NiO + 0.1% $CeO_2/\gamma\text{-}Al_2O_3$ (II), 37.5% NiO + 10.2% $CaO/\gamma\text{-}Al_2O_3$ (III), 37.5% NiO + 0.3% $Li_2O/\gamma\text{-}Al_2O_3$ (IV), and 7.5% NiO/TiO_2 (Degussa P25) (V). The catalysts were investigated by methods BET, XRD, TPR, and hydrogen pulse titration. Experiments were carried out in gradientless systems at 180-240 °C at atmospheric pressure. Partial pressures of CO and H_2 are changed in the following limits 0.025-0.30 and 0.17-0.67 atm respectively. The values of kinetic isotope effects (the relation of the rates with the participation of light and heavy-weight isotopes) at replacement of H_2 by D_2 are 0.63; 0.86; 1.1; 1.3, and 1.4 for catalysts I, II, III, IV, and V, respectively. The data of adsorption-desorption and kinetic experiments show that strength of H_2 adsorption increases in the following sequence: I, II, III, IV, and V. The strength of CO adsorption changes in inverse sequence. Kinetic equation of CO methanation is the same over studied catalysts, but the constants are different for various ones:

$$r = \frac{k_1 P_{CO}^{0.5} P_{H_2}}{P_{H_2}^{0.5} + k_2 P_{CO} + k_3 P_{H_2O} + k_4 P_{CO}^{0.5} P_{H_2}^{0.5}}$$

The step-scheme of the process was proposed on the basis of all data. The slow step is the interaction of the adsorbed intermediate compound HCOH with adsorbed hydrogen atom. The values of inverse kinetic isotope effects are explained on the basis of proposed step-scheme in which the increase of the rates in the steps, previous of the slow step, overlaps the decrease of the slow step rate at the replacement of H_2 by D_2. The weaker H_2 adsorption and the stronger CO adsorption is over studied nickel catalysts, the more the increase of the rates before the slow step in this process is observed.

References:

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Mechanism of Propane and Isobutane Oxidative Dehydrogenation in the Presence of Carbon Dioxide over Chromium-Oxide Catalysts

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During the recent decade, progress was made in the understanding of the mechanism of oxidative dehydrogenation of light alkanes in the presence of O_2 [1, 2], while data on the mechanism of paraffin dehydrogenation in the presence of CO_2 are still missing. This work reports on some conclusions about the mechanism of propane and isobutane oxidative dehydrogenation over chromium-oxide catalysts in the presence of CO_2, based on the results of transient response and adsorption-desorption studies. In the previous work, the resistance of various samples of chromium-oxide catalysts to deactivation in this process was studied and reversible-reactivation catalysts were chosen [3]. Unstationary phenomena were studied in the flow step of small volume at atmospheric pressure. The step contained 3 independent lines and was connected with mass-spectrometer. Relaxation curves describing a transition of the system to a new steady state were obtained by a jump change of the corresponding concentrations. CrO_x/SiO_2 (prepared by impregnation methods) and CrO_x/MCM-41 (prepared by direct hydrothermal synthesis) were used for the investigation. The catalysts contained 1.0% (wt.) Cr. The partial pressures of paraffins and CO_2 are changed in the limits 0.125-0.33 and 0.30-0.75 atm., respectively. The temperature interval was 500-600 °C. Some adsorption experiments have been done at 200 °C.

The shapes of the relaxation curves obtained in the responses with different paraffins and carbon dioxide concentrations indicate that paraffins and carbon dioxide enter the reaction in the adsorbed state. The form of responses $He/[CO_2+C_3H_8\ (i\text{-}C_4H_{10})]$ and $He/[He+C_3H_8\ (i\text{-}C_4H_{10})]$ (a slope line means a change of the reaction conditions), where the amount of methane was measured, is practically coincident. It means that CO_2 didn't participate in the formation of cracking products and they are formed from paraffins. The experiments on CO_2 adsorption/desorption showed that CO_2 is quickly adsorbed over CrO_x/SiO_2 CO_2 surface (4 s) while the desorption process is rather slow (90 s). The adsorption and desorption times are 15 and 30 sec., respectively, for CrO_x/MCM-41, it means that CO_2 is tied with CrO_x/SiO_2 surface tightly, than with CrO_x/MCM-41 but amount of adsorbed CO_2 is higher over CrO_x/MCM-41 surface. Olefins are tied more strongly with CrO_x/MCM-41, than CrO_x/SiO_2.

Mechanism of propane and isobutane dehydrogenation is the same over studied catalysts, but the adsorption abilities of the reaction components are different. The step-schemes of olefins and cracking products formation were proposed.

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Influence of Coordination State of the Nickel Ions in the Activity of NiO/B_2O_3-Al_2O_3 Catalysts for Ethylene Dimerization

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Dimerization of ethylene is an important process for production of higher alkenes which find extensive application as intermediates for manufacture of detergents, plasticizers, transportation fuels, etc. In this paper we report about new bifunctional catalytic system of NiO/B_2O_3-Al_2O_3 for ethylene dimerization. The aim of this work was to test these catalytic materials in this reaction performed in continuous fixed bed reactor under temperature 150-200 °C. The catalytic behavior was investigated in connection with NiO content and physicochemical properties of catalysts (DSC, XRD, BET, TPD NH_3, FTIR, UV-VIS).

Catalyst without NiO was inactive in ethylene dimerization. Catalyst without B_2O_3 (NiO/Al_2O_3 catalyst) was less active, than NiO/B_2O_3-Al_2O_3 sample with the same NiO content. Thus, active sites for ethylene dimerization consist of nickel ions and acidic centers formed by interaction between B_2O_3 and Al_2O_3. Catalytic activity of NiO/B_2O_3-Al_2O_3 system increases with increasing NiO content, reaching a maximum in the interval between 4.9 and 9.3 wt.%. When NiO loading is 38.3 wt.%, catalyst is inactive. It is related to coordination state of nickel ions. The IR, IR CO, and UV-VIS spectra were examined to clarify the formation of the active nickel ions. Catalytic activity is closely correlated with presence of Ni^{2+} ions formed on the catalyst surface by interaction of NiO with borated alumina and coordinated to borate species.

The observed dimerization product distribution points at the occurrence of two types of mechanism, one based on coordination chemistry on nickel sites (formation 1-butene) and the second based on acid catalysis (double bond isomerization and butenes oligomerization).

PP-I-53

Mechanism of Chlorobenzene Reductive Transformation on the Ni and Pd Catalysts Supported on Alumina Modified by Heteropolyacid Salts

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Modification of oxide supports by heteropolyacids (HPA) derivatives gives possibility for the construction of new catalytic systems. Chemical and structure features of such modified systems make it possible to produce nanoparticles of the metal which are systematically arranged on the surface of support [1]. Such arrangement could play very important role for the mechanisms of hydrodechlorination (HDC) due to structure effects of the second type [2].

In this work, mechanisms of reductive transformation of chlorobenzene in vapor phase in the presence of 6% Ni/HPA salt/γ-Al_2O_3 systems were investigated. Comparison was made for the catalysts on different samples of Al_2O_3, with different modifiers (Si,W) or (W, Mo, Si) HPA salts; two catalysts contained additionally 0.03 or 0.015% Pd.

All catalysts are effective in chlorobenzene HDC to benzene in flow-type system in the presence of H_2 at 100-300 °C. The catalysts on the base of type 1 alumina were very selective in benzene formation; other performed also benzene hydrogenation to cyclohexane. Selectivity of cyclohexane formation has extremal dependence on the temperature. The catalysts modified by (W, Mo, Si) HPA salt were much more active, than other. TPR method was used to investigate the reasons of such behavior. Thus, modification of alumina by HPA salts gives the instrument for the tuning of HDC or hydrogenation activity of the catalysts. This work was maintained by RFBR (07-03-01017).

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Activity of Ni and Pt Catalysts in Sorption-Enhanced Reforming Process

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Hydrocarbons reforming over an admixture of a catalyst and CO_2 absorbent is often called sorption enhanced reforming (SER). The SER process is periodic, because of necessity of the absorbent regeneration. While different solutions are being considered, use of steam or air as a purge gas looks the most probable solution in an autonomous reforming unit. However, periodic contact of the catalyst with reducing and oxidizing atmospheres may affect its catalytic activity. This paper focuses on the catalytic activities of platinum and nickel based reforming catalysts subjected to the repeating reduction/oxidation cycles.

Commercial nickel catalyst, containing 12% NiO supported on calcium aluminate (NIAP-18, Novomoskovsk, Russia), and a lab made catalyst 0.5% Pt/α-Al_2O_3, prepared via α-Al_2O_3 impregnation with H_2PtCl_6 solution was used in tests. In a reference experiment the preliminary reduced Ni catalyst was tested in conventional continuous steam reforming. On the contrary, the same catalyst under RedOx cycles of the SER process demonstrates high and stable activity for more than 50 hours. The enhanced stability of the Ni catalyst in the SER process was attributed to self-dispersion of the active component. During regeneration step at high temperature the air readily and completely oxidizes supported Ni particles to NiO. During reforming step the NiO particles are reduced by the gas-steam mixture. Importance of the RedOx cycling of active component is further evidenced by a comparison of long-term stability of the Ni and Pt based catalyst.

The RedOx cycles enhance stability of the Ni catalyst in the SER process as compared to conventional continuous reforming. The oxidation-reduction cycles of active component prevent sintering of the Ni particles and corresponding loss of catalytic activity.

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PP-I-55

Formation of Alkyl Benzenes during Ethanol Conversion over HZSM-5 Zeolites

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Benzene and its alkylated compounds are important raw materials in the chemical industry. These compounds can be obtained via crude oil processing or by alkylation of aromatic compounds. However, the uncertainty of petroleum prices is likely to affect the production of other substances obtained from the primary and secondary processes of crude oil refining. It is, therefore, essential to ensure that possible substitutes of fossil fuels could also serve as sources of raw materials for the petrochemical industry. Bioethanol – obtained by fermentation of agricultural products and wastes could be dehydrated to ethylene which could subsequently be transformed into various valuable compounds similar to those obtained from crude oil.

Zeolites under certain experimental conditions are capable of converting ethanol, which is renewable, into valuable hydrocarbons. The conversion products of ethanol vary depending on the reaction conditions. Using ZSM-5 as catalysts, ethanol is usually dehydrated to ethylene first before other processes such as oligomerisation, aromatization, and alkylation among others take place. Benzene, toluene, xylenes, ethyl benzene, and ethyltoluenes are important hydrocarbons that are obtainable from the conversion of ethanol over zeolites and are widely applicable in different spheres of human activities.

With the aim of studying the mechanism of the formation of benzenes and their methyl and ethyl alkylated compounds, ethanol conversion was carried out under different temperatures, concentration of ethanol in the feed varied, ethanol was used as a mixture with other aromatic compounds, and the effect of Si/Al ratio was also studied.

Benzene, toluenes, xylenes, and ethyl benzenes were obtained in all runs. Concentration of ethyl toluene decreased with an increase in temperature, whereas that of other methyl benzenes increased. It is likely that high temperatures do not favour formation of ethyl radicals that could attack aromatic compounds. Introducing benzene into the feed practically had no change on the concentration of methyl benzenes, however an increase in the concentration of ethyl benzene was observed, showing that methylbenzenes are formed via a different route to that of ethylbenzenes. Conversion of ethanol over HZSM-5 with Si/Al = 30, 50, and 90 conforming to 3, 2, and 1 Al atom per elementary cell was studied, it was observed that at different pressures the catalyst with Si/Al = 50 yielded the minimum liquid hydrocarbons, this probably has to do with the possibility of the formation of Lewis acidic site which promotes the dehydration activity [1] but does not favour selectivity for liquid hydrocarbons.

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PP-I-56

The Role of C_2H_5I Promoter in the Process of Ethylene Glycol Partial Oxidation

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Halogens and halogen-containing compounds are widely used as promoters in the partial oxidation processes. It is known that the promoting effect of halogens in the oxidation processes of olefins and alcohols takes place over polycrystalline silver as well as aromatic hydrocarbons over oxide catalysts. Promotion of catalysts or reaction mixture with halogens leads to increasing of main products selectivity and decreasing of deep oxidation product yields, simultaneously. In the present work an influence of ethyl iodide addition into reaction mixture in the process of ethylene glycol partial oxidation was investigated.

The catalytic tests showed that the addition of ethyl iodide into the reaction mixture leads to increasing of glyoxal selectivity and decreasing of carbon dioxide yield. Using the TPD with MS, it was shown that the ethyl iodide forms two states of iodine, when adsorbed. The first state is the surface silver iodide and the second one is subsurface dissolved iodine. It is shown by means of MS that the surface silver iodide is thermally unstable and decomposes with isolation of molecular iodine. The subsurface dissolved iodine is more stable and desorbs in form of hydrogen iodide with treatment of catalyst by reducing agents. Thus, we concluded that the role of promoter lies in decreasing of concentration of surface and subsurface oxygen forms, which are responsible for deep oxidation and carbon deposition processes on the silver surface. Moreover, the promoting effect of ethyl iodide is the prevention of carbon deposit formation on silver surface: the SEM results showed, the formation of carbon deposits on the Ag surface is the result of long-time catalyst treatment by reaction mixture, and the addition of C_2H_5I into reaction mixture prevents carbon deposition on the catalyst surface.

Mechanism of Alkylation of Naphthalene by iso-Propanol

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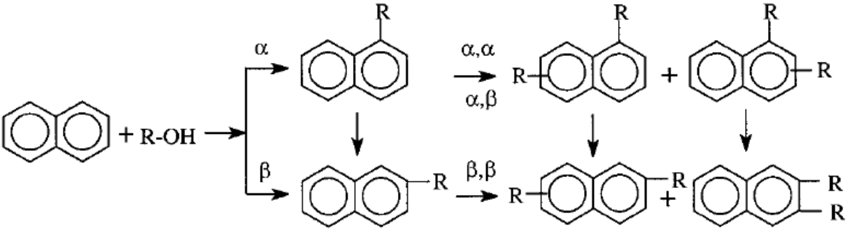
Process of alkylation of naphthalene plays the important role in the industry as products of reaction are applied for manufacture of valuable polymers. This process should use more environmentally friendly reagents including reactants and catalysts. It may be desirable to replace the processes employing corrosive catalysts such as HF/BF_3. Process should be as selective as possible, so that the amount of by-products can be minimized. In this context zeiolites are the best eco-friendly and selective catalysts.

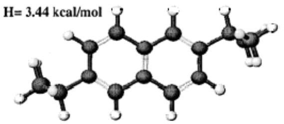
Alkylation and dialkylation of naphthalene by alcohols can proceed according to the following scheme in several directions:



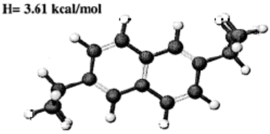
The structure of molecule of naphthalene promotes mainly formation of α-mono- and α,α-di-isomers of alkylated naphthalene. In β- and β,β-directions more valuable products are formed, especially, 2,6-dialkylnaphthalenes. Low selectivity and yield of β,β-isomers in alkylation process of naphthalene results in necessity of search for new ways of their production.

The basic factors that affect the selectivity of reaction are pore structure, pore size, and surface acid characteristics of the catalysts, type of alkylating agents, and reaction conditions. In this aspect for naphthalene alkylation by iso-propanol modified mordenite were studied which could carry out this process with high shape-selectivity and 65-80% yield of β,β-isomers.

Computational analysis of the molecules of naphthalene and products of alkylation was carried out using quantum-chemical program MOPAC. According to the frontier molecular orbital theory the most reactive position has the highest frontier electron density. Molecule of 2,6-diisopropylnaphthalene has two conformations: A and B. The A conformation is more stable, than B conformation.



2,6-diisopropylnaphthalene (A)



2,6-diisopropylnaphthalene (B)

2,7-diisopropylnaphthalene

Calculations show that formation of 2,6-diisopropylnaphthalene inside catalyst channel is more favoured, than 2,7-diisopropylnaphthalene, because position 6 has higher frontier electron density and higher reactivity for electrophilic substitution.

Formation of Oxygen-Containing Products from Methanol on the Supported Catalysts with Heterogeneous Structure of Active Surface

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Use is made of methanol as a raw material to produce complex hydrocarbons, dimethyl ether, methyl formate, and formaldehyde, in particular. In the present paper we have investigated the supported catalysts which allow their composition and properties to be easily altered by changing the ratio of the components, while impregnating a carrier – γ-Al_2O_3 and the regime of the heat treatment to follow. Use has been made of copper, molybdenum, and potassium compounds as active components.

The results of studies on catalytic properties and IR- spectra of surface compounds have been interpreted in terms of the following pattern of a catalytic reaction. Being absorbed on the surface, methanol decomposes to form methoxy- and hydroxyl groups, followed by their transformation into formate through formyl particles being active sites to form the compounds with an aldehyde group. Active centers with metal particles and Brensted bases are absolutely necessary for such transformations. It is on these sites of the surface that atomic hydrogen passes and then evolves in a molecular form. A formate group is an intermediate in the route of carbon monoxide conversion. In contrast to copper catalysts, no formate structures are available on molybdenum-containing specimen. Only dimethyl ether, methane, and formaldehyde are present through the products of methanol decomposition. Formation of methyl formate seems to occur via combination of methoxy- and formyl groups via free oxygen center. One can explain decreasing in catalyst activity as to methyl formate in high hydrogen concentration medium by interaction of the latter with an active oxygen center to form surface hydroxide, which prevents these groups from combining. Carbon monoxide forms formate ion on the surface of potassium-containing catalysts, which is one of the intermediate particles being formed through formyl groups. This fact results in decreasing the intensity of their consumption and increasing in the rate of formaldehyde and methyl formate formation.

PP-I-59

The Influence of the Support and Modifier's Type (HPC) on the Formation of the Active Surface of Alumina Supported Ni Catalysts Defining Their Selectivity in Unsaturated Hydrocarbon Hydrogenation

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As it was demonstrated before [1, 2] on the basis of investigations in wide range of reactions of hydrogenation activity for the Ni catalysts supported on the alumina modified by heteropolycompounds (HPC), such systems have adjustable activity. Tuning of the activity could be achieved by the changes in pore structure of the support, the nature of HPC as modifiers, Ni/HPC ratio, and the use of preparation know-how. Using this patented method the effective Ni nanocatalysts for olefin and aromatic compound hydrogenation on HPC modified alumina have been produced [3].

In this work, the results of the 1-heptene (10%) and benzene (30%) in heptane mixture hydrogenation in the temperature region of 100-400 °C are presented. The set of Ni catalysts supported on aluminas of different porous structure modified by HPC of the Keggin's structure – HPC (W) and mixed HPC (Mo, W), HPC(Cr, W), HPC (Cu, W), etc. was used as the catalysts. It was found that some catalysts, containing 4% Ni modified by HPC (W) in the different forms demonstrates high selectivity in 1-heptene hydrogenation (up to 100%) and no benzene transformation, whereas another group of catalysts with the same Ni content performs both olefin and benzene hydrogenation. These data point out the different mechanism of these reactions depending on HPC peculiarities and on the structure of support.

Early O.V. Krylov [4] proposed the mechanism of hydrogenation on analogous catalysts that implies direct participation of HPC in metal-containing active center formation. Such active centers serve for hydrocarbons adsorption, whereas diffusion of hydrogen from Ni surface proceeds through spillover mechanism by the help of OH-groups of modifiers.

However, such explanation does not consider the effect of porous structure and surface properties of the alumina, but both factors seem to be important for the concrete reaction mechanism realization. As modifiers of different nature were used in this work, it is obvious that the result of H_2 activation is different, just as the arrangement and dispersion of metal active centers on HPC.

All listed factors define for example the reaction mechanism of structure-sensitive reaction of benzene hydrogenation. The reaction mechanism of olefins is different. The former depends on heptene adsorption as π-complex on HPC and H_2 adsorption on the Ni centers connected with HPC and surface OH-groups.

The results obtained in this work are explained using the approach described here and confirmed in [5] by the additional results of active surface investigations by IRF-spectroscopy, NMR, porometry etc.

These catalysts are perspective for optimization and reduction of prices for several large-scale processes including hydrogenation stages [6].

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PP-I-60

Catalytic Etching of Polycrystalline Palladium in the $CO+O_2$ Atmosphere

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To determine the mechanisms how the reaction atmosphere affects the catalyst structure, it is necessary to study the surface microstructure of platinum metals in the reaction atmosphere in a wide temperature range. The surface reconstruction of polycrystalline palladium (Pd(poly)) in the $CO+O_2$ atmosphere at 500-1000 K was studied by scanning electron microscopy (SEM). It was found that palladium oxide particles, microcrystals, elongated fibers, and large palladium crystals are formed on the Pd(poly) surface as the sample is heated in the $CO+O_2$ atmosphere. Detailed analysis of scanning electron images of polycrystalline palladium surface and comparison with the amount of absorbed oxygen show that the Pd(poly) surface microstructure during the sample heating from 500 to 1000 K in the $CO+O_2$ atmosphere is determined by the formation and decomposition of PdO. For instance, at T = 600-800 K oxygen penetrates in the palladium lattice resulting in intense oxidation of the palladium surface to from PdO oxide particles with dimensions 50-100 nm. At 800 K the oxide particles decompose to form clusters smaller than 3-5 nm. It increases the mobility of metal atoms on the surface and leads to gradual formation of 100-500 nm metal microcrystals. The microcrystals form a continuous layer with a cellular structure. At T = 900 K elongated fibers with the diameter ~ 50 nm and length ~ 5000 nm are formed on the surface of this layer. The interlaced fibers form a continuous layer up to 5000 nm thick. At $T \geq 1000$ K the formation and decomposition rates of PdO clusters grow considerably. As a result, the concentration of mobile palladium atoms on the surface of the sample substantially increases. The higher concentration of the mobile metal atoms accelerates the reconstruction of the polycrystalline sample surface. So, palladium crystals with dimensions 500-5000 nm are formed on the Pd(poly) surface at 1000 K. The crystals are ordered and form a continuous layer that covers the whole palladium surface.

Enantioselective Hydrogenation of Dimethyl Itaconate

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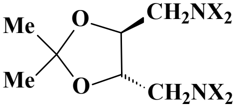
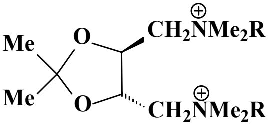
Colloid metals stabilized with chiral species are known to be capable of inducing enantioselectivity in catalytic hydrogenation [1].

We have performed hydrogenation of dimethyl itaconate on complex [Rh(cod)(**1a**)]Cl under various conditions.



1a, X=H,
1b, X=Me



2a, R=benzyl
2b, R=octyl

For this, optically active quaternary salts **2a,b** prepared by the reaction of diamine **1b** with two equivalents of benzyl chloride or octyl chloride were introduced into the reaction mixture.

*Hydrogenation of dimethyl itaconate on complex [Rh(cod)(**1a**)]Cl*
(C_{Rh} = 2 mol/l, Sub/Rh=158; solvent – methanol, P_{H2}=1 atm)

Run	System	r_{max}, mmol/l h	$(A)_{max}$, mol/g-at Rh h	*ee*, % (conf.)
1	[Rh(cod)(**1a**)]Cl	1050	684	2.1 (S)
2	[Rh(cod)(**1a**)]Cl + toluene	238	154	11.3 (S)
3	[Rh(cod)(**1a**)]Cl + toluene + **2a**	213	138	11.0 (S)

The rate of the reaction and the optical yield for hydrogenation of the substrate in the system $RhCl_3 \cdot 3H_2O$ + **2a,b** depend on the nature of the quaternary salt: in the presence of salt **2b** it is 10 times as large as in the presence of **2a** (35.0 and 3.3% of the S-enantiomer, respectively).

Reference:

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PP-I-62

Stability of Pd in Homogeneous Catalyst (Pd + Mo-V-P Heteropoly Acid) for Oxidation of n-Butenes to Butanone with Dioxygen

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We have developed a homogeneous catalysts (Pd + HPA) [1], where HPA is Mo-V-P heteropoly acid, for two-stage oxidation of *n*-butenes with O_2:

$$n\text{-}C_4H_8 + {}^1/_2\,O_2 \xrightarrow{\text{Pd + HPA}} CH_3COC_2H_5 \qquad (1)$$

The HPAs are reversible oxidants as much as their reduced forms, H_mHPAs, can be easily oxidized with O_2. The first step of process (1) is n-C_4H_8 oxidation with HPA at ~333 K catalyzed by Pd. The second step is regeneration of HPA with O_2 at 423–443 K. For execution of process (1), the redox potentials of all involved systems must be in the relation:

$$E_{O_2/H_2O} > E_{HPA/H_mHPA} > E_{Pd^{2+}/Pd^0} > E_{butanone/C_4H_8}.$$

To prevent precipitation of Pd in the reduced catalyst solution, we propose to use stabilizers of Pd. These stabilizers must be stable to oxidation at temperatures of the catalyst regeneration. As stabilizers, dipicolinic (2,6-pyridinedicarboxylic) acid [2], 3-pyridinesulfonic acid [2], and pyromellitic (2,3,5,6-benzenetetracarboxylic) acid [3] are investigated. In the presence of these stabilizers, activity of the catalyst is diminished, but an interval of the catalyst homogeneity is essentially extended. Furthermore, complexes of Co with phthalocyaninesulfonic acids are tested as Pd stabilizers in process (1) [4].

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Investigation of Mechanism of Singlet Oxygen Generation in the Decomposition of Dimethyldioxirane Catalyzed by Chloride Ion

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Singlet-oxygen (1O2) chemistry has been an attractive topic of intensive research over the years. Recently a new efficient source for singlet-oxygen generation has been reported: decomposition of dioxiranes catalyzed by anionic nucleophiles. Quantitative yield of 1O2 has been recorded by means of infrared chemiluminescence (IR-CL). Herein we report our study of kinetics of the chloride ion induced decomposition of dimethyldioxirane (DMD), which extend our knowledge on the mechanism of such a catalytic peroxide decomposition. Kinetics of the reaction has been studied by IR-CL method. Activation parameters of the process were determined. It was shown that the catalytic decomposition of the DMD into 1O2 is in competition with the oxidation of chloride ion. Kinetics studies have been complemented by the quantum-chemical modelling [MP4(SDTQ)/6-31+G(d)//MP2/6-31+G(d)] of interaction of chloride ion and DMD in acetone solution. The research was supported by the Ministry of Education and Sciences of RF, the Branch of Chemistry and Material Sciences of the RAS (№1-OKh), Federal Agency for Science and Innovations (№ 02.513.12.0050).

PP-I-64

The Method of Determination of Stationary States Number of Catalytic Reactions

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In this message a new determination method of internal stationary states (ISS) of catalytic reactions is given. This method include: 1) researched system stages rates constants (instead of intermediate substances concentration) are determined; 2) the set of all possible values of concentration is broken on n-dimensional (as a rule rectangular) “areas”; 3) for each of these areas possible values stages rates constants (“constants values area”) are counted up; 4) then maximum ISS number is determined on the a condition that it does not surpass number of “areas” for which the values stages rates constants can be the same identical. The given method applied for the reaction $2CO+O_2 \rightarrow 2CO_2$ proceeding under classical scheme 1. $CO+K=KCO$, 2. $O_2+2K=2KO$, 3. $KCO+KO \rightarrow 2K+CO_2$. It is known that this scheme is characterized by 3 ISS and described by the following system of equations stationary:

$$k_{-1}x_2 + r = k_1[CO]x_1,\ 2k_{-2}x_3^2 + r = 2k_2[O_2]x_1^2,$$

$$r = k_3 x_2 x_3,\ x_1 + x_2 = x_4,\ x_4 + x_3 = 1$$

After introduction of new variables

$$y_1 = r/(k_1[CO]x_1),\ y_2 = r/(2k_2[O_2]x_1^2),$$

$$y_3 = r/k_3 x_2 x_3,\ y_4 = x_2/x_4,\ y_5 = x_3$$

the system will become

$$\begin{aligned} &y_1 + k_1' \cdot y_1/y_5 = 1, \qquad y_2 + k_2' \cdot y_2^2 \cdot y_5^2/y_1^2 = 1,\ y_3 = 1, \\ &y_4 + k_4' \cdot y_4 y_5/y_1 = 1,\ y_5 + k_5' \cdot y_1^2/(y_2 y_4 y_5) = 1, \end{aligned} \tag{1}$$

where $0 \le y_1, y_2, y_4, y_5 \le 1$ $y_3 = 1$. Values of all variables y_i, except for y_3, were broken into 5 intervals ($a_i^j < y_i \le b_i^j$), the general areas number was equal $5^4=625$. Unambiguity of areas was checked on the basis linearization of the equations of system (1). The number the crossed “areas of values of constants” at the given stage was equal 4. The further splitting of areas with crossed values allowed us to establish realization of no more than 3 crossings. This means that the realization is no more than 3 ISS.

On the Role of Oxygenates on the Surface of Carbon Catalysts in the Catalytic Wet Peroxide Oxidation of Organic Contaminants

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This work focused on the investigation of the possible correlations between the presence of oxygenated species on the surface of carbon catalysts after an oxidative treatment and the performances of such catalysts in the catalytic wet peroxide oxidation (CWPO) of formic acid.

Catalysts were prepared by oxidation of a mesoporous graphite-like carbon (Sibunit) with either oxygen, nitric acid, hydrogen peroxide or sodium hypochlorite. Catalysts were characterized by BET, Boehm titration, XPS, FTIR and tested in CWPO of formic acid at pH ca. 3 in the absence or in the presence of iron, using a batch reactor.

Substantial differences in the catalytic performances of these catalysts were observed in both series of experiments. Catalytic activity in the formic acid oxidation appeared inversely proportional of the total amount of surface oxygen groups but no direct relation with the concentration in one specific type of functional groups was observed. We supposed that the surface functional groups were responsible for the scavenging of the free radicals. In the case of the deeply oxidized samples, it was observed that the reaction completely stops after being initiated by the iron ions in solution. The creation of strong iron complexes at the surface of these samples appeared to be responsible for it. In addition, the initial reaction rates seemed to correlate with the catalyst surface area and their iron adsorption capacities.

Acknowledgements. This research was supported by the RFBR-CNRS grants 05-03-2200, RFBR grant 06-03-32969 and PhD student fellowship from the French Embassy in Russia.

PP-I-66

Research of Kinetic Regularities for Catalytic Hydrodefluorination of Pentafluoroacetanilide

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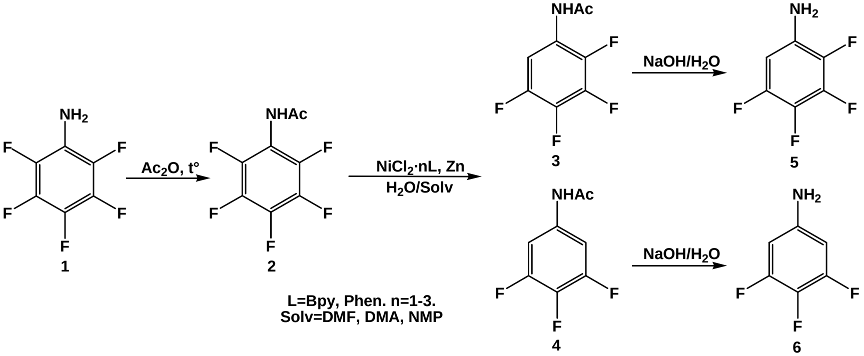
In previous papers [1, 2] we reported a method for preparation of the partly fluorinated amines **5** and **6** through selective hydrodefluorination of pentafluoroacetanilide **2** under the action catalytic reductive system NiCl2 – 2,2'-bipyridine (Bpy) or 1,10-phenantroline (Phen) – Zn. (Scheme 1)



Scheme 1.

In the present work we investigated the kinetic features for catalytic hydrodefluorination of **2**, depending on different factors. We observed that the composition of the nickel complexes and the nature of solvents influence on rate and selectivity of hydrodefluorination. The obtained data were used for interpretation of the possible mechanism of the reaction and improve of the catalytic process.

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Mechanism of Catalytic Polymerization of Caprolactam by Microaddition of Polyfluorocompounds

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Mechanism of catalytic polymerization of caprolactam by such catalytic systems as polyfluoroalcohols, carbonic acids, complex cupric compounds were examined.

Peculiarities of the step of opening caprolactam cycle in homolytical and hydrolytical polymerization were studied. The synergism of catalytical action of system polyfluoroalcohol - carbonic acid, which leads to high rate of olygomerization, growing of macromolecular chain and structure reorganization of macromolecular system by influence of nano-centres, which form in polymer system, was found.

It leads to increasing of the area of coherent dispersion (from 25 to 50 Angstrom unit for non modified and modified by microaddition of polyfluorocompounds fibers), which increases structural perfection along the macromolecular backbone, which gives rise to improvement on the thermal stability and oxidative destruction resistance of modified fibers.

Polycaproamide materials with higher thermo-, light-, threadbare stabilities, for production of cord and textile materials with better performance characteristics were obtained.

PP-I-68

True Heterogeneous Mechanism of the Heck Reaction in Ion Liquid Media

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C-C coupling of an aryl halide with an olefin mediated by supported metal Pd is commonly believed to proceed as a quasi-homogeneous process [1-3]. This mechanism suggests Pd particles hosted within a porous solid to interact with reaction media and form small Pd nanoclusters or molecular complexes that are transferred into the liquid phase, where they perform homogeneous catalytic cycles. There are only a few papers, where the possibility of direct involving of Pd atoms, located at the vertexes and edges, as well as atoms at the crystal faces, into the catalytic cycles has been addressed. In this communication, we reports on the uncommon catalytic properties of Pd nanoclusters immobilized onto the specific carbon material – the mesoporous acetylene soot, using the tetraalkylammonium-based IL as a solvent to arylate styrene with bromobenzene. First, Bu_2NH additive is 2 times more efficient as base then NaOAc in contrast to the reaction performed in molecular solvent [2]. Second, the preactivation of carbon-supported Pd in the tetraalkylammonium IL takes place in the presence of Bu_2NH which is quite the reverse for imidazolium-based IL solvent. At last, unambiguous evidences in favor true surface Heck chemistry are (i) no traces Pd were detected in the IL solvent, and (ii) neither general appearance of metal Pd entity nor the average Pd nanoparticle size showed significant changes after performing the reaction in IL solvent.

This work was supported by the RFBR (grant No. 08-03-00544).

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PP-I-69

Formation, Composition and Catalytic Properties of Ni-, Cu- and Pt-Containing Oxide Layers

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Here we report the results of the investigation of the alumina alloy composition effect on catalytic properties of coatings, formed by micro arc oxidation (or plasma electrochemical oxidation, PEO) technique with nickel and copper additions. The data of platinum building-up into oxide layers on aluminium and titanium under PEO will be presented as well.

The strongest activity in CO oxidation have been showed by the Ni-Cu-containing oxide compositions, based on alumina alloys containing Cu, Mg and Mn simultaneously.

The possibility of Pt introduction into PEO layers on alumina and titanium has been established. The films have been investigated with EPXMA and XPS. The films obtained contain up to 1 at. % Pt. It should be noted that the oxidation level of Pt is 0 (zero) in surface layers on alumina and +2 in ones on titanium.

The results show the possibility of PEO-deposition of catalytic activity coatings on different alumina alloys. The obtained films with Pt are promising for catalytic testing in different processes.

PP-I-70

Catalytic Performance of Reinforced Nickel Cr_2O_3-Free Catalysts for Methane Steam Reforming to Synthesis Gas

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To carry out the endothermic methane steam reforming reaction (MSR), intensive heat transfer from an outer source to the reaction zone is required. Therefore, the catalyst must have a high thermal conductivity. It is most promising to use catalysts on metallic supports. The reinforced nickel catalysts with addition of chromium oxide were studied in detail in [1]. To compare the MSR performances of reinforced Cr_2O_3-doped and Cr_2O_3-free nickel catalysts we studied in the present work the peculiarities of the formation of composite reinforced nickel catalysts free of chromium oxide additive, and their catalytic properties in the reaction of MSR.

To prepare reinforced catalysts, a mixture of components containing 87,5 wt.% Ni,12,5 wt.% commercial GIAP-3 or NIAP-18 catalyst was mixed with a rubber-based adhesive and applied to reinforcing gauze followed by sintering in a vacuum oven at 760°C for 2 h.

It was found that a metal matrix, in the pores of which supported catalyst particles were distributed, was formed in the composite catalysts. The NIAP-18 based catalyst exceeded the GIAP-3 based catalyst by the activity for the reaction of MSR. The NIAP-18 based catalyst was as active as the Cr_2O_3-doped NIAP-18 based catalyst. A Cr_2O_3 additive increased the activity of GIAP-3 based catalyst. The conversion of methane on catalytic layers remained stable over the entire period of testing (30 h). According to TEM studies of NIAP-18 based catalytic layers exposed to MSR, the Cr_2O_3-doped sample contained amorphous carbon which was detected in the initial sample also; the sample without Cr_2O_3 additive contained small amounts of carbon filaments together with amorphous carbon.

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Oxidation and Recrystallization of Polycrystalline Rhodium, Palladium and Silver in Oxygen Atmosphere

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Oxidation and recrystallization of polycrystalline rhodium, palladium and silver samples in the oxygen atmosphere at T=500-1500 K were studied by scanning electron microscopy (SEM) and thermal desorption (TD). Different microstructures were observed to form on the surface of Rh, Pd and Ag foils at increasing temperatures. Particles with dimensions of 50-60 nm were observed on the surface of the samples at $T \leq 800$ K. At $T \geq 800$ K the surface of the samples loosens considerably. Further temperature increase to $T \geq 1000$-1200 K led to the gradual growth of grains and formation of crystalline facets. Detailed analysis of scanning electron images of the polycrystalline Rh, Pd and Ag samples and comparison with the amounts of absorbed oxygen showed that the surface microstructure of polycrystalline Rh, Pd and Ag samples during the temperature growth from 500 to 1500 K in the O_2 atmosphere was determined by the formation and decomposition of the corresponding oxides Rh_2O_3, PdO and Ag_2O. For instance, at T = 600-800 K oxygen penetration into the metal lattice results in intensive oxidation of the metal surface to form oxide particles with typical dimensions 50-60 nm. At $T \geq 800$ K the oxide particles decompose to form clusters smaller than 3-5 nm. As a result, the mobility of metal atoms on the surface increases, and metal microcrystals with dimensions 100-300 nm are gradually formed. At $T \geq 1000$ K for Ag, $T \geq 1200$ K for Pd and $T \geq 1400$ K for Rh the formation and decomposition rates of the oxide clusters substantially increase. This increases the concentration of mobile metal atoms on the surface of the sample. The growth in the concentration of mobile metal atoms accelerates the surface reconstruction of the polycrystalline foil. Thus, At $T \geq 1000$-1200 K a grain boundary appears on the surface of polycrystalline Rh, Pd and Ag samples. The grains gradually grow, and crystalline facets are formed and cover the whole surface of the grains.

PP-I-72

Strategy for the Synthesis of Highly Effective Nanoscale Palladium Hydrogenation Catalysts Modified with Elemental Phosphorus

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The mechanisms of the formation and functioning processes as well as the nature of highly effective nanoscale palladium hydrogenation catalysts modified with elemental phosphorus are considered1,2]. The key stages determining the composition, the structure and the catalytic properties of the nanoparticles have been experimentally substantiated. These ones include the reduction of Pd(II) compounds to Pd(0) species by elemental phosphorus and hydrogen, the oxidation of Pd(0) owing to interaction with white phosphorus resulting in different palladium phosphides, and clustering. The nature of the products: nanoparticles of palladium phopsphides (PdP_2; Pd_5P_2; $Pd_{4.8}P$; Pd_6P), palladium nanoclusters and core-shell type nanoparticles (core – Pd_6P, shell – Pd(0)) depends on anion nature of Pd-precursor and modifier concentration. It was found that if $PdCl_2$ was used as precursor then nanoparticle formation was accompanied by side process of solvent (DMF) catalytic hydrolysis with formation of the stabilizers – ammonium salts in the reaction system. Reasons of promoting or inhibitory action of elemental phosphorus are considered also ways of the purposive synthesis of highly effective in hydrogenation nanoparticles are offered.

The selectivity analysis of various substrates catalytic hydrogenation as well as different methods of distinguishing homogeneous hydrogenation catalyst nature from microheterogeneous one, have allowed to draw a conclusion in favour of the latter. The general schemes of nanoscale palladium hydrogenation catalyst formation and of catalytic hydrogenation are given.

The Reactivity of Arenes in Hydrogenation Processes on Homogeneous and Nanoscale Catalysts

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Valuable information about a catalytic process mechanism can be obtained by reactivity investigating of compounds with similar structures, the molecule size and shape of which successively changes. The results on studying of hydrogenation reaction rates for a number of arenas under mild conditions on homogeneous and nanoscale cobalt- and nickel-catalysts, including the conditions of earlier found by us conjugated hydrogenation of alkenes with monocyclic arenas are presented. The satisfactory correlation between hydrogenation rate and localization energy of radicals formed by addition of first hydrogen atom to arene is established for $Ni(acac)_2 – LiAlH_4$ nanoscale catalyst. It is consistent with the ideas about the rate-controlling stage and the determining role of electron factors on mono-, bi- and tricyclic arene hydrogenation rate. Further increasing of the cyclicity reduces the hydrogenation rate, which is probably due to steric factors.

The homogeneous cobalt catalyst $Co(acac)_2 – PBu_3 – AlEt_3$ is catalytically inert in benzene hydrogenation, but is active in hydrogenation of polycyclic arenes, the reactivity of which decreases in the following series (TOF, min^{-1}): naphthalene (3.6) > anthracene (2.1) > phenanthrene (0.9) > benzanthracene (0.6) > triphenylene (0.2) > 9,10-dihydroanthracene (0.15). While under the conditions of conjugated hydrogenation with alkene arenes are disposed as follows: benzene (0.16) ≤ naphthalene (0.19) < anthracene (0.041) < phenanthrene (0.019). The kinetics corresponds to the first order for hydrogen, close to the first order – for the catalyst, and zero one – for arene. It was found that in the case of conjugated hydrogenation of benzene not only alkenes and dienes can act as inductor, but also polycyclic arenes. A number of the theses about conjugated hydrogenation mechanism were formulated. The results on studying of the formation mechanism and the nature of catalytically active forms of the used catalytic system are reported.

PP-I-74

Modification of the Catalytic Systems $(C_5H_5)_4Zr$ – MAO and $(C_5H_5)_4Ti$ – MAO by Metalalkyls

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Control under the characteristics of metallocene catalytic systems for ethylene polymerization and copolymerization and polymer properties is an actual fundamental and industrial problem. These questions can be solved on the basis of deep understanding of polymerization mechanism. In one’s turn information about mechanism can be obtained during investigation of kinetic regularities (activity, productivity and selectivity of the catalytic system) and properties of products (structure, MWD, nascent properties, density). Now for variation of catalytic system characteristics and polymer properties using various regulators: H_2, butene-1, hexene-1 and organometallics.

We have reported [1] about investigation of the new catalytic system for ethylene polymerization based on $(C_5H_5)_4Zr$ and MAO, which showed high polymerization activity (2200 kg PE/ g Zr per hour) in the presence of H_2. It was shown that H_2 additives allow to regulate molecular weight of PE in broad range and additives of butene-1 and organoaluminum allow to regulate structure of PE. We have studied the possibility of partial MAO replacing by other organoaluminum because of it’s high cost and difficulty to obtain.

When MAO was replaced by equimolar mixture with trimethylaluminum, triethylaluminum or triisobutylaluminum (TIBA) increase of activity and decrease of molecular weight was observed in all cases. These effects were developed significantly in the case of TIBA. Optimization of concentration and molar ratio of additive allow to increase productivity of catalytic system at 60°C and 0.6 MPa in toluene from 791 kg PE/ g Zr per hour (without TIBA) to 2366 kg PE/ g Zr per hour with simultaneous decrease of molecular weight from 220 to 100 kg/mol. Using diethylzinc as additive allow decrease molecular weight to 15 kg/mol, productivity 1600 kg PE/ g Zr per hour.

We observed decrease of productivity from 416 to 106 kg PE/ g Zr per hour and increase of molecular weight from 60 to 128 kg/mol when studied catalytic system $(C_5H_5)_4Ti$ – MAO, modified by TIBA.

Differences in studied effects agree with obtained earlier facts and could be concerned with difference in structure of metallocene precursors. Molecule of $(C_5H_5)_4Zr$ in contrast to $(C_5H_5)_4Ti$ contains three $(\pi\text{-}C_5H_5)$-groups. It allows regarding it as a model of active site with stable fragment $(\pi\text{-}C_5H_5)_3Zr$.

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PP-I-75

Investigation of Catalysts and Organic Compounds Oxidation Mechanisms in Biphasic Systems by SAXS Method

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Method of Small-angle X-ray scattering (SAXS) was used for the direct structural and dispersed analysis of chemical reaction components in studying of organic substrates catalytic oxidation mechanisms.

It is known that peroxopolyoxotungstates, for example $\{PO_4[WO(O_2)_2]_4\}^{3-}$, are used for various organic substrates oxidation [1, 2]. Catalysts on basis of effective mentioned above anion in combination with quaternary ammonium cations – phase-transfer catalysts, were used in our investigations.

Investigated samples represent a totality of nanoparticles (electron density non-uniformities), which follows from the results of catalytic systems analysis in organic solvents by SAXS method. It is ascertained that $[(n\text{-Bu})_4N]_3\{PO_4[WO(O_2)_2]_4\}$ complex (**I**) is similar to monodisperse, while $[Me(n\text{-}C_8H_{17})_3N]_3\{PO_4[WO(O_2)_2]_4\}$ (**II**) represents a binary mixture of two fractions. It is most probable, that observed differences are related to different nature of complex cation.

It is established that specific changes of SAXS roentgenograms, evidencing of complexes dispersed composition modification of initial catalyst molecules, occur under conditions of organic substrates oxidation reactions by hydrogen peroxide in the presence of catalyst II.

The investigations will be performed in order to establish the reaction mechanisms of the phase-transfer oxidation catalysis using specially improved analysis method.

The investigation was carried out at Department of Chemistry and Sciences on New Materials RAS support (project 5.7.3).

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Catalytic Ozonation of Oxalic Acid with Copper/Copper Oxides Catalyst

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Catalytic ozonation is one of more effective methods of water treatment. This technique uses oxidation of water pollutants by ozone in presence of catalysts, e.g. different metals, metal oxides. There are many researches of such processes were carried out some last decades. But mechanism of catalytic ozonation is not clear yet. Some authors point out that the mechanism depends on type of using catalyst. That's why it is very important to investigate the process way for every type of catalyst.

This work deals with a new type of catalysts – copper with copper oxides on its surface. Catalytic activity of this material for oxalic acid decomposition was studied and mechanism was proposed. Such indirect methods, as UV-Vis Spectroscopy, FTIR-ATR Spectroscopy, XRD, SEM were used.

As it shown in Table 1, the presence of this catalyst increases oxalic acid decomposition from 7 to 84 %.

Table 1 – Oxalic acid decomposition depending on kind of treatment (initial content of oxalic acid – $1*10^{-3}$ M).

Kind of treatment	O_2 without catalyst	O_2 with catalyst	O_3 without catalyst	O_3 with catalyst
Oxalic acid decomposition, %	3	3	7	84

It's supposed that the mechanism of oxalic acid decomposition in this case has an oxidation-reduction nature. Oxalic acid decomposition in presence of copper catalyst concerns with its oxidation by copper oxides, which formed on catalyst surface under ozone action.

PP-I-77

The Mechanistic Study of 1,2-Dichloroethane Conversion on Catalysts Surface by in situ FTIR Spectroscopy

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The reactions of halogen substituted hydrocarbons (RCl) in homogeneous catalysis can be considered as studied more fundamentally than the other reactions. It is known that reactions of substitution and dehydrochlorination in RCl are dependant on substrate structure, nature of the solvent and catalyst and proceed via one of classical mechanism: SN1, SN2 (E1, E2).

1,2-dichloroethene is used for industrial production of vinyl chloride by dehydrochlorination process. Therefore, the study of the mechanism of 1,2-dichloroethene dehydrochlorination on surface of catalysts is interesting for revealing the interrelation between homogeneous and heterogeneous catalysis at the molecular scale and simultaneously for searching of industrial catalyst of vinyl chloride producing .

The objective of this work is studying the mechanism of 1,2-dichloroethane dehydrochlorination on well characterized acid (γ-Al_2O_3, H-ZSM-5 zeolite) and basic (MgO) catalysts by means of in situ FTIR spectroscopy. As the catalyst, H-ZSM-5 zeolite with strong Broensted acid sites was chosen. Alumina catalysts have strong Lewis sites. MgO is basic catalyst.

Adsorption of 1,2-dichloroethane on H-ZSM-5 zeolite, γ-Al_2O_3 and MgO was studied in the temperature range of 25-400^{o}C. 1,2-dichloroethane conversion started on zeolite at 200^{o}C whereas on MgO, and alumina already at 100^{o}C.

It was shown that the formation of H-bond between 1,2-dichloroethane and acidic OH groups of H-ZSM-5 preceded to dehydrochlorination process at 200^{o}C. The formation of these complexes was proved by band shift from 3602 cm^{-1} (attributed to acid OH groups in channels) to 3350 cm^{-1}. Vinyl chloride converted into oligomers directly at adsorption. Besides, it was shown that vinyl chloride interacted with AlOH groups or water converting into acetaldehyde. On alumina surface, vinyl chloride converted into

1,3-dihlorbutene-2 and acetaldehyde. Both 1,2-dichloroethane and vinyl chloride form donor-acceptor bond with Lewis acid sites. The formation of 1,3-dihlorbutene-2 occurred with participation of weak Lewis acid sites. Both vinyl chloride and 1,3-dihlorbutene-2 converted into oligomers on weak Lewis acid sites which resulted in catalyst deactivation. Side reaction of acetaldehyde formation occurred with participation of AlOH groups, similar to zeolite. The same species as on γ-$Al_2O_3$are found on MgO, but vinyl chloride is adsorbed on surfaces with formation of allyl-type complexes. The schemes describing main direction of 1,2-dichloroethane conversion on acid and basic were proposed.

PP-I-78

The Mechanism of Ultrafast Deactivation of Kynurenine Excited States

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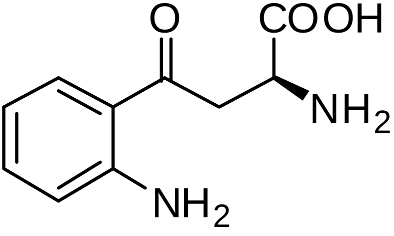

Kynurenine (KN)

The lens of the human eye contains low-molecular weight compounds which act as UV filters. These molecules – kynurenine (KN) and its derivatives – are natural metabolites of the amino acid tryptophan; they absorb UV light in the 300-400 nm spectral region. For a long time, kynurenines were believed to be photochemically inert: they exhibit low fluorescence quantum yield and short fluorescence lifetime, low yield of reactive oxygen species under aerobic photolysis. These observations point to the presence of a fast radiationless transition $S_1 \rightarrow S_0$ in KN molecule, the mechanism of this process being still unknown.

We present here our investigation of the origin of the ultrafast deactivation of KN excited states, using femtosecond-resolved optical spectroscopy combined with steady-state techniques. The main goals of this study are: (i) to investigate the mechanism of the efficient UV protection provided by KN and its derivatives and (ii) to examine the influence of the substituent on this efficiency.

The excited state dynamics of KN were examined in various solvents. The S_1 lifetime of KN amounts to 30 ps in aqueous solutions, increases by more than one order of magnitude in alcohols, and exceeds 1 ns in aprotic solvents such as DMSO and DMF. Internal conversion (IC) is shown to be the main deactivation channel. The IC rate constant is pH independent, but increases with temperature with an activation energy of about 7 kJ/mol in all solvents studied. The dependence on the solvent proticity together with the observation of a substantial isotope effect indicates that hydrogen bonds play the crucial role in the rapid non-radiative deactivation of KN in water.

The covalent attachment of KN to the antioxidant glutathione and to the amino acids cysteine, histidine and lysine results in an increase of the S_1 state lifetime. The binding to a more bulky substituent – a protein lysozyme – leads to a 7-fold increase of the fluorescence quantum yield as compared to free KN. The observed time profiles of the excited state dynamics reveal a multi-component decay, which corresponds to KN attached to protein in different positions. The weakening and/or blocking of intermolecular hydrogen bonds between KN and solvent molecules should be responsible for the changes in photochemical properties of KN. These results give a new insight into the origin of KN efficiency as an UV filter and its role in cataractogenesis.

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The Bulk Porous Electrode Material with Controllable Geometrical Parametrs of the Structure

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On the carrying out of electrochemical processes which proceed with participation and formation of the gaseous products or other electrochemical redox reactions, one can require the gas and liquid permeability of electrode material, its substantial surface area available for an electrochemichal reaction, corrosion resistance and mechanical stability. The electrode material consisting of one- or multicomponent conducting base, having a bulk porous structure with the holes uniformly allocated on all electrode surface is considered. The formation of the bulk porous structure can be carried out by the bulk structure modifying of electrode material base by the controllable manner with the use of physical and chemical methods (for instance, chemical or electrochemical etching, laser technology of the material treatment, lithography with the suitable linear precision). The formation of such bulk porous structure makes it possible to achieve the substantial increasing of the electrode material surface area and permeability of electrode material for the gas and liquid (See detailed in [1]).

For instance, it was calculated that the specific surface area of the electrode material (with thickness **h** and density **ρ**) after the creation of the equidistant cylindrical holes (with radius **r**) net is equal: $\mathbf{(S_1)_{spec} = 2/\rho*[1/h + (\pi/(9 - \pi))/r] \sim 2/\rho*(1/h + 0.536/r)}$ **(Eq. 1).** The relation of the specific surface area of the electrode material after the creation of the equidistant cylindrical holes net to the initial specific surface area of the electrode material without the holes may be expressed by the next equation as a result: $\mathbf{(S_1)_{spec}/(S_{in})_{spec} = 1 + \pi/(9 - \pi)*h/r \sim 1 + 0.536\ h/r}$ **(Eq. 2).**

Electrocatalitic activity, corrosion resistance, other necessary electrode material properties can depend not only on the base structure and properties but also on the properties of one- or multicomponent coverage with the submonolayer, monolayer or multilayer thickness. The coverage is deposed on the electrode surface after the bulk structure modifying of electrode material base. In the case of nanodispersional coverage the substantial additional increasing of the electrode material surface area can be achieved.

The electrode material with perforated cylindrical equidistant holes and with the deposited dispersional (nanodispersional) coverage was considered. The carried calculation led to equation: **$(S_1)_d/S_{in} = S_1/S_{in}*(1 + \pi*N_d*)$ (Eq. 3)**, where **$(S_1)_d/S_{in}$** is the relation of the result surface area of the bulk porous electrode material with the coverage to the initial surface area of the electrode material without the holes and without electrode coverage; **S_1/S_{in}** - the relation of the result surface area of the bulk porous electrode material without dispersional electrode coverage to the initial surface area of the electrode material without the holes and without dispersional electrode coverage; **N_d** – the number of nanodispersional layers of the electrode coverage. The calculated results may be seen in Table.

If the spherical particles in the layer are disposed uniformly and occupy the part D of the bulk porous electrode material surface area then the relation $(S_1)_d/S_{in}$ may be expressed in equation: **$(S_1)_d/S_{in} = S_1/S_{in}* (1 + 4D)$ (Eq. 4)**, for D = 0.1 $(S_1)_d/S_{in} = S_1/S_{in}*$ 1.4, for D = 0.2 $(S_1)_d/S_{in} = S_1/S_{in}*$ 1.8, for D = 0.4 $(S_1)_d/S_{in} = S_1/S_{in}*$ 2.6, for D = 0.6 $(S_1)_d/S_{in} = S_1/S_{in}*$ 3.4.

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PP-I-80

2-Propanol: Solvent or Reagent in the Hydrodechlorination of Chlorobenzene and Its Derivatives over Pd/C Catalysts?

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Catalytic hydrodechlorination is presently acknowledged as the most universal and promising method for treatment and neutralization of chlorine-containing organic waste, since this process makes it possible to convert hazardous compounds to useful products under mild conditions.

In this work, the study of liquid-phase hydrodechlorination of chlorobenzene and its derivatives over of Pd/C catalysts at different conditions was performed. Isopropanol or H_2 gas were investigated as a hydrogen sources. Hydrodechlorination process was carried out at 20-50ºC at 1 atm in solvent system containing toluene, 2-propanol or 2-propanol-toluene mixture. Isopropanol was found to be more efficient than toluene. It was shown that the addition of 2-propanol to toluene in the amount stoichiometric toward chlorobenzene leads to significant process fastening. Probably, the observed increase of activity when 2-propanol was added is due to its ability to form active hydrogen-transfer species. The discussed mechanism includes the 2-propanol catalytic dehydrogenation as a key stage of chlorine-containing substrate hydrodechlorination. The advantages and disadvantages of carrying out this process in absence (or presence) of molecular hydrogen were shown.

It was shown that toluene-alcohol solvent mixture may be effectively used for hydrodechlorination of heavy polychlorinated aromatic compounds which are poorly soluble in 2-propanol.

Investigation of the Linoleic Acid Isomerization over Gold Catalysts

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Linoleic acid (C18:2), which has double bonds located on carbons 9 and 12, both in cis configuration, can be isomerized to conjugated linoleic acids (CLAs), that in their turn are widely used as a healthy promoting agents in food and pharmaceuticals due to their anticarcinogenic and antioxidative properties [1]. In the isomerization reaction small quantity of hydrogen is needed to enhance activity. Thus, selective isomerization under hydrogen atmosphere is challenging due to hydrogenation of a C=C bond over typical metal catalysts (e.g. ruthenium) and consequent formation of stearic acid instead of CLAs. In a recent work performed at Åbo Akademi it was demonstrated for the first time that isomerization of linoleic acid is possible over heterogeneous catalysts [1, 2]. The reaction was carried out under nitrogen atmosphere after pre-adsorbtion of hydrogen on the catalyst surface. In fact, selective isomerization under hydrogen atmosphere has been carried out by using Ag/SiO_2 as a catalyst [3]. Gold is a potential catalyst for the selective isomerization reaction as it is reluctant to hydrogenate C=C double bond.

There are several advantages using gold as a metal in catalysts compared to other precious metals [4]: the cost is lower and price stability is greater. However, improvements in preparation of the gold catalysts are needed. It is well known that the efficiency of gold nanoparticles depends largely on the size, therefore catalyst activity appears to depend strongly on the method of synthesis, the nature of the support, the size of the gold particles and the thermal history of the catalyst. In this work we aim to develop a nanosized gold catalysts preparation to be active in the synthesis of fine chemicals from wood.

Samples of gold catalysts were prepared by deposition-precipitation method (DP) with urea (1-5 wt % Au/Al_2O_3, TiO_2, SiO_2) and by immobilization of gold sols stabilized by polyvinyl alcohol (PVA) (1-2 wt % of gold on mesoporous carbon Sibunit). Gold particle size was measured by TEM and XRD techniques. It was shown that the highest dispersion of gold particles was reached on silica.

Activity and selectivity of synthesized catalysts towards hydrogenation, conjugation and desired conjugation were investigated. 1 wt % Au/Al_2O_3 showed the highest activity while the highest yield of the desired CLAs was observed over silica supported gold catalysts. The highest selectivity towards conjugation was observed over carbon supported gold catalyst, although the overall yield is low. Gold particle size in Au/C catalysts is larger than for gold particles supported on oxides, while carbon supported gold catalysts seem to be more promising catalysts for linoleic acid isomerization than gold supported on metal oxides.

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Influence of the Precursor Structure on the Properties of Ni-Cr Catalysts in the Hydrogenation Reactions

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The study is devoted to the effect of the Ni:Cr proportion on the structure of co-precipitated Ni-Cr hydroxycarbonates and their transformations during subsequent heating in the inert gas and hydrogen flows. X-ray powder diffraction and thermogravimetric analysis were used. Catalytic properties in benzene hydrogenation to cyclohexane and preferential CO methanation were studied. Ni^{2+}:Cr^{3+} ratio varied from 1:3 to 3:1. Ni-rich precipitates have hydrotalcite-like structure, Cr-rich precipitates are amorphous.

Thermal treatment at 675 K results in decomposition of hydroxycarbonates and a cubic NaCl-like structures are forming. Parameter of the elementary cell slightly increases from 4,180 to 4,186 ± 0,005 Å when increasing Ni content. For samples with high Ni content diffraction lines intensity distribution is close to that, characteristic for NiO (ICDD, PDF-2, 00-047-1049). Diffraction patterns of the samples with high Cr content had some differences in intensities ratio. The most intensive is (311) line, that allows presuming the forming of some amount of spinel-like phase. Further calcination at higher temperature (upto 875 K) is accompanied with appearance of the well crystallized spinel structure with the lattice parameter a = 8,320 ± 0,005 Å (ICDD, PDF-2, 00-023-1271). The main compound in Ni-rich samples has NiO structure with unit cell parameter 4,177 Å, coinciding with standard parameter.

Reductive treatment of the Ni-rich oxide precursor in hydrogen at 625-675 K results in appearance of the metallic nickel particles with the mean size ca. 55 Å. The specific surface area of the Ni^0 is ca. 6 m^2/g. In Cr-rich oxides, nickel cations also reduce when heated in hydrogen and form metallic nickel. However, specific catalytic activity of Cr-rich oxides in hydrogenation reactions are much worse than Ni-rich ones.

PP-I-83

Formation of Active Structures in NaWMn-Silica Catalyst for Oxidative Coupling of Methane

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Oxidative coupling of methane (OCM) is an attractive way of direct transformation of natural gas into valuable chemical products via ethylene. The development of active and selective catalyst is the key stage of its practical implementation, and detailed information on the mechanism of active catalyst formation and catalytic action is required for their optimisation. Mixed oxide systems containing Na, W and Mn on silica are known to be among the most efficient OCM catalysts [1]. In this study, we applied various preparation procedures and physical characterisation methods (XRD, EPR) to elucidate the nature of active phase and active sites in NaWMn-silica system responsible for its efficiency in OCM reaction.

A series of samples with different combinations of doping elements (Na, W, Mn) and different intermediate treatments was prepared. It was shown that the presence of Na is crucial for the formation of highly-crystalline samples containing α-cristobalite phase. The presence of this phase in the system on a certain stage of preparation is essential for the formation of highly efficient catalyst. However, the high performance can be achieved only if this phase is formed in the presence of W and Mn in the catalyst precursor. In other words, if α-cristobalite is formed when Na is solely present in the precursor, any subsequent addition of W and/or Mn does not lead to the formation of efficient catalyst. Further details of the formation of active sites and their atomic organisation can be derived from EPR spectra of Mn^{2+} and Mn^{4+} cations. It is worth noticing that the formation of such active structures is not essential for other processes catalysed by the same mixed oxides (e.g. CO oxidation).

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Features of Catalyst Processes at Use of 'Spin-on Glass' Films

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Possibility to prepare the nanosized oxide and silicate layers containing diverse catalysts (Pt, Pd, Mn, etc.) is advantage of sol-gel technology. Such thin films spin-coated on silicon and other electronics wafers are named by 'spin-on glass' films. They are used in manufacture of cheap metal-oxide gas sensors on a basis of SnO_2 [1,2]. Unsatisfactory reproducibility of their parameters is one of the problems preventing the organization of such sensors manufacture. To overcome this obstacle, along with necessity of the decision of some other problems, it is necessary to achieve the stable high catalyst activity of films-catalysts. It can be made only on a scientific basis. Here the results of researches carried out by the AFM, ESXA etc. using chips of primary elements of SnO_2-derived gas sensors will be presented. The analysis and interpretation of the received data will allow defining the influence of catalyst elements as well as molecular and phase structure, charging and energy states of catalyst composites on kinetics and balance of processes on interphase border "metal oxide-multicomponent gas mix". Analytical characteristics of test structures will be investigated using the precision automated analytical equipment.

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PP-I-85

Mechanism of Catalytic-Adsorptive Purification of Wet-Process Phosphoric Acid

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Purification of wet-process phosphoric acid (WPA) is proposed to be fulfilled by means of catalytic-adsorptive method on a concentrating stage. Activated coals are desirable to use as a catalyst-adsorbent.

The analysis of changing the admixtures concentration during the purification without using an adsorbent allow to state that the process is limited by fluorine complexes hydrolysis. The application of a catalyst-adsorbent allows to accelerate the decomposition of fluoride complex compounds with alumina, iron and silicon.

Using IR-spectroscopy and potentiometric methods it was found, that carboxyl, phenolic, alcoholic groups were active centers which initiate the decomposition process of fluorine complexes. Hydrolysis of those complexes with the use of carbon material proceeds according to a catalytic mechanism at the expense of fluorination of coal surface by ion-exchange reactions.

Surface groups containing C-F binding are formed as a result of a hydrolysis reaction which was initiated by an activated coal. This statement has been confirmed by the appearance of similar absorption bands on IR-spectrum of a catalyst being analyzed. Partial hydrolysis of surface fluorine containing groups with reduction of initial acid forms of surface groups and the evolution of HF molecules into WPA solution has been observed in the purification process.

It was shown that hydrated ions of alumina, iron and silicon were formed in the solution during the hydrolysis of fluorine complexes. These ions form solid hydrolysis products which crystallize in pores and on an adsorbent surface. Thus active centers of carbon material responsible for fluorination process lose significantly their strength. Therefore the decomposition of fluorine complexes was decreased. Regeneration of coal is necessary for restoration of its catalytic activity.

Kinetic Peculiarities of Vapour-Phase α-Pinene to Camphene Isomerization over Gold Catalyst

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Camphene is an important intermediate for camphor synthesis, which is a valuable product for the pharmaceutical and perfumery industry. The main source for camphene production is α-pinene isomerization [1].

The objective of this work is to study general kinetic regularities and perform kinetic modeling of the vapour-phase α-pinene isomerization to camphene over supported gold catalysts.

The experiments were carried out in the fixed bed glass reactor at atmospheric hydrogen or nitrogen pressure at the reaction temperature between 180 and 210°C. Such catalytic properties as activity, selectivity and stability in α-pinene isomerization were elucidated. The effect of temperature, residence time and initial α-pinene concentration on the conversion and the camphene selectivity over gold metal catalysts was determined. It has been established that after neutralization of acidic sites in Al_2O_3 by alkaline treatment, Au/γ-Al_2O_3 catalyst exhibited high and stable activity: conversion of α-pinene (98-99%) and camphene selectivity (80-90%) were constant during 1-3 hours. Subsequently the kinetic modeling of vapour-phase α-pinene isomerization over the nanosized gold catalyst has been performed.

The part of research work was supported by RFBR Grant № 08-03-91758-AF.

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PP-I-87

Mechanism of Selective Catalytic Pyrolysis of Light Hydrocarbons on Ni-Cu Catalysts

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The process of production of highly concentrated CO_x-free hydrogen and nanofibrous carbon (NFC) by catalytic propane decomposition on Ni-Cu catalysts at relatively low temperatures (500-700°C) was investigated. It was ascertained that the mixture with high H_2:CH_4 ratio (much higher than that at thermodynamic equilibrium) can be obtained under given conditions [1]. Based on experimental data obtained and analysis of the literature we suppose that decomposition of propane over Ni-based catalyst occurs on active centers of two types (S1 and S2). This process is accompanied by chemisorption with the formation of strongly-held species. Depending on the strength of C-S (carbon-center) bonds in chemisorbed species (S-CH_x) either the progressive loss of H atoms with the formation of carbon on the catalyst surface (mainly on centers S1) or bonding of H atoms from gaseous phase with the formation of methane (mainly on centers S2) could happen.

The possible scheme of C, H_2 and CH_4 formation in the process of selective catalytic pyrolysis of C_2–C_4 hydrocarbons is shown in Fig. 1.

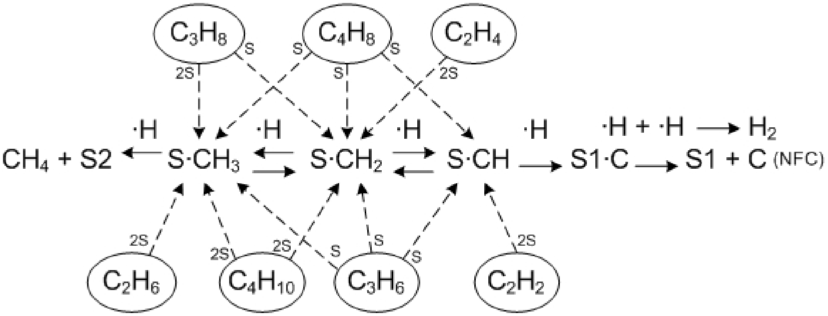

Fig. 1. Scheme of selective catalytic pyrolysis of C_2–C_4 hydrocarbons (S is common sign of centers S1 and S2).

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$MgCl_2$-Supported Ziegler-Natta Catalysts for Propylene Polymerization: Structure of Surface Species

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The “internal” electron donor (ID), for example ethyl benzoate (EB) is a key component which provides the high stereospecificity of Ziegler-Natta catalysts. Several molecular models were proposed to explain the stereoregulating role of ID. However, the data on the quantity and structure of the ID and $TiCl_4$ surface species are still not enough to build the appropriate molecular models of catalytic surface.

In this work adsorption of various ID and coadsorption of these ID with $TiCl_4$ on an activated $MgCl_2$ sample has been studied by DRIFT and analytical technique. As a result coordination of the ID with the surface Mg cations as well as the ID packing on the $MgCl_2$ surface was clarified. Particularly, the monoesters were coordinated by both the oxygen atoms with the $MgCl_2$ surface. The steric factor was significant only for the (104) $MgCl_2$ surface: the larger size the ID had, the less complexes ID formed on this surface. It was observed that $TiCl_4$ could not substitute the ID on the $MgCl_2$ surface. Obviously, $TiCl_4$ occupies the adsorption sites which are inaccessible for the ID because of the steric reasons (the big size of the ID molecules). The surface species of EB which are followed from the experimental data were analyzed by DFT calculations within periodic and cluster approaches.

PP-I-89

Nonequilibrium Mechanisms of Interplay between Heterogeneous and Homogeneous Catalytical Reactions

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The recognized ways of the reactor wall's impact on the homogeneous reactions follow from the chain theory of many of such reactions (H_2 burning in O_2, or Cl_2 and so on). These ways include: a) break of a chain due to loss of gas free radicals at the surface; b) "exit of the reaction from the surface" into the volume of the vessel due to generation of radicals by the walls.

There are some mechanisms involved in these processes discovered or examined by us, which are associated with energy exchange on the surface in the course of homogeneous reactions. The products of exothermic heterogeneous reactions are bearing a plenty of energy as created on the surface. Our group advocates the important role of subsequent energy transfer between excited intermediates (precursors with excess of energy) and the surface of the catalyst. The chemical energy released is first concentrated mainly on the vibrational degrees of freedom of the product molecules, then it is transferred to both vibrational and electronic degrees of freedom of the catalyst. The electronic channel of accommodation of chemical energy manifests itself in a number of nonequilibrium electronic effects examined by us, such as extra thermal radiation of the surface (heterogeneous chemiluminescence – HCL) and a range of electrophysical effects for which however the only chemoexcitation is responsible (these effects are analogous to photoconductivity and photovoltaic effects).

In this report we focus on those effects under chemical excitation of the catalyst (which will be referred to as chemoeffects) that links the heterogeneous processes and the homogeneous ones. Among the chemoeffects of the interest in the context of the Symposium scope we would discuss such effects as nonequilibrium desorption of neutrals as well as electrons and ions emission due to chemical energy released. 1) The ion emission discovered by us is the most intriguing chemoeffect since the lattice components escape the surface during the chemical reaction being ejected from the surface lattice into the gas phase. For example, we found by molecular beam method combined with mass-spectrometry that the reaction of recombination of hydrogen atoms on powdered CaO with Bi-impurity is accompanied by emission of Bi^+, Ca^+, CaO_2^+ ions. The ion emission was also observed in the same reaction on ZnS-Tm. Simultaneously the HCL with the characteristic impurity spectra was observed. A number of the type II – VI and III – V semiconductors were also examined. In the case of atomic oxygen recombination the emission of negative ions also takes place from some catalysts. One of the mechanisms of the emission is associated with nonadiabatic electronic transitions initiated by reactive collisions and transition of the system after that into the antibonding state. The emission of ions due to the exothermic surface reaction comprising the units of the surface lattice has far going consequences. The phenomenon reveals that the reagents from the gas phase participating in the homogeneous process can actively modify the surface properties relevant to catalysis. Physical etching under consideration elucidates on the one hand the mechanism of influence of reactive media on the catalyst (it is of importance for heterogeneous catalysis) and explains on the other hand why the impact of the walls on the homogeneous reaction (e.g. ability to break chains by the particles emitted). The physical etching during a reaction (knocking out of the lattice constituents), making the surface unstable, may cause dramatic effect on the nanocatalysts. It is worth notice that the chemoeffects under discussion (in particular, HCL) were developed by us into powerful tool for *in situ* monitoring the modification of the surface during the catalytic process. 2) We have found that the reaction can stimulate with high efficiency nonequilibrium desorption from the surface of both foreign and its own adparticles. For example, the reaction of recombination of H-atoms causes nonequilibrium desorption of water molecules or adsorbed H-atoms (from Teflon) with the yield of ~ 5 particles per recombination event. We established the V-T mechanism of nonequilibrium desorption and found by mass-spectrometry the isotope effect in desorption of HDO, D_2O and H_2O molecules. The nonequilibrium desorption (chemodesorption) may provide extraequlibrium densities of active particles in the gas phase and may serve as a mechanism for interplay between gas phase (homogeneous) and surface (heterogeneous) reactions. Summarizing, the phenomena under consideration shows that there exists the intensive nonequilibrium mass and charge interplay between the surface and the gas phase due to surface reactions themselves giving rise to mutual influence of homogeneous and heterogeneous factors in catalysis.

PP-I-90

Carbonilation of Olefins in the Presence of the Phosphin-Palladium Complexes

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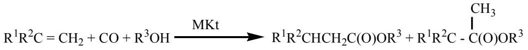
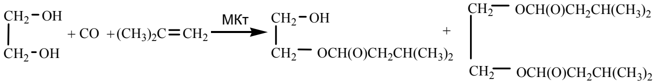
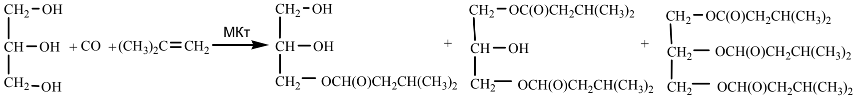
We investigate the catalytic activity of a series of two and three-components systems on the basis of the phosphin-palladium complexes in hydroalkoxycarbonylation of α-alkenes with carbon monoxide and mono- and polyhydric alcohols. The reaction was carried out without use of the solvents.



$$R^1R^2C = CH_2 + CO + R^3OH \xrightarrow{MKt} R^1R^2CHCH_2C(O)OR^3 + R^1R^2C - \overset{CH_3}{C}(O)OR^3$$





R^1=Me, C_5H_{11}; R^2=H, Me; R^3=Me, Et, Pr, i-Pr, Bu, C_5H_{11}, i-C_5H_{11}, C_6H_{13}, C_7H_{15}, C_8H_{17}, C_9H_{19}, CH_2Ph, $(CH_2)_2Ph$, L-menthyl, L,D-menthyl. MKt=PdCl-L-AH, $PdCl_2(PPh_3)$-TsOH, $PdCl_2(PPh_3)$-L-AH, $Pd(PPh_3)_4$-TsOH, $Pd(PPh_3)_4$-L-AH, $Pd(Acac)_2$-L-AH (L-various mono- and bidentate phosphines, A-RCOO, $ArSO_3$)

The high catalytic activity in olefin hydroesterification at low pressure of carbon monoxide (≥ 20 atm) of the system was demonstrated. The most suitable are systems $Pd(PPh_3)_4$-L-TsOH, $PdCl_2(PPh_3)_2$-L-TsOH and $PdCl_2$-L-TsOH (L-PPh_3).

We applied hydroalkoxycarbonylation of α-alkenes (2-methylpropene, 1-heptene, 1-nonene) with carbon monoxide and alconols in the presence of the catalytic systems to prepare a series of esters of isovaleric, caprylic and capric acids, many of which are widely used as perfumes (ethyl isovalerate, pentyl isovalerate, etc.) The reactions were performed in a stainless-steel autoclave (20 atm, 100°C, 4 h). The [alkanol]:[olefin]:[Pd]:[PPh_3]:[p-TsOH] ratio was 435:565:1:7:12. The autoclave at room temperature was charged with the catalytic system and alcohol. The autoclave was hermetized, purged in duplicate with carbon monoxide for deaeration, and charged with olefin, after which required carbon monoxide pressure was effected, and stirring and heating were started. The reaction products were isolated by fractional distillation.

The yields of the target products were 61-93%. The isolated product fraction was analyzed by GLC to determine the linear-to-branched product ratio. The selectivity linear reaction product was 80-100%. Such a high regioselectivity is apparently provided both by the structure of the starting alkenes (α-alkenes) and by the reaction mechanism. The probable mechanism of the reaction was proposed.

It was found that carbonylation of isobutylene with CO in the presence of ethylene glycol yields a mixture of mono- and diglycol esters of isovaleric acid, irrespective of the initial reactant ratio. During the hydroalkoxycarbonylation of isobutylene with glycerol, either mono- and di- or mono-, di, and triglycerides of isovaleric acid are formed depending on the reactant ratio.

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PP-I-91

The Mechanism Reactions of the Epoxidation of Propylene and Allyl Chloride with Titanium Silicalite

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The work presents the mechanisms of epoxidation propylene and allyl chloride by aqueous solution of hydrogen peroxide in medium of organic solvent in the presence of heterogeneous catalyst – titanium silicalite.

While studying it was found that the epoxidation of presented olefins by hydrogen peroxide is performed on the titanium atoms being in tetracoordinate state and runs through formation of the five-member cyclic framework, where a molecule of hydrogen peroxide has the active oxygen atom and can transfer it to olefin molecule. It is important to note that the solvent is not only a homogenizer of the mixture of initial reagents of the epoxidation process, but it takes an active part in the stabilization of Ti-peroxo complex formed by molecule of hydrogen peroxide in of titanium's center of catalyst.

The proposed mechanism of the epoxidation of olefins agrees with the kinetic model process of the epoxidation of propylene and allyl chloride.

PP-I-92

Surface Reconstruction of Polycrystalline Palladium in Oxygen Atmosphere

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To understand the effect of the oxidative reaction atmosphere on the catalyst structure and composition it is necessary to study the surface microstructure of platinum metals in oxygen atmosphere in a wide temperature range. Surface reconstruction of polycrystalline palladium foil in the oxygen atmosphere in the temperature range of 500-15000 K was studied by scanning electron microscopy (SEM) and thermal desorption (TD). Different microstructures were observed to form on the palladium foil surface as the temperature increased. PdO oxide particles with dimensions of 25-50 nm were formed at $T \leq 800$ K. Palladium microcrystals with dimensions of 100-300 nm were formed at 800-1200 K. At $T \geq 1200$ K a grain boundary appeared with gradual growth of grains and formation of crystalline facets. Detailed analysis of scanning electron images of the polycrystalline palladium surface and comparison with the amount of absorbed oxygen showed that the microstructure of the palladium sample surface during the temperature growth from 500 to 1500 K in the O_2 atmosphere was determined by the formation and decomposition of PdO. For instance, at $T \leq 800$ K palladium is readily oxidized to form PdO particles with typical dimensions 25-50 nm. At 800-1200 K the palladium oxide particles decompose to form PdO clusters smaller than 3-5 nm. As a result, the mobility of palladium atoms on the surface increases, and palladium microcrystals with dimensions 100-300 nm are formed. At $T \geq 1200$ K the formation and decomposition rates of PdO clusters substantially increase. This increases the concentration of mobile palladium atoms on the surface of the sample. The growth in the concentration of mobile metal atoms accelerates the surface reconstruction of the polycrystalline foil. Thus, at $T \geq 1200$ K a grain boundary appears. The grains gradually grow, and crystalline facets are formed and cover the whole surface of the grains.

PP-I-93

Oxygen Forms and $La_{1-x}Ca_xMnO_{3+\delta}$ Perovskite Reactivity in Ammonia Oxidation Reaction

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Mixed oxides adopting the perovskite structure form an interesting class of compounds, as their structure and oxygen stoichiometry can be turned to investigate structure-property relations in catalysis. In this work we studied the effect of manganese valence (Mn^{3+}/Mn^{4+}) and oxygen forms in $La_{1-x}Ca_xMnO_{3+\delta}$ depending on perovskite composition (x) on its catalytic properties in ammonia oxidation reaction.

The series of oxides $La_{1-x}Ca_xMnO_{3+\delta}$ (T_{calc} = 900-1100 °C) was prepared by mechanical activation route. The basic features of phase and surface compositions of these oxides have been presented earlier [1]. Several surface oxygen species were determined as separate maxima in the H_2-TPR spectra [2]. The samples were used as catalysts for the oxidation of ammonia to N_2, N_2O, and NO at 200 - 850°C.

The catalytic activity of $La_{1-x}Ca_xMnO_{3+\delta}$ in ammonia oxidation reaction at 200-400 °C was found to be directly proportional to the concentration of Mn^{4+} ions that are suggested to adsorb and activate ammonia molecules. The selectivity to N_2O correlates with the amount of reactive oxygen that released in TPR-H_2 below 420 °C. Probably, ammonia oxidation to N_2O on perovskites occurs via the alternating reduction and reoxidation of the catalyst surface that is in a good agreement with the mechanism proposed for oxide catalysts. However, perovskites show maximum selectivity to N_2O at higher temperatures.

The NO selectivity for studied perovskites at 750-850°C reduces with the increase of the amount of strongly bound oxygen species that did not released in TPR-H_2 up to 700 °C. Thus there seems to be a direct interrelation between catalyst activity and the surface oxygen concentration depending on the perovskite composition, crystal structure and defects in the solid.

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Relationship between the Structure of the Active Sites Inside Fe- and Cu- Containing Zeolites and Their Activity in Fenton-Type Reactions

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Here, we report our studies of the influence of Fe- and Cu-containing zeolites structural topology, acidity and surface properties on their performance of differing in CWPO of *Rhodamine G and Methyl Orange* dyes in water. The catalysts were prepared *via* the ion exchange using Y, Beta, ZSM-5 (MFI) and mordenite zeolites as the parent materials or by direct incorporation of Fe^{3+} or Cu^{2+} heteroatoms in the MFI framework during the synthesis.

The catalyst-composition *vs.* catalyst-reactivity relations and the influence of zeolite structural topology on the catalytic behaviour were determined. The activity of the catalysts strongly depends on the surface properties (hydrophobicity/hydrophilicity, point of zero charge) and texture of the parent zeolite. The catalyst activity is also affected by the metal loading and dispersion of the metal-formed species, reaction temperature, pH and H_2O_2 addition rate. At least three conditions must be fulfilled to make zeolite-base catalysts active towards the dyes CWPO decomposition: (i) the zeolite textural properties should allow existence of metal-containing species; (ii) the possibility of the reversible redox transformation of those species; (iii) providing an optimal rate dye adsorption- desorption. These conditions can be accomplished by variation of the zeolite composition (Si/Al ratio), metal loading and controlling pH level of the reacting medium.

Acknowledgements. This research was supported by the RFBR-NASU grant 08 03 90435 and Integration project SB RAS 31.

PP-I-95

Research of the Mechanism of Nanosized Metal Oxide Action on Regio- and Stereoselectivity of the Hantzsch Reaction

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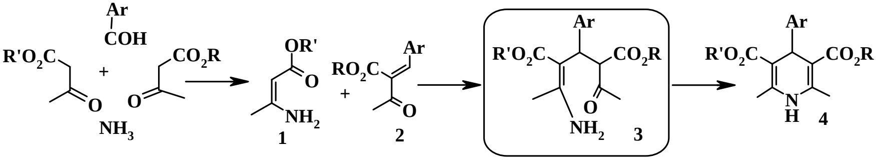
For the first time the mechanism of the Hantzsch reaction in heterogeneous catalysis conditions was investigated. It was shown that in heterogeneous catalysis conditions the reaction runs via product of addition of enamine **1** to chalcone **2**, which (**3**) is not fixed in conventional conditions.



The coordination processes of the Hantzsch reaction participants and basic intermediates on metal nanooxide surface are investigated and it has been found, that activation of initial reagents and intermediates results in increase of selectivity and rate of reaction. It is shown, that simultaneous use of metal nanooxide and chiral modifier results in increase of regio- and stereoselectivity of the Hantzsch reaction. A new one-pot method of synthesis of nifedipine with yield of 87 % is developed. The samples of nitrendipine enriched by S-enantiomer more than on 30% are obtained.

Work is executed with financial support of the Russian Foundation for Basic Research (grants № 07-03-96111, 07-03-96113); the Presidium of the Russian Academy of Science (the project «Heterogeneous catalysts with the use of nanosized metals and their oxides»), and also Korea Atomic Energy Research Institute (contract 01/06 «Development of new chiral catalytic systems on the basis of nanocrystalline metals and metal oxides»).

Development of the Conception on the Nature of the Catalytic Action Effective in the Transformation of Unsaturated Hydrocarbons Systems Based on Pd(acac)$_2$ and BF$_3$OEt$_2$

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The quantative characteristics that prove fundamentals of the basic conceptions on the nature of catalytic action, effective in the transformation of unsaturated hydrocarbons systems, based on palladium beta-diketonates and complexes of boron trifluoride with oxygen containing compounds modified with PR_3 and protonodonors (HBF_4, AcacH, ROH, H_2O), was considered. In view of the aforesaid, the active complexes(**AC**) are hydride complexes $HPd(L, L'_n)BF_4$ (L=substrate; L'=L or PR_3; n=1, 2) in which fragment BF_4 can be bonded to Pd in the form of charge transfer complex $HPd(L, L_n')F{\cdot}BF_3$ (n=0,1) or in the form of ion pair $[HPd(L, L_n')]^+BF_4^-$. In particular, the key precursor of AC $[(Acac)Pd(PPh_3)_2]BF_4$ (II) was identified and isolated with yield of 96% from the products of interaction of $Pd(acac)_2/PR_3/BF_3OEt_2$. XRD analysis showed that complex II has square-planar structure and two organophosporus ligands are coordinated in cis-position to each other. Preliminary experiments showed high activity of the catalyst system $[(Acac)Pd(PPh_3)_2]BF_4/BF_3OEt_2$ in the selective (up to 100%) styrene dimerization into 1,3-diphenylbutene-1 (TON=153000, it in a multiple number of times exceeds literature data). On the base of obtained data two originals techniques for synthesis of cationic complexes $[(Acac)Pd(PR_3)(PR'_3)]^+A^-$ were developed. They allow varying in wide range nature of an anion and organophosphorus ligand.. It has been established that proposed catalyst systems $[(Acac)Pd(PR_3)(PR'_3)]^+A^-/BF_3OEt_2$ can be applied not only in the selective styrene dimerization, but in additive norbornene polymerization too.

Acknowledgment. This work was supported by the joint grant of the Russian Foundation for Basic Research and the Ministry of Education, Science and Culture of Mongolia (Grant No. 07-03-90104).

PP-I-97

On the Mechanism of Methanol Transformation into Hydrogen-Rich Gas Mixtures over Cu-Based Oxide Catalysts

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Currently, processes for H_2-rich gas mixtures production with the view of using them in fuel cells are of significant researchers interest. Such mixtures can be obtained by catalytic transformation of methanol.

In this work, research results are presented on the studies of methanol decomposition, steam reforming and oxidation over Cu-Zn-Al (Al_2O_3; Cu/Al_2O_3; commercial catalyst SNM-1) and Cu-Ce-Zr (CeO_2; $Cu/CeO_2.ZrO_2$; Cu/ZrO_2) catalysts using *in situ* spectrokinetical method.

For Cu-Zn-Al system, spectrokinetical measurements showed that the main intermediates in methanol transformation are bridge and linear methoxy groups which form in breaking of the methanol C-O bond in interaction with surface OH-groups. Over alumina surface, the bridge methoxy group forms dimethyl ether (DME); the linear one forms (through a formate and an aldehyde complexes) CO and CO_2. With copper supported by alumina, hydrogen formation proceeds through recombination of atomic hydrogen forming in mutual transformations of surface complexes over copper clusters. Addition of water into the reaction gas leads to a significant increase in hydrogen formation rate and a decrease in CO formation rate due to more hydrogen atoms and hydroxyl groups adsorbing over the surface.

SNM-1 catalyst (Cu-Zn-Al) has copper oxide interspersed with alumina and zinc oxide. Over its surface, methoxy groups form during interaction of methanol with coordination-unsaturated atoms due to the breakage of the O-H bond in methanol. These methoxy groups are highly reactive, showing a tendency for a change of the reaction route in their transformations, forming methyl formate (MF) in the place of DME which is absent in reaction products. Formate and carbonate are the rapidly-formed intermediates of methoxy groups transformation. In turn, they give hydrogen (through recombination of atomic hydrogen over copper clusters) and CO_2. In the interaction of a methoxy group and a formate one, MF is formed which undergoes decomposition into CO and H_2.

Regarding the Cu-Ce-Zr-O system: over the 5%Cu/CeO_2 catalyst, the following species were found under the conditions of methanol transformation: bridge and linear methoxy groups, formate and carbonate complexes. CO, CO_2, H_2, CH_4 and MF were found in the products. Under similar conditions, over the ZrO_2, Cu/ZrO_2 catalysts there were two types of linear methoxy groups, a bridge methoxy group and a formate complex found. The products were as above with the addition of DME. The difference in product composition is due to the peculiarities of mechanisms responsible for methoxy groups formation. Over 5%Cu/CeO_2, methoxy groups are formed in interaction of methanol with basic hydroxyl groups (with breakage of the O-H bond in the alcohol); over 5%Cu/ZrO_2 – with both basic (breakage of the O-H bond in the alcohol) and acidic hydroxyl groups (breakage of the C-O bond in alcohol). Linear methoxy groups of the first type due to the condensation reaction with the formate complex form MF which gives further CO and H_2. Methoxy groups of second type are the intermediates in formation of DME. The consideration given here shows that the main reactions of hydrogen formation are recombination of its atoms over copper clusters as well as decomposition of MF. CO_2 in gas phase is derived from formate and carbonate complexes, while CO forms in MF decomposition.

In generation of hydrogen-rich gas mixtures from methanol formation of MF is not a desirable reaction, because MF forms down the line CO which is poisonous for fuel cells. In this case, addition of water and oxygen to the feed is of great use – hydrogen yield remains constant, but MF (hence, CO) formation is inhibited. This scenario is caused by a shift toward oxidation of catalyst surface, and over the oxidized surface, the reaction of oxidative transformation of a methoxy group into CO_2 and H_2 (through a formate and a carbonate) dominates over the condensation reaction of a methoxy and a formate into MF (and CO, H_2).

PP-I-98

The Formation of Structure of Meso- and Micro-Mesoporous Metal Silicates in the Catalytic Template Syntheses

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Introduction In spite of the fact that escalating attention to mesoporous oxide materials on the basis of silicates, mechanisms of gelation in a course of template synthesis remain poorly studied. Earlier [1] we reported about the research of influence of initial magnitude of OH^-/Si^{4+} relation on morphology of the mesoporous titaniun-silicates obtained by base hydrolysis in organic-aqueous mediums. In the report we provide some new results about an influence of temperature and duration of synthesis, the nature of metal (Al, Ti, Zr) and character of the metal-containing precursor for size, form and structure of xerogel particles, architecture and the size of mesopores of the calcinated silicates, and also a role of structure directed agents in the course of formation of the structure of silicate at atom-molecular level.

Experiment The synthesis of metal silicates by basic and acidic hydrolysis (OH^- or H^+ as catalysts) in organic-water mediums were carried out at 80-150°C in an autoclave at autogenic pressure. As silicon sources tetraethoxysilane and silicic acid have been used. As metal sources the Al_2O_3, $Ti(OC_4H_9)_4$ and $ZrO(NO_3)_2$ have been used. Ammonium-chloride, N,N-dimethyloctylamine, hexamethylenetetra-amine were used as the structure-directed agents. The texture and morphology of synthesized objects were investigated by XRD, FT-IR, TEM, SEM, AFM, BET methods.

Results We modified the conventional template method by applying of the low-molecular structure-directed agents which forms the olygomer templates during the formation of supromolecular gel. The three-dimensional structure of *in situ* obtained templates defines morphology of received metal-silicate. Fig. 1 shows how the form and the size of $Al_{0.25}Si_{0.75}O_{2+\delta}$ particles differ with the replacement of structure direct agents. Obvious distinctions in morphology of calcinated powders

$Al_{0.25}Si_{0.75}O_{2+\delta}$ are caused, apparently, by various characters of used structure direct agents which define the structure of supramolecular gel-intermediate.

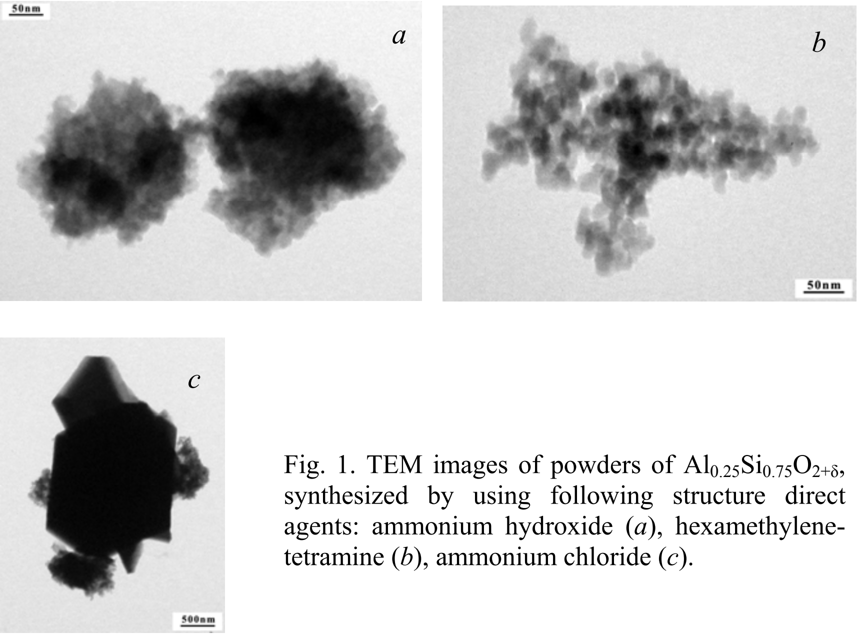

Fig. 1. TEM images of powders of $Al_{0.25}Si_{0.75}O_{2+\delta}$, synthesized by using following structure direct agents: ammonium hydroxide (*a*), hexamethylene-tetramine (*b*), ammonium chloride (*c*).

Also influence of a charging condition of metal (Al, Ti and Zr) on morphology of synthesized silicates was shown by using TEM. The possible schemes of formation of meso- and micro-mesoporous structures of gels and metal silicates under the influence of the considered factors are resulted.

Conclusion A facile, effective and good reproducible method was developed for the preparation of meso- and micro-mesoporous silicates without using of expensive traditional templates. The proposed approach provides to realize a variable mechanism of the formation of porous structures with specified parameters: form and size of pores and nanoparticles, crystalline or amorphous structures of latter and so on.

Acknowledgement This study was supported by the Program № 27 of Presidium of RAS and the Program №7 of the Department of Chemistry and Materials Sciences of RAS.

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PP-I-99

Silica Based Composites in Catalysis of Methane Oxidative Coupling: Influence of Phase Composition

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Introduction

The necessity of natural gas conversion into more valuable or easily transporting products boosted both the applied and academic research activity. Among the methods proposed for the methane upgrading single-stage process of catalytic methane conversion to C_{2+} products (ethylene, ethane, propylene, propane, butenes) - oxidative coupling of methane (OCM) seems very perceptive [1-5]. In this work we report an enhanced method of synthesis of OCM reaction catalysts – silica-based composites Mn/W/Na (Li, K, Rb, and Cs)/SiO_2 [1, 2].

Experimental

Instead of using traditional incipient wetness impregnation method [3, 4] we synthesized these catalysts from dry salts and oxides mixture using ceramic method. The Rb and Cs containing catalysts were synthesized using this method for the first time.

The catalytic properties in OCM were tested in a 650-mm-long flow differential quartz reactor 8 mm i.d. with an external thermocouple pocket 4 mm o.d. under atmospheric pressure using CH_4 - O_2 mixtures. To reduce the space upstream and downstream of the catalyst, the reactor was filled with quartz glass inserts, which were tightly put on the thermocouple pocket. Conversion and selectivity values were calculated from results of gas-chromatography analyses.

Results

Fig. 1 shows that the catalysts obtained by new ceramic synthesis (except Cs-containing sample) demonstrate high methane conversion – 40-49% and high C_{2+} selectivity – 52-66%. The reached C_{2+} yield values (25-29%) are close to the limiting values calculated from kinetic data [5].

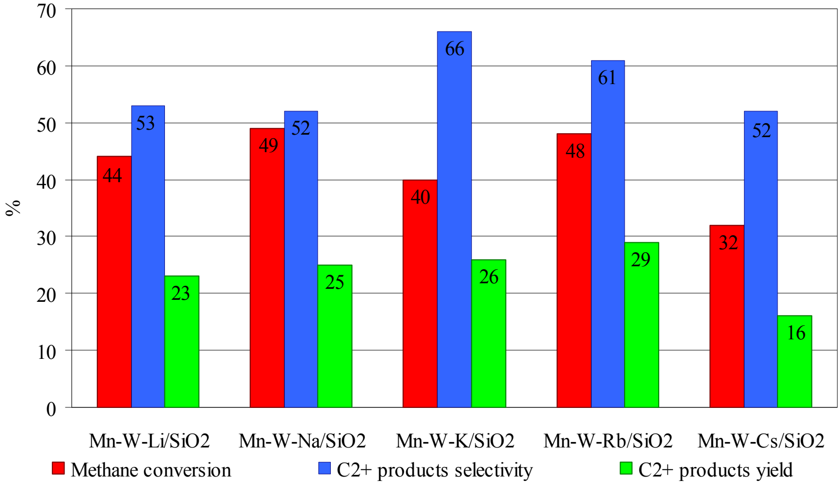

Fig. 1. Results of OCM catalytic experiments with catalysts, synthesized using ceramic method. (CH4/O2 = 2/1 ÷ 3/1; W = 50 – 60 l/(g·h); T = 840 – 900°C).

XRD investigation of the catalysts shows that in fresh composites silica crystallized in a form of metastable tridymite-cristobalite mixture. When this materials undergo long anneal it occurs a silicon oxide transformation into a stable tridymite-quartz state.

Simultaneous existing of two crystalline SiO_2 phases in the temperature range conforming to maximal yield of C_{2+} products authenticates that SiO_2 polymorphism possibly influences on the catalytic activity of the composites studied. Supposedly the existence of the nonstoichiometric tridymite phase promotes the efficiency in methane OCM-conversion. Building a schematic diagram of the quasi-binary system $Na(K, Rb, Cs)_2O – SiO_2$ for phase states with polymorphic SiO_2 modifications (quartz – *Q*, tridymite – *T*, cristobalite – *C*) and melt – *L* (Fig. 2) allows to explain above-said experimental facts.

Conclusions

Thus, the high activity in methane transformation in the presence of catalysts produced by solid-phase synthesis (Fig. 1) can be related to the presence of a forming tridymite–cristobalite mixture in the catalyst structure. An increase in the duration of heat treatment of the oxide composite at 800°C from 6 to 18 h does not lead to a decrease in the C_{2+} yield and the catalyst productivity. In the Mn–W– Li(Na K, Rb, Cs)/SiO_2 catalysts obtained by solid-phase synthesis, there can be a thermodynamic exchange of alkali metal cations between the polymorphic modifications of SiO_2. In turn, this promotes the generation of surface-active oxygen-containing intermediates, which activate the formation of methyl radicals that further enter the dimerization reaction. On the one hand, Mn and W oxides (or salts) act as precursors in the synthesis of composite, and, on the other, they (especially manganese salts) can be involved in redox transformations of methane and oxygen molecules.

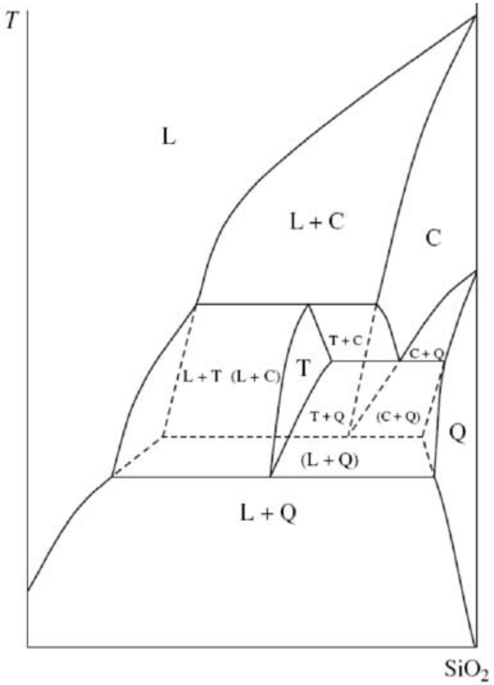

Fig. 2. Fragment of a hypothetical T-x phase diagram of the Na2(K,Rb,Cs)2O/SiO2 system (Q, quartz; T, tridymite; C, cristobalite; and L, melt).

Acknowledgements

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PP-I-100

The Formation of Benzotriazole Cycle in a Liquid Phase Hydrogenation of Substituted Nitrobenzenes on the Heterogeneous Catalyst

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Substituted 2H-benzotriazoles (BT) find wide use as UV absorbers of polymers thanks to their strong photostability activity. The liquid-phase hydrogenation of the corresponding nitroazobenzenes (NAB) on skeleton nickel catalysts is an effective and ecologically pure industrial method for the production of BT. The molecule of NAB includes two reactive groups, which are able to react with hydrogen adsorbed on the catalyst surface. Therefore there are two possible, parallel directions of process. The azo group hydrogenation leads to the nitrohydrazo compound (NHB), and the nitro group leads to the nirosoazo compound (NSAB).The formation of NSAB due to the oxidation of the catalyst surface is not excluded. The hydrogenation di-rection of NHB and NSAB transformation ends with the formation of the corresponding amines, and their benzotriazole cyclization ends with the formation of the benzotriazole N-oxide (NO). The cyclization of NSAB is most probable on a contact surface and the cyclization of NHB occurs directly in bulk solution. This fact complicates treatment of kinetic regularities of the hydrogenation. The NHB homogeneous transformation is connected with the possibility of hydrazo group to give a -proton from β proton to nitrogen atoms of nitro group. The transfer of a nitrogen atom is the most probable process in alkaline media. It is accompanied by the removal of a water molecule and the formation of the benzotriazole cycle. In acidic media, the proton transfer may be hindered due to the nucleophility decreasing of oxygen atoms of nitro-group. Therefore breaking of nitrogen–carbon bonds in NHB occurs with the formation of 3-amino-4-hydroxytoluene or 2-nitroaniline and corresponding radicals. The recombination of the radicals leads to the formation of initial NAB. The NO is the main intermediate compound in NAB hydrogenation, and the BT yield at its reduction is virtually quantitative. Thus a selectivity of BT is determined by the ratio between the rates of heterogeneous and homogeneous stages, which mainly depend on nature of the solvent and its composition.

PP-I-101

Isomerization of Linear Crude Oil Paraffins over Zr-ZSM-5

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Crude oil contains a considerable amount of linear paraffins C_{5+}. So the reaction of isomerization of n-paraffins is very important in obtaining high-octane motor fuels from the straight-run gasoline. This reaction runs over bifunctional zeolite catalysts according to the following pathway: $n\text{-}C_5H_{12} \rightleftarrows n\text{-}C_5H_{12}(HDC) \xrightarrow{-2H(HDC)}$ н-$C_5H_{10}(HDC) \rightleftarrows$ н-$C_5H_{12} \rightleftarrows n\text{-}C_5H_{10}(AC) \rightleftarrows C_5H_{11}^{+}(AC) \rightleftarrows iso\text{-}C_5H_{10}(AC) \xrightarrow{+2H(HDC)} iso\text{-}C_5H_{12}(HDC) \rightleftarrows iso\text{-}C_5H_{12}$, where HDC is the hydro-dehydrogenating center, containing Zr^{4+} cation; AC is the zeolite acidic center.

The condition of the reaction was the following: T=300-380 °C, V=2 h^{-1}, P=1 atm. The feed stock composition was the following (wt. %): arenes – 9.4; iso-alkanes – 25.4; n-alkanes – 31.3; the octane number was 64. The results of isomerization are given in Table 1.

Table 1. Yield of isoalkanes C_{5+}, formed over ZSM-5.

$T_{\text{of the process}}$, °C	300	340	380
Conc. of ZrO_2, wt. %	Yield of isoalkanes C_{5+}, wt. %		
–	29.7	22.0	18.5
2.0	37.3	38.2	36.6
4.0	36.6	36.2	35.0

The modification of zeolite with zirconium stimulates the isomerization reaction. The high octane gasolines, obtained over the zeolite with addition of 2 % ZrO_2, contain their maximal amounts.

Ni-, Cu-Containing Oxide Catalysts of CO Oxidation

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Earlier it was shown, that catalytic active systems on metals can be obtained by plasma-electrolytic oxidation (PEO) method (oxidation in conditions of electric discharge action) [1, 2].

In the present work we investigated some properties and catalytic activity in oxidation CO of Ni-, Cu-containing compositions obtained by an impregnation method of oxide films, formed on titanium by PEO in various electrolytes, with the subsequent annealing. PEO-layers, formed in various electrolytes, have various water uptake (*B*, %), on what the total content of Ni and Cu in the impregnated PEO-layers depends.

Electrolyte	PBW	Na_3PO_4	Na_2SiO_3	K_2SO_4
B, %	0.13	0.08	1.87	0.00
$C_{\sum(Ni,\ Cu),}$ at%	9,0	7,7	29	3,7

The increase in the content of Ni and Cu from 4 up to 29 at, %, leads to decrease of T_{50} by 100°C (from 350 to 250^{0}C), what is possibly connected with increase in a part of the surface containing NiO and CuO which have more easy connected oxygen in comparison to TiO_2 and obviously accompanied also by change of the mechanism of investigated reaction. Influence of an initial PEO-layers surface structure on composition and catalytic properties of catalysts is established.

In the number of investigated samples the best results on catalytic properties are obtained for Ni-, Cu-containing compositions on the basis of the PEO-layers formed in silicate electrolyte.

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PP-I-103

Conversion of Natural Gas over Zr-Mo-Zeolites

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The development of gas processing in Russia for the purpose of the most comprehensive and economic utilization of all components of natural and associated gases is a critical and urgent topic. The uses of the zeolites, which are characterized by high activity and selectivity and are easy to regenerate by oxidative treatment, make the process of aromatization of light hydrocarbons promising for industrial application. The objective of this work was to study the effect of addition of nanosized zirconium and molybdenum powders on the catalytic properties of high-silica zeolite (HSZ) during the direct aromatization of natural gas components.

The investigation has shown that the 4.0% Mo-0.5% Zr/HSZ (SiO_2/Al_2O_3=40) catalyst system exhibits the highest activity and selectivity in the process of conversion of natural gas into aromatic hydrocarbons. Based on the composition of the products obtained on different catalyst systems, may propose the following scheme of transformation of C_1-C_5 lower alkanes on the given polyfunctional catalyst: the activation of methane molecules and C–H bond dissociation occur at the active centers containing molybdenum particles; the zirconium-containing centers mediate the dehydrogenation of saturated C_2-C_5 hydrocarbons present in natural gas, as well as intermediate products formed; and the acid sites of the zeolite per se mediate the cracking of C_3-C_5 alkanes and the oligomerization and cyclization of intermediates yielding aromatic compounds. It is this combination of the zeolite properties with the properties of the transition metals introduced in the form of nanosized powders that is likely to result in the most effective catalyst, a development that can ultimately lead to resolving in the near future the important problem of proper use of natural gas as an inexpensive and available feedstock for the manufacturing of valuable chemicals.

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Hydrogen Production via Ethanol Steam Reforming on CeO_2-Based Catalysts

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Today, hydrogen is considered the most ecologically friendly fuel taking into account cognizance that water which does not pollute the environment is the only by-product when hydrogen is used in fuel cells. There are different ways of producing hydrogen. Hydrogen can be obtained from the electrolysis of water but this process is energy-consuming. Steam reforming of methane and gasification of coal produce synthesis gas, a mixture of CO and hydrogen which can not be used for fuel cells as a result of polymer membrane destruction by carbon monoxide. Methanol conversion which produces relatively pure hydrogen is not suitable for domestic purposes because of the high toxicity of methanol. Alternatively, hydrogen could be obtained from the reforming of ethanol. The advantage of using ethanol is that it is obtained from biomass, i.e. it's renewable

$$CH_3CH_2OH + 3\ H_2O \rightarrow 2\ CO_2 + 6\ H_2 \qquad (1)$$

However a number of side reactions exist leading to formation of other compounds:

$$CH_3CH_2OH + H_2O \rightarrow 2\ CO + 4\ H_2 \qquad (2)$$

$$2\ CH_3CH_2OH + H_2O \rightarrow (CH_3)_2C{=}O + CO_2 + 4\ H_2 \qquad (3)$$

$$CH_3CH_2OH \rightarrow C_2H_4 + H_2O \qquad (4)$$

The most important are CO production (2), ethanol to acetone conversion (3), ethanol dehydration (4), and some others leading to formation of acetaldehyde, methane, and other carbon containing compounds. Reaction (1) need high temperatures $> 500\ ^oC$ and the catalysts are ceria supported transition metals. The properties of supported ceria catalysts are very sensitive to the ceria structure, particle sizes, and surface area.

Currently, we have developed the method based on ceria precipitation from water/alcohol mixtures producing near uniform ceria samples with high surface area and particle sizes between 4-8 nm. After incipient wetness impregnation of ceria with corresponding amount of metal nitrate, followed by calcination at 400 ^{o}C in air flow. The achieved ethanol conversion values show that all of the metals promotes hydrogen yield in comparison with pure ceria to 2 molecules of hydrogen per one molecule of ethanol. The lowest CO yield (< 1%) was achieved on Cu/CeO_2 system but the quantity of acetone and acetaldehyde was rather high (17%). Nickel promotes CO formation, but the yield of H_2 is higher and production of oxygenates is low.

The effect of the size of cerium oxide particles on the conversion of ethanol and the difference in activity of catalysts promoted with copper and nickel are studied in this work.

$LaSrFeO_4$ Nanophases in $La_{1-x}Sr_xFeO_{3-y}$ Perovskites: Formation Specialities and Catalytic Properties

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Mixed oxides with perovskite structure appear to be suitable for high-temperature catalytic processes. Mechano-chemical (MC) method is known as very promising approach for perovskite catalysts preparation. In this communication the influence of Sr containing precursor taken for MC synthesis on catalytic properties of $La_{1-x}Sr_xFeO_{3-y}$ oxides in deep oxidation processes is discussed.

Different series of $La_{1-x}Sr_xFeO_{3-y}$ system ($0 \le x \le 1$) were prepared by preliminary mechanical treatment following by calcination at 1100 or 1200 °C for 4 hours. Preparation details of “N-series” and “C-series” are in using of $Sr(NO_3)_2*6H_2O$ or $SrCO_3$ as Sr containing precursor. Detailed investigations of the surface/bulk composition, structure, catalytic properties and reactivity of samples were carried out by using XRD, differential dissolution method, SAXS, SIMS. Phase composition and microstructure specificity of N-series are in formation of supported $LaSrFeO_4$ nanophase on the surface of $La_{1-x}Sr_xFeO_{3-y}$ perovskites.

Studies on catalytic performances of $La_{1-x}Sr_xFeO_{3-y}$ systems in methane oxidation process revealed different catalytic behavior of N-series and C-series. In perovskites of C-series the Sr-substitution leads to the decreasing of specific catalytic activity (SCA) value in CH_4 oxidation process, approximately in two times (for x=0.2), all other substituted samples show a similar SCA with selectivity (CO_2) = 100 %. For samples of N-series SCA value reaches its maximim on the sample with x=0.75 characterized by maximum amount of randomly situated anion vacancies and presence of supported $LaSrFeO_4$ nanophases on the surface. Assumed methane activation on $LaSrFeO_4$ nanophases is discussed in the terms of acid-base reaction. It was suggested that SrO layers of $LaSrFeO_4$ nanophase could act as strong base - active sites for hydrogen abstracting, and anion vacancies could play a role for regenerating of surface oxygen forms $O_{(s)}^{2-}$ in the process $O_2^- \rightarrow O_{(s)}^{2-}$.

PP-I-106

Dimerization of Isobutene on Superacid Catalysts

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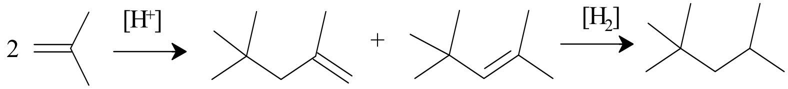
Oligomerization of gaseous olefins is a process widely used in industry for a preparation of different useful products and for a “liquification” of gaseous fractions for fuel production [1]. Isooctane is one of the most important and ecologically friendly components of fuels. Isobutene can be effectively dimerized into an isooctenes mixture under the action of different solid superacids - sulfated metal oxides [2, 3].

This work is dedicated to isobutene oligomerization on novel superacidic catalyst – sulfated tin oxide.



№	Catalyst	Temperature, ^{0}C	Yield, %		
			C_8	C_{12}	C_{16}
1	5% $NiSO_4$/ SnO_2	18	7	87	6
2	H_2SO_4/SnO_2	18	2	68	30
3	H_2SO_4/SnO_2	120	48	48	4
4	5% $NiSO_4$/ SnO_2	150	54	44	2
5	H_2SO_4/SnO_2	150	54	43	3
6	H_2SO_4/SnO_2	180	73	27	0

It is clearly seen from the table above that the temperature increase from 18 to 180 ^{0}C seriously increases the isooctenes content and decreases the content of C_{12} and C_{16} olefins. The comparison of 4 and 5 entries reveals that the presence of Ni^{2+} ion does not effect the process.

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PP-I-107

Abietic Acid in the Synthesis of New Chiral Catalysts of Asymmetric Reactions

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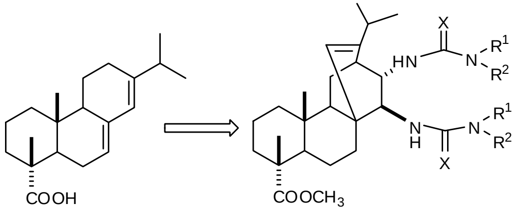
Phytogenic diterpenes have been under intensive investigation for many years. Procedures of synthesis of P-, N-containing ligands starting from tricyclic diterpenes, levopimaric and dehydroabietic acid were described in literature. The prepared chiral diphosphines, diphosphinites, amines, azomethines and ureas were used as ligands for catalysts of asymmetric reactions [1]. As a result of our further investigations we developed the new schemas of the synthesis of nitrogen containing ligands on the basis of the transformations of abietic acid.

Synthesis of chiral ureas and thioureas was developed starting from the adduct of abietic acid (**1**) with fumaric acid.



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X - O, S; R^1- H, Met, Et; R^2 - Met, Et, Bn

Chiral nitrogen-containing ligands were synthesized from abietic acid and used for preparation of chiral Ru and Rh complexes. It was demonstrated that Ru and Rh complexes with these chiral ligands were active as catalysts for asymmetric reduction of acetophenone. Depending on the conditions in which the reaction of the acetophenone reduction was carried out, the mixture enriched by R- or S- phenylethanol was obtained.

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PP-I-108

Kinetics and Mechanism of Ozone Decomposition on Catalysts Based on Transition Metal Oxides

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Heterogeneous catalytic ozone decomposition is the best way to destroy residual quantity of this unique, non-polluting, but highly toxic (MPC = 0,1 мг/м^3) oxidant from gas emission. Highly active cement-containing catalysts based on transition metal oxides (Ni, Cu, Mn, Co, Fe, V) are widely used in practice. These catalysts are developed in the chemical department of M.V.Lomonosov Moscow State University [1].The catalysts activity in ozone decomposition decreases when passing from Ni to V. The fraction of active collisions of ozone with surface is ~10^{-4}. For example, for low-active materials like stainless steel and quartz this value is 10^{-7}-10^{-9}.

The first order and macro kinetic properties of ozone decomposition reaction are determined experimentally.

Two-stage process is one of the possible mechanisms of ozone decomposition on the surface of catalysts [2]:

$$\begin{aligned} O_3 + (Z) &\xrightarrow{k_1} (ZO) + O_2 \\ O_3 + (ZO) &\xrightarrow{k_2} (Z) + 2O_2, \end{aligned} \quad (1)$$

which is correspondent to the equation for velocity of ozone decomposition reaction:

$$-\frac{d[O_3]}{dt} = \frac{2k_1k_2[Z_0]}{k_1 + k_2}[O_3], \quad (2)$$

where Z = Z_0 – (ZO); Z_0 – is an initial number of centers.

The first stage isn't worked out in detail, although evidently, it consists of several elementary stages: chemical adsorption of ozone with a break of molecular bond and formation new Z-O bond and molecular oxygen. Transfer of electronic density from active centers – metal ions in the molecular of oxide to ozone increases its dipole moment and makes the molecule of ozone unstable. If the temperature is low, ion radical O_3^- can be formed. The second stage is proved by the fact that the signal of

ESR from electron, localized on atomic adsorbed oxygen ZO, disappears in the result of reaction with ozone while entering in the sample of ozonized air. Scheme (1) explains both mentioned above monoxides catalysts activities: in ozone decomposition reaction and toxic action of water fume.

Activity of catalysts based on transition metal oxides is determined by electronic donor properties of the surface, which is opposite to bond’s energy of oxygen with the surface. These values are determined experimentally [3]. Actually, for metal oxides with strong bonding of oxygen with the surface (for example, Fe, V), $k_1 >> k_2$ and velocity of ozone decomposition reaction is not so high. Many researchers consider the stage of desorption of molecular oxygen to be the limiting stage in ozone decomposition process.

During the adsorption of water, governed by the transfer of oxygen’s electronic pair of water molecule to catalysts, displacement of ozone from active centers takes place. Catalysts with high electronic donor properties, for example, containing nickel and noble metals are less exposed to being poisoning by water.

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PP-I-109

Regeneration of the Catalysts Based on Aqueous Solutions of Mo-V-P Heteropoly Acids under O_2 Pressure

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The solutions of Mo-V-P heteropoly acids, $H_{3+x}PMo_{12-x}V_xO_{40}$ (HPA-x), are well-known reversible oxidants in numerous catalytic processes of organic substrates oxidation with dioxygen. HPA-x regeneration (*i.e.* oxidation of their reduced forms with O_2) is the *key* stage of the processes. Therefore, it was important to find optimal conditions for fast regeneration of the HPA-x solutions.

Regeneration of 0.1–0.4 M aqueous HPA-x (x = 2–4) solutions with O_2 proceeds fairly fast at 393–413 K and $P_{O_2} \leq 8$ atm [1]. When temperature is increased, rate and depth of regeneration rise. The often used 0.2 M HPA-4 solution, however, turns unstable at T>413 K yielding vanadium-containing deposits. The 0.2 M HPA-2 solution is regenerated slower, but it is thermally stable up to 463 K. Features of mechanism of the HPA-x solutions regeneration are considered. It was found that the apparent activation energy of the regeneration strongly increases as its depth rises. This is because a change of limiting stage of this reaction.

Recently we have developed new compositions of Mo-V-P heteropoly acids (named as HPA-x') solutions that are stable up to 443 K [2]. During long exploiting at temperature interval 333–443 K, catalysts based on the HPA-x' solutions remain homogeneous. Regeneration of the catalysts is carried out at 433–443 K, P_{O_2}=3–4 atm during 20 min.

The fast regeneration of catalysts based on the HPA-x' solutions permits to realize a whole series of processes of various organic compounds oxidation.

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PP-I-110

Cumene Hydroperoxide Cleavage Catalyzed with 5-Substatuted 2-Hydroxybenzene Sulfoacids

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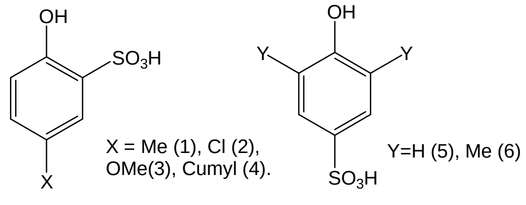
Acid-catalyzed cleavage of cumene hydroperoxide (CHP) is the main stage of phenol and acetone mutual production commercial process [1]. Nowadays, sulfuric acid is used as a catalyst of this process at each plant, while the cleavage is carried out in reaction products media. Maximal selectivity of the process can be reached decomposing CHP within two stages: at 50 and 130 °C [2].

Investigating CHP cleavage parameters at pilot laboratory installation, allowing to model the two-stage technology, reaction mass obtained by phenol and sulfuric acid intermix was discovered to be a more active CHP cleavage catalyst, comparing to the acid itself. Considering that phenol can easily be involved in sulfurization reaction, giving phenolsulfoacids, one can assume that a catalytical particle has been changed in this case, providing the effect observed.

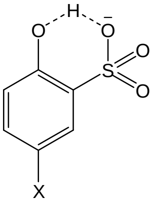
Aimed to check up this hypothesis, which is not described in literature, we have synthesized serial of substituted ortho- and para-phenolsulfoacids. Structure and purity of the obtained acids was proved by NMR-spectroscopy methods.

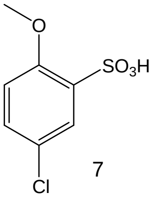


Kinetic experiments for the acids catalytic activity investigation were carried out at constant CHP conversion at first stage. This condition was reached varying the catalyst concentration in flow reactor. As the results show, various molar concentrations of the investigated acids are needed to keep one and the same CHP cleavage velocity.

Comparing to sulfuric acid all the tested ortho-phenolsulfoacids show 3 – 3,2 times higher catalytic activity; while para-phenolsulfoacids appeared to be 2-2,2 times less active. It is interesting to note, that in both cases no aromatic ring substituent influence were found using modern experimenting methods.

Probably, in phenol-aceton media, which does not have high level of dielectric coefficient, solvation effects are more favorable for better delocalized anions. Among other ortho-phenolsulfoacids, these, first of all, should be the anions, which can form intramolecular hydrogen bond with circular conjugation. These conclusions can indirectly be proved with acid 7 catalytic activity data, as this anion cannot have itramolecular hydrogen bonds. Experiments show acid 7 activity in CHP cleavage process is approximately equal to the one of sulfuric acid, i.e. 3 times lower comparing to other ortho-phenolsulfoacids. Arilsulfoacids having no hydroxyl-groups demonstrate close activity, e.g., p-toluenesulfoacid.





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This low activity of para-phenolsulfoacids can be explained by the following factors: impossibility to stabilize anion due to intramolecular hydrogen bonds, mesomeric effect of sulfo-group and oxy-group of an aromatic ring conjugation.

Commercial phenol quality depends mainly on the following two micro-admixtures concentrations: hydroxyacetone and 2-methyl-benzofurane. The latter can form because of hydroxyaceton and phenol condensation. We have found that using ortho-phenolsulfoacids as the process catalysts, one decreases hydroxyacetone yield down 3 – 3,5 times. Hydroxyaceton formation is well-known from literature to be an acid-catalyzed process. [3]. Most probably, this time we observe common acidic-catalysis, where by-product yield depends on total acid concentration in system.

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PP-II-1

IR-Spectroscopic Evaluation of Surface Intermediates of Propane Partial Oxidation by Nitrogen Monoxide over Fe-ZSM-5

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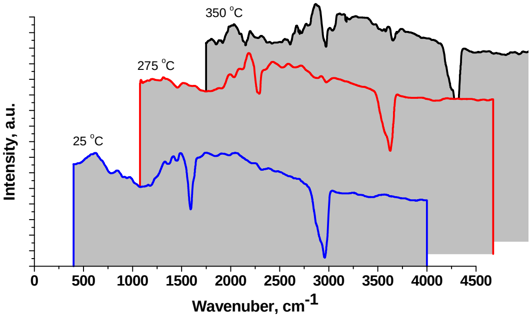
Activation of light alkanes for the purpose of production of valuable products is an actual direction of oxidative catalysis. Last years the achievement of certain successes in direct oxidation of light alkanes is connected with application of nitrogen oxides (NO_x) as oxidants [1]. Earlier it has been shown [2], that Fe-ZSM-5 catalyzes the partial oxidation of C_3-C_4- alkanes by nitrogen oxides (NO, N_2O) with formation oxygen-containing products (C_2-C_4-oxygenates), also the compounds containing atoms of C, O, H and N(III) – *amines* and *nitriles* (CH_3CN, $C_2H_5NH_2$, $HOCH_2CH_2NH_2$) were identified by mas-spectrometry methods. For the purpose of definition of the surface intermediates for propane oxidation by NO in the present work the (co)adsorption of NO and C_3H_8 on Fe-ZSM-5 is studied by the IR-spectroscopy method.



On Fig. 1a the IR-spectrum of the catalyst Fe-ZSM-5 after adsorption of a reactionary mixture (NO+C_3H_8) and holding at a room temperature is resulted. At a spectrum there are the absorption bands, characteristic for nitrogen (II) oxide and the propane, observed at their individual adsorption. Step rise in temperature to 250°C did not lead to appreciable changes in spectra whereas at 275°C in the IR-spectrum of the sample (b) the absorption bands with maxima at 1750, 1850, 1960, 2070 and 3430 cm^{-1} are shown, that, possibly, is connected with formation of intermediate compounds. So, items in the field of 1620-1720 cm^{-1} can be connected with adsorbed on the active centers acetone, propanile ($\nu_{C=O}$), acrolein or propene ($\nu_{C=C}$). Absorption in the field of 2100 cm^{-1} is characteristic for the compounds containing *nitrile*-group [3]. The wide absorption band with a maximum at 3430 cm^{-1} can be connected with formation of hydrogen bands (SiAl (OH) ··· HOC-CH_2-CH_3) [4]. Rise in temperature to 350°C leads to appreciable change of spectra of absorption in the field of 1600-2100 and 3400-3610 cm^{-1} (c). Occurrence of the absorption band in the field of hydroxyl group fluctuations at 3740 cm^{-1} (ν_{O-H} of the zeolite catalyst) simultaneously with decrease of intensity of items of hydrogen bands of 3400 cm^{-1},(ν_{O-H}) and occurrence of items at 3610 sm^{-1} (ν_{O-H}), can be connected with desorption of the formed products of reaction, in particular alcohols, to what more difficult character of absorption spectra in the field of valence fluctuations of CH-, CH_2-, CH_3-groups also testifies. Redistribution of items in the field of 1600-2100 cm^{-1} can be connected with formation of alcoxy, carbonilic intermediates and also the structures containing CN-bands [3].The obtained data taking into account literary show possible sequence of the reagents transformation in reaction of partial oxidation C_3H_8 - NO:

C_3H_{8ads} +(NO_2^-/NO_3^-)$_{ads}$→[-CH_x, -CN, -COOH]$_{ads}$→CH_3CN, C_3H_6O, C_3H_7OH, C_2H_5OH, C_2H_5COOH.

Activation of the propane can occur on the acid centers of the catalyst, in our case on proton (H^+) centers of zeolite Fe-ZSM-5. NO is activated on the Fe-containing redox-centers with formation of nitrates-ions, interaction of the last with the C-H bands of propane weakened as a result of adsorption, leads to formation of adsorbed intermediates, containing C, N and O atoms. So, formation of alcoxides and carbonilic compounds, and also amines and nitriles begins at 275°C, with raising of temperature to 350°C they are desorbed from a surface of the catalyst with formation of oxygenates - ethanol, propanol, acetone, propionic acid, as well as acetonitrile and etilamine.

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Study of the Process of Aluminium Activation by Liquid In-Ga Eutectic

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It is known that alumina activated by liquid In-Ga eutectic can interact with alkyl chlorides and form active Lewis acids as potential catalysts of transformations of alkanes and alkenes under moderate conditions [1]. Earlier in the work [2] it was demonstrated by ATR FT-IR that liquid In-Ga eutectic produced disappearance of oxide layer from metallic alumina surface. At the same time accumulation of oxide components (Al and O) was observed by SEM/EDS on In-Ga eutectic. These results point to destruction of the oxide layer.

In this report the main results in the study of composition of the surface layer on aluminium at the contact with liquid In-Ga eutectic by using Auger Electronic Spectroscopy (AES) are presented.

Spectral data analysis has revealed that only the oxide layer is observed on Al surface with the depth to 20 nm. After the contact of an alumina plate with a drop of liquid In-Ga eutectic AES signals from the eutectic components are registered from the depth ~ 2-3 nm up to the maximum depth ~ 170 nm. The antibate dependence is observed: with the increasing of eutectic components contents by depth, oxide layer components contents decrease. This result confirms destruction of the oxide layer at the aluminium interface by In-Ga eutectic.

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PP-II-3

Dry Reforming of Methane over Intermetallides

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The methane reforming with CO_2 seems to be a promising reaction system useful to reduce the greenhouse contribution of both gases into the atmosphere. On this basis, and considering the potentiality of this reaction system, the dry reforming reaction has been carried out in an tubular flow reactor using new type of catalysts which are intermetallides.

Catalytic systems based on the Ni_3Al intermetallic compound and modified with different transition metals were studied in methane reforming with CO_2. The catalysts were prepared by the method of self-propagating high-temperature synthesis. The X-ray diffraction patterns were measured at room temperature using diffractometer Shimadzu XRD-6000 Morphology of catalysts was investigated using two high-vacuum microscopes: SEM Philips 515 and Jeol 6460LV. The surface areas (BET) were determined by nitrogen adsorption using an automated gas adsorption analyzer (ChemiSorb 2750, Micromeritics, USA) linked with mass-spectrometer QMS-300 (Stanford Research System, USA). DTA-TG measurements were conducted using STA 409 Luxx (NETZSCH, Germany).

In summary, it was shown that the intermetallides are active catalysts of DRM and it was proposed the mechanism of CO and H_2 formation.

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Propane Conversion on Zn-Modified Zeolite BEA Studied by MAS NMR in situ Spectroscopy

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High-silica zeolites modified with Zn attracted much interest as the catalysts of light alkane aromatization. Despite intense studies a detailed mechanism of alkane aromatization and the role of zinc species on the reaction network remains a subject of debates. In this paper *in situ* ^{1}H and ^{13}C MAS NMR, which was proved to be a powerful technique for the investigation of the mechanisms of hydrocarbons conversion, was applied to study propane transformation into aromatic hydrocarbons on Zn-modified zeolite BEA.

The use of reagents with selective ^{13}C- labels allowed observation of olefinic intermediate characterized by the signals at 165, 110 and 20 ppm and Zn-allyl species with the signals at 165, 94 and 26 ppm. These intermediates transformed further to aromatics, as well as to ethane and methane. The kinetics of propane conversion has been studied *in situ* at temperatures 623-673 K by ^{1}H MAS NMR. The mechanism of propane conversion was analyzed by comparing the experimental and simulated kinetics based on analysis of the possible kinetic schemes of alkane to aromatics conversion.

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PP-II-5

Resting States in Methylalumoxane (MAO)-Activated Zirconocene Catalysts for α-Olefin Polymerization – an *in-situ* NMR-Study

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Reactive species in MAO-activated zirconocene *pre*-catalyst systems have been characterized in detail [1], but surprisingly little is known about catalyst species which are present when such a polymerization catalyst is actually at work in the presence of excess monomer. Resting states to be considered for such catalysts include species with Zr-bound polymer chains stabilized by contact ion pair formation [2], by an agostic interaction [3] or by $AlMe_3$ adduct formation [4], as well as Zr-bound polymer chains ending in a secondary unit [5] or in an allyl group [6].To gain information with regard to the species actually present under realistic reaction conditions, we have studied $Me_2Si(ind)_2ZrMe_2$/MAO catalysts by NMR methods while these are actively polymerizing 1-hexene. We show that species of the types $Me_2Si(ind)_2Zr(\mu\text{-}Me)_2Al(Me)_2^+$, $Me_2Si(ind)_2Zr(\mu\text{-}R)(\mu\text{-}Me)Al(Me)_2^+$ and $Me_2Si(ind)_2ZrMe^{+}\cdots MeMAO^{-}$, and a fourth, NMR-silent species are present in comparable quantities in these "working" catalyst systems.

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Influence of Strong Electric Fields on the Growth of Platinum Nanooxides and Their Interactions with Molecular Hydrogen

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In high-vacuum experiments the influence of strong electric fields, which were created by the scanning tunneling microscopy tip, on the growth, modification, and disruption of platinum nanooxides and their interactions with molecular hydrogen was studied by the «nanolaboratory» method. Dependencies of platinum oxidation rates on applied contact voltage, as well as on its polarity, were established and interpreted. The possibility of reversible changes stimulated by field in the atomic structures of oxide phases was demonstrated. It was found for the first time, that the field-accelerated damped self-oscillations of chemical reactions, which took place at the interaction between molecular hydrogen and PtOx, was polarity-dependent. Obtained results, modeling the influence of charges of small metallic particles on their catalytic activity, introduce the new size parameter determining maximum sizes of nanoparticles, whose reactivity depend on the local electric fields, into the theory of applied catalysts.

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PP-II-7

The Influence of Gold Addition on Carbon Deposition Formed on Ni-Au/Al_2O_3 Catalysts in POM Process

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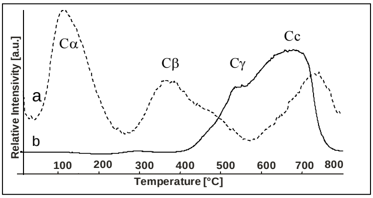
The high affinity of nickel to nickel carbide formation and following transformation and growth of graphite like deposition caused the danger of carbon deactivation for these catalysts. The formation of several types of deposition: polymeric, filamentous and graphitic carbon was observed on the surface of nickel catalyst during the CH_4 reforming reactions [1]. The limitation of carbon deposition could be achieved by electron and/or structure changes of Ni active sites [2].

The aim of this work was to prepare active and stable bimetallic 5%Ni-x%Au/Al_2O_3 (x = 0,1-2) catalysts and find correlation between gold addition and type and amount of carbon deposition formed during partial oxidation of methane (POM).

The monometallic 5%Ni/Al_2O_3 catalyst showed 20% of CH_4 conversion at 900°C and after several hour at this temperature it showed about 80% of conversion. The gold (0.1-2%) doped catalysts showed the CH_4 conversion in the range 40-100% at 900°C and optimal composition of catalyst was achieved for 5%Ni - x%Au/Al_2O_3 (x = 0.5, 1), for which about 100% of CO yield and above 95% of CH_4 conversion was observed.



The 24h stability test in POM reaction lead to 23% wt. of carbon deposition on monometallic 5%Ni/Al_2O_3 system. The tree times lower deposition demonstrated catalysts doped by gold. Furthermore bimetallic systems showed only slight amount of graphitic (Cc) and filamentous (Cγ) carbon – responsible for deactivation, while dominate were adsorbed (Cα) and polymeric (Cβ) species taking part in synthesis gas production.

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PP-II-8

Lanthanide's Luminescent Probe – the Efficient Instrument of a Mechanism Studying of C-C Bond Cycloalkanes Activation and Splitting

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The new one-pot method of the cycloalkanes (C_5-C_{10}) hydrogenolysis to appropriate acyclic (linear) alkanes by using as the catalyst the new bimetallic lanthanide and aluminum-containing catalyst $TbCl_3{\cdot}3H_2O{\cdot}3(EtO)_2AlOH$ (**CAT**) in combination with i-Bu_2AlH and also lanthanide's luminescent probe for the mechanism studying of this catalyst's action have been developed. The hydrogenolysis proceeds selectively (the yields of alkanes are 70-80%) in simple technological equipment and very mild conditions (80ºC, 760 mm Hg), in difference from known methods. The interaction **CAT** with i-Bu_2AlH on the first stage of the mechanism's researching for monitoring the changes in coordination neighboring of Tb^{3+} ion in catalytic process was studied. The photoluminescence spectrum of **CAT** has maxima at 493, 546, 586, 593 nm and shoulder at 550 nm. The Tb^{3+*}ion lifetime - τ (Tb^{3+*}) is 900 μs in **CAT**. The i-Bu_2AlH addition to **CAT** solution in dioxane causes intensive formation of i-BuH and change of luminescent parameters of Tb^{3+} ion: τ (Tb^{3+*}) = 10-20 μs, maxima of photoluminescence – 492, 543, 580 and 590 nm. The formation of i-BuH occurs in reaction of crystalline water of **CAT** with i-Bu_2AlH. The view of photoluminescence spectra after **CAT** and i-Bu_2AlH interaction indicates on the preserving of oxidation state ion Tb^{3+} and significant changes of it's coordination sphere as a result of water molecules remove and formation of bridge structures, containing Tb-Cl-Al and Tb-H-Al fragments.

PP-II-9

About the Reaction Mechanism of the Aniline Condensation with Butyraldehyde Catalyzed by $LnCl_3{\cdot}6H_2O$ Crystalline

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The new type of chemiluminescent-catalytic conversion – reaction of condensation of aniline with butyraldehyde, catalyzed by crystalline $LnCl_3{\cdot}6H_2O$ (Ln = Ho, Tb, Eu), in which Ln^{3+} ion is a radiating and highly efficient catalytically active center was found. Reaction is carried out in DMFA; the yield of the basic product 2-propil-3-ethylquinolin 94 %. The mechanism of $LnCl_3.6H_2O$ action was studied with application of luminescent methods: photoluminescence, chemiluminescence (CL) and Ln^{3+*} ion lifetime measurement and also by quantum chemical calculations (AM1/RHF), modeling the separate stages of reactions and a complex of analytical methods. The probable scheme of condensation is suggested. The active form of the catalyst is complex $LnCl_3{\cdot}4DMFA$. Cl emitter nature depends on Ln nature. For catalyst were Ln = Tb, Eu emitters are electronically excited states Tb^{3+} (λ_{max} = 485 and 545 nm) and Eu^{3+} (λ_{max} = 610 nm) ions generated by energy transfer from the reaction condensation the key intermediate 1,2-dehydro-2-propil-3-ethylquinolin. When Ln = Ho emitter is electronically excited states of 2-propil-3-ethylquinolin (λ_{max} = 450 and 515 nm).

In situ FTIR Study of 3-Cyanopyridine Transformation on V-Ti-O Catalyst

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Nicotinic acid and nicotinamide are vitally important B_3 vitamin. Nicotinamide is produced via hydrolysis of 3-cyanopyridine (3-CPy) obtained by oxidative ammonolysis of β-picoline (β-P). Nicotinic acid is produced via oxidation of β-P by air oxygen; measurable amounts of 3-CPy are formed as a side product. Both syntheses employ the V–Ti catalyst. In the present work transformation of surface complexes of 3-CPy on V–Ti catalyst are studied by in situ FTIR spectroscopy.

A sample containing V_2O_5 in amount of 20 wt. % and TiO_2 in amount of 80 wt. % was prepared according to [1]. The catalyst surface area was 100 m^2/g. In situ FTIR experiments were performed in a flow IR cell-reactor with a Bomem BM-102 FTIR spectrometer. The catalyst powder was pressed into a self-supported 1×3 cm wafer. The wafer was mounted into a quartz IR cell-reactor with a CaF_2 window and was activated in air flow at 300°C for 60 min. 3-CPy used for the adsorption was from Aldrich Chemical Company, Inc. (purity 99%). The adsorption was carried out at 130°C by injecting 3-CPy into air flowing through the reactor cell.

In the temperature range of 130–290°C two types of adsorbed 3-CPy bound to different sites (V^{5+} or H^+) were found to transform into surface nicotinamide by the mechanism of surface hydrolysis involving lattice oxygen and Brønsted acid sites. At 220–290°C the surface heterocyclic complexes decompose to form carboxylates and ammonium ions. Carboxylates are a source of deep oxidation of heterocyclic compounds, and formation of ammonium (due to decomposition of heterocomplexes) explains a remarkable yield of 3-CPy in the absence of ammonia in the reaction mixture at the β-P oxidation.

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PP-II-11

Co- Catalytic Effect of Re- and W-Contained Oxides in Alcohols Cross-Coupling Reaction

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Based on homo- and heterometallic W-, Re- alkoxide complexes as precursors the catalyst containing nanostructured W and Re oxides on γ-Al_2O_3 surface was prepared and studied in novel cross-coupling reaction of aliphatic alcohols to form a fraction of alkane-olefin.

The relationship between composition and structure of metal-contained sites and catalytic activity and selectivity in this reaction was studied. It was found that the catalyst obtained from heterometallic alkoxide complex possessed the highest activity and selectivity toward alkane-olefine fraction compared to the catalysts prepared based on homometallic or mix of monometallic alkoxide complexes. In the presence of that catalyst ethanol conversion reaches up to 85–95%, alkane-olefin fraction $C_5 – C_{9+}$ yield is 30–45% with 50 wt. % content of aliphatic hydrocarbons with branched structure [1].

By X-Ray diffraction, molecules-probes, thermo desorption, and infrared spectroscopy it was shown that the catalytic active sites of the polymetallyc system are nanosize mixed oxides clusters with the structure of solid solutions of isomorphic substitution distributed on the γ-Al_2O_3 surface. The surface of active catalyst is characterized by maximum concentration of Brønsted acidic sites with average energy of 128,71 kJ/mo in comparison with Re- and W- contained catalysts.

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Oxidation of Chlorobenzene with Mixtures of Hydroxides or Chlorides with V_2O_5

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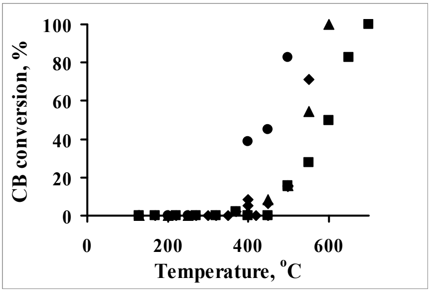
Alkali metal hydroxides and chlorides doped with transition metal oxide were shown to be suitable for deep oxidation of halogenated organics [1]. Methods of GC, Raman spectroscopy, HPCE were employed to study process of deep oxidation of chlorobenzene (CB) with the help of following catalytic blends: NaOH–KOH (eut.) (I), NaOH-KOH (eut.) + 10 wt.% V_2O_5 (II), NaCl–$CaCl_2$ (eut.) + 10 wt.% V_2O_5 (III) at 200–700 °C.

Catalyst (III) shows high conversion degree (38.5%) at temperature as low as 400°C. Conversion degree grows with the increase of temperature, O_2/CB molar ratio and surface of catalyst film. Coke formation process was found to be the least intensive when catalytic blend (II) was used.



♦ – I, ■ – II, ● – III, ▲ – III'(greater weight of catalyst)

In the course of halogenated arenes oxidation reaction Cl^--ions are formed. Transition metal oxides promote oxidation of Cl^--ions into gaseous Cl_2, this process allows to extend life of tested catalytic systems

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PP-II-13

Partial Oxidation of Methane to Synthesis Gas on Ribbon Porous Nickel Based Catalysts

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At present, the process of catalytic partial oxidation (POM) is considered to hold much promise for generation of synthesis gas. POM is an exothermal reaction, thus in order to decrease local overheating of catalysts and to develop mechanically strong catalysts, the use of catalysts on metallic supports is one of the most promising ways. The aim of this work was studying peculiar features of formation of nickel catalysts supported on the ribbon porous nickel with a MgO carrier and their catalytic properties in the reaction of POM to synthesis gas.

To prepare nickel supported catalysts, ribbon porous nickel (Ni_{rb}) (h=0.1 mm) ($S_{sp} \sim 0.15$ m^2/g, $V_\Sigma \sim 0.1$ cm^3/g, $r_{preval} \sim$ 5-50 µm) was used as a support. MgO carrier (5 wt. %) was supported by impregnation with solution $Mg(NO_3)_2$ and calcination at 550°C in a flow of N_2. Nickel (2 wt. %) was supported by impregnation with solution $Ni(NO_3)_2$ and calcination at 450°C in N_2.

The as-prepared catalysts were characterized by the following methods: XRD, low-temperature adsorption of nitrogen and TEM HR in combination with EDX analysis. Reduced supported catalysts contained phases of metallic nickel and solid solution NiO in MgO. In the supported nickel catalysts nickel particles were epitaxially bonded with support MgO which was evidenced by the Moire picture. There is not an oxide layer in the dispersal nickel particles (2–7 nm) epitaxially bonded with MgO.

The catalysts were tested in POM for 100 h (flow method, $P = 1$ atm, $T = 800$°C, $O_2/CH_4 = 0,75$, $\tau = 5$ ms). The methane conversion value of catalysts decreased on 15–20 %. The dispersal nickel particles epitaxially bonded with MgO were detected in catalysts tested in the reaction. Oxide layer in these particles (2–7 nm) was absent. No carbon deposition was observed by TEM in tested samples.

Microstructure Changing Research of Solid Solutions $La_{1-x}Ca_xMnO_3$ Synthesized by Pechini Method after Methane Oxidation Reaction

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Solid solutions like $La_{1-x}Ca_xMnO_3$ are widely used as catalysts of high-temperature oxidizing processes. In this work, a high resolution transmission electron microscopy (HRTEM), X-ray energy-dispersive spectroscopy (EDS), and X-ray powder diffraction (XPD) are used to study microstructure changing in the solid solutions $La_{1-x}Ca_xMnO_3$ synthesized by Pechini method (polymer-salt composition) in the methane oxidation reaction.

Depending on parameter of replacement (x) morphotropic transitions inside of the sample series are observed. At $0 \leq x \leq 0.4$, it is possible to characterize samples by orthorhombic symmetry of space group Pnma, at $0.5 \leq x \leq 0.8$ symmetry increases to tetragonal group I4/mmm, $0.9 \leq x \leq 1$ goes down to monoclinic symmetry $P2_1$.

As the result of catalytic reaction the structure of the some samples were transformed. $LaMnO_3$ changed the symmetry from orthorhombic (Pnma) to hexagonal (R3c), also samples with $x = 0.5 – 0.8$ assumed the orthorhombic modification (Pnma).

According HRTEM data, multiple planar defects were formed under the forcing of catalytic reaction starting from $x = 0.3$, the amount of the defects is growing with the rise of x. Also appearing of CaO and Mn_3O_4 oxides was observed starting from $x = 0.5$.

In sample with the $x = 0.9$ areas of the planar defects segregation and superstructure formation was observed. According EDS in these areas the deficit of Mn cations containing (approximately 20%) was detected. The superstructure is characterized by quadruple period of the crystal lattice in [001] direction.

PP-II-15

Investigation of Oxygen Mobility in Ce- and Sr- Modified La_2CuO_4 Phase by TPR and CO Oxidation

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Perovskite-type complex oxides have a potential interest as a catalyst for oxidation processes [1]. Their catalytic properties potentially associated with oxygen nonstoichiometry, oxygen storage capacity and oxygen mobility.

In this work the mechanisms of lattice oxygen mobility in Ce- and Sr- doped lanthanum cuprates was studied. All samples were prepared by co-precipitation of corresponding nitrates by ammonia at pH=10. Calcination temperature was determined by DSC-TG analysis. All samples have relatively high specific surface area about 20 m^2/g. Phase composition was studied by X-ray diffraction.

Total amount of weakly coupled oxygen was measured by temperature programmed reduction. For all catalysts two reduction peaks at 350–400°C and 600°C were observed. The first peak corresponds to oxygen mobility at surface; the latter peak mainly attributes to bulk oxygen diffusion. It was found that increase of Ce content in $La_{2-x}Ce_xCuO_4$ from $x = 0.05$ to 0.2 the amount of mobile oxygen at surface significantly increases.

Oxygen mobility was investigated in CO oxidation by lattice oxygen as well. Reaction was performed by a pulsed microcatalytic technique. Impulses of reaction mixture (5% CO in He) were passed through the catalysts. CO oxidation in this case proceeds due to lattice oxygen. Such method allows to qualitative study of oxygen mobility. Different results were obtained for Ce- and Sr-doped lanthanum cuprates. For $La_{2-x}Sr_xCuO_4$ the initial CO conversion during first 8 impulses is about 80% and then it goes to steady value 35%. In contrary, for $La_{2-x}Ce_xCuO_4$ initial CO conversion is close to zero, then, after 6 impulses it increases up to 30%. Obtained results points that in Sr-doped samples mobile oxygen accumulates generally on the surface; but in $La_{2-x}Ce_xCuO_4$ bulk mobile oxygen is prevailed.

Additional CO oxidation was investigated in impulse microcatalytic technique with 5% (O_2–CO stochiometric ratio) He. Results were compared with literature data obtained under the same reaction conditions [2] for undoped La_2CuO_4. In [2] total conversion CO to CO_2 was reached only at 550°C. In the presence of La_2CuO_4, prepared in our work, CO conversion was 87% at 200°C, and at 350°C total CO oxidation was achieved.

We thank Dr. G.P.Murav’eva for help in performing of XRD.

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PP-II-16

Nb Role in Active Phases Formation in MoVTeNbO Catalyst for Ammoxidation and Oxidation of Propane

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The most effective catalysts to date in the propane ammoxidation to acrylonitrile and oxidation to acrylic acid are MoVTeNbO oxide catalysts reported by Ushikubo et al. [1]. The aim of current study is elucidation of Nb role in active phase formation and in catalytic properties in ammoxidation and oxidation of propane.

$Mo_1V_{0.3}Te_{0.23}Nb_n$ (n = 0–0.3) catalysts were prepared by the spray drying of the aqueous suspension of starting chemicals using lab spray-dryer (Buchi-290) and next heat treated at 600°C in He flow. An aqueous niobium oxalate solution was added to an aqueous solution of ammonium metavanadate, telluric acid and ammonium heptamolybdate at 40°C (pH =3.0).

The samples were characterized by XRD, IR and Raman spectroscopy, TEM and differential dissolution (DD) methods.

The catalytic experiments were carried out at atmospheric pressure in a fixed-bed tubular reactor with on line gas chromatography.

Injecting Nb in MoVTe slurry changes the mechanism of the catalyst formation and improves the catalytic properties. Despite of the same structure of liquid and solid precursors (heteropolyanion Anderson-type) orthorhombic M1 phase forms mainly in the MoVTeNb and M2 phase forms in the MoVTe system upon subsequent thermal treatment.

MoVTeNb is more active and selective in the propane ammoxidation to acrylonitrile and oxidation to acrylic acid than MoVTe catalyst.

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Application of SEM, SIMS and XPS for Studying Adsorption of CO and O_2 on Surface of Invar Alloy Fe-0,3Ni

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Fe–Ni alloys with the content of nickel about 30% have the Curie temperature of several tens of Celsius degrees. It enables one to experimentally study the adsorption of gases on ferro- and paramagnetic surfaces of alloys, and in the temperature range of the phase transition. Samples of the invar alloys with the Curie temperature of 75 and 160°C were obtained by fusion of powders of iron and nickel in a corundum crucible in vacuum (below 10^{-2} Pa). The SEM studies showed that the surface of the samples consists of blocks of several tens of microns in size. The XPS studies were carried out at temperatures 25, 75 and 125°C for the sample with the $T_C = 125°C$. It was found that the 3s core level spectra of the sample in the ferromagnetic state have components B and B', which are the result of superposition of two spin-multiplet splittings of the line 3s. The origin of these two components consists in two available positions for atoms of both iron and nickel with various electronic surrounding. It was found that iron interact with carbon more intensely than nickel. In the range of the Curie temperature, the peak due to carbide disappears. Heating of oxygen adsorbed at room temperature on a surface preliminary subjected to ion bombardment results in the appreciable oxidation of an alloy. The SIMS experiments were carried out at temperatures 25–400°C with both the samples. It was established that the adsorption of CO results in an increase in the ion currents Fe^+ and Ni^+, as well as in the emission of molecular ions: FeC^+, NiC^+, $FeCO^+$, and $NiCO^+$, whose intensities increase with an increase in the CO coverage. Since the intensity of the FeC^+ ions is much higher than that of NiC^+ the degree of dissociation of CO on iron atoms is much higher than that on nickel atoms. Adsorption of CO on Ni into tightly bound state goes through a weakly bound state.

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PP-II-18

Molecular Dynamics in Ionic Liquids

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Ionic liquids (ILs) are unique solvents: all their components are electrically charged, and are either cations or anions of different nature [1]. Because of their properties ILs can be used as special so-called "green solvents" for carrying out different chemical processes: organic synthesis, catalysis, adsorption; they are also applied in electrochemistry, analytical chemistry, etc. In the paper we describe the main results of our investigation of ILs with the use of spin probes method. The following two ILs were studied: $[\text{1-butylmim}]^+[PF_6]^-$ (IL1) and $[\text{1-octylmim}]^+[BF_4]^-$ (IL2), where mim is 3-methylimidazolium fragment.

Three types of molecular dynamics of ILs were studied: rotational and translational diffusion, and intramolecular conformational motions. Nitroxide radical TEMPOL and biradicals $R_6{-}C{\equiv}C{-}p{-}C_6H_4{-}C{\equiv}C{-}R_6$, $R_6{-}C{\equiv}C{-}C{\equiv}C{-}R_6$, $O{=}S(OR_6)_2$, $(H_5C_6)O{=}P(OR_6)_2$, $(CH_2)_5[CONHR_6]_2$ were used as spin probes. In the paper, we will discuss regularities and peculiarities of the molecular dynamics of spin probes in ionic liquids.

Acknowledgement: This work was supported by RFBR (08-03-00478).

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Exoemission, Accompanying the Methanol Decomposition over the Zinc Oxide and Alumina

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Methanol is an important reagent in the dimethylether and methylformiate synthesis and in the manufacture of hydrogen-containing gaseous mixture for fuel cells. The aim of the present work is the use of exoemission technique to perform a detailed study of methanol decomposition reactions and to analyze how these reactions are related to the electronic structure of the surface active sites of ZnO (during the dehydrogenation) and Al_2O_3 (during the dehydration). The reactions were investigated “in situ” in adsorption layer using the chamber for registration of exoemission with the secondary electron multiplier (SEM) as a detector of negative charges. The temperature and the intensity of thermostimulated emission maxima T_{max} were the decisive parameters for the characterization of active centers of methanol decomposition. These maxima coincided with the maxima of the thermodesorption accompanying the methanol decomposition. The most intensive peaks of the thermostimulated emission spectrum of ZnO and Al_2O_3 have been found in the same temperature intervals (T_{max} = 130–150°, 190–210°, 310–330° and 360–380°C). These peaks coincide with those observed in our previous studies [1] for the majority of oxides. We have proposed that the exoemission centers are the surface hole V_k-centers – weakly bounded surface oxygen ($O^{\delta-}$).

According to [2], during the methanol decomposition in adsorption layer over the SNM-1 catalyst ($CuO/ZnO/Al_2O_3$) or on its component (Al_2O_3), the intermediate $HCOO^-$, CH_3OH^-, and final H_2, CO_2, CO products are formed. The formation of $CH_3–O–CH_3$ may be displayed by the scheme:

$2\ CH_3O^- \rightarrow CH_3–O–CH_3 + O^- + e\uparrow$

According to our data this reaction is accompanied by the emission of negatively charged species.

It is suggested [3] that the adsorption and decomposition of methanol take place over the low-coordinated surface ions Al^{3+}

(Zn^0, Zn^+). We have discovered [1] that V_k-hole centers ($O^{\delta-}$) represent the exoemission centers (O_2^-, O_2^{2-}, O^-, O^{2-}_{surf}) on the oxide surfaces. The adsorption of methanol may occur on Al^{3+} (Zn^+) low-coordinated surface centers, but its decomposition proceeds by participation of $O^{\delta-}$ (V_k) surface centers and is accompanied by the emission of negatively charged species.

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The Adsorption-Calorimetric Method of Determination of Liquid Phase Hydrogenation Reactions Kinetic Parameters, Taking Place in Surface Layers of Heterogeneous Catalysts

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The results of researches of hydrogen adsorption laws on metals are the base to work out the methods for choosing optimum catalytic systems used in liquid phase hydrogenation reactions. According to the method developed kinetic parameters for liquid phase hydrogenation reactions of organic compounds can be determined from adsorption-calorimetric experiment with hydrogen adsorbed on skeletal nickel catalyst. The thermal emission rates were determined for the hydrogenation reactions of sodium maleate proceeding in the skeletal nickel adsorption layers in sodium hydroxide aqueous solutions at different pH values. Description of the experimental data within the limits of Vant-Goff classical method was shown to be formal. The best results were obtained by analyzing the experimental kinetic data in Roginsky-Zeldovich's and Elovich's linear coordinates. The strong heterogeneity of the surface of skeletal nickel essentially influences the kinetic laws of hydrogenation reactions. Computer modeling was performed to obtain the reactivity of individual forms of hydrogen according to two basic chemical mechanisms on the catalyst surface in the wide range of concentrations.

PP-II-21

XPS, EM, IR, TPD-MS and Kinetic Studies on Mechanisms of H_2, CO and CH_4 Oxidation

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Transition metal oxides attract an increasing interest due to their ability to be reduced and, upon this, form dislocations and other extended defects. Easy conversion between oxides of different stoichiometry at gas-surface interface and in near-surface layer, reduction at gas medium containing H_2, CO and CH_4 and formation of oxygen vacancies allow the oxides to function as a catalyst. Heterogeneous catalytic systems based on H_2-reduced M_2O_5 oxides ($M = V$, Nb, Ta) with supported Pt (Pd) were prepared and tested in H_2, CO, and CH_4 oxidation reactions. Some of the catalysts were comprehensively characterized by physical methods (XPS, EM, CO(CH_4) FTIR, TPD-MS) sensitive to the surface structure of the catalyst and adsorbates on the surface. Activity tests and kinetic studies on mechanisms of H_2, CO and CH_4 oxidation in oxygen excess gas mixtures were performed. Different surface structures were found and the better conversion was achieved when MO_x $(4 < x \leq 5)$ was predominant in the layer. The impact of the non-stoichiometric oxides on elementary transformations on the surface of the catalytic systems was determined. The conversion increased with a rise in the amount of nonstoichiometric oxygen over the series of catalysts. H_2, CO and CH_4 adsorption processes were investigated, the active sites and intermediates were determined from FTIR and TPD-MS data. It is concluded that oxygen nonstoichiometry and redox M^{4+}/M^{5+} couples facilitate the oxidation over these catalysts.

A New Approach to Study Kinetics and Mechanism of Solid-State Tranformations

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It is impossible to study mechanism and kinetics of catalytic reactions without detailed knowing structure and composition of catalysts. Usually actual catalysts show evidence of an inhomogeneity in these fundamental characteristics. Inhomogeneity can appear during preparation of the catalysts resulting from many factors. It may be a result of the absence of effective transport between different parts of a complex mixture, of different forms of the distribution function of reacting particles by size, of irregular temperatures in the active reaction zone. Other chemical transformations, being in parallel with target and often irreversible, lead also to the inhomogeneity. Studying mechanisms and kinetics of solid-phased transformations is highly improbable when suitable methods are absent to identify phases and to determine their amounts in complex mixtures of solids, not matter whether they are in intermediate or terminal products of interaction. This phenomenon is typical for the systems with unknown before phases including amorphous phases, phases of varying composition and phases of a low content. At present only qualitative and incomplete information on the phase composition of products of such type may be obtained.

A stoichiographic method of differential dissolution (DD) represents new potentialities to study mechanism and kinetics of solid-state transformations [1]. The potentialities of the DD method are unique due to its ability to determine simultaneously the stoichiometric composition and amounts of phases in multi-element and multiphase solids without isolating these phases in a pure form and being in the full dark about the phase composition of subjects under study. Reference-free nature of the DD method differentiates it from all known physical and chemical methods of the phase analysis. This method allows substances of unknown phase composition being as disperse powders, ceramics, crystals, thin films and complex nano-systems to be studied.

The kinetics of formation of $CaTiO_3$ from $Ca(OH)_2$ and $TiO_2 \cdot aq$ by soft mechanical-chemical synthesis was studied first [2]. Currently unique results were obtained studying processes of such type in the system Mo-Te-V-Nb-O [3]. By now the great amount of factual information was accumulated on application of the DD method to practical use [1].

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Chromium-Aluminum Binary Oxides – Promising Support Material for Various Catalytic Reactions

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Binary oxides are often used as a support material for many catalytic reactions. The main goal of this work was the preparation of binary chromium-aluminum oxidic systems with various Cr/Al ratio (from 1:10 up to 10:1). In our work we tested the catalytic behavior in: partial oxidation of methane, methanol synthesis, oxidation of CO with oxygen or water vapor. Metal $Cr_xAl_{1-x}O_3$ supported catalysts were much more active (up to 3 times) in comparison to the same systems based on appropriate monoxides (Al_2O_3, Cr_2O_3). We have not found straight correlation between chromium content and catalytic performance, however it seems that the most optimal composition have samples with the Al/Cr ratio equal 3. It seems to be connected to the quantity of superficial isolate chromium species which have the donor-acceptor ability for oxygen. The formation of interoxide compounds ($CrAlO_3$, CrAlO and other ions present in secondary ion spectra) was confirmed by TOF-SIMS techniques. SEM-EDS investigations confirm high homogeneity level of samples with low chromium content (for Cr/Al ratio below 1). For chromium rich samples two type of agglomerations were observed rich and poor chromium regions. In the case of chromium rich samples the presence of α-Cr_2O_3 and γ-Al_2O_3 was confirmed by XRD technique. This fact seems to be confirmed also by BET measurements. Specific surface area for samples with the low chromium content was similar as for alumina (230–160 m^2/g), for samples with the high chromium content it decreased rapidly (>50m^2/g).

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PP-II-24

The Mechanism of Sorption Sulphur Dioxide on the Vanadia-Zeolite DESOx Catalysts

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The studied DESOX type catalysts based on synthetic zeolite Sipernat A 820 doped vanadia may be used to the catalytic process of SO_2 removal from combustion gases which takes place on the grain plane of hard coal.

This paper reports the study of relationship between sulphur dioxide sorption and sulphur dioxide removal degree from exhaust gases on DESOX type catalysts based on synthetic zeolite. SO_2 sorption on prepared catalyst mechanism was studied. Taking the results of SO_2 adsorption into account, a probable mechanism of interaction of SO_2 with the surfaces area can be proposed as:

i) $SO_2 \rightarrow SO_{2(a)}$,
ii) $O_2 \rightarrow \text{oxygen}_{(a)}$,
iii) $SO_{2(a)} + \text{oxygen}_{(a)} \rightarrow SO_{3(a)}$.

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PP-II-25

Catalytic Utilization of Methane from Coal Mine Ventilation Air

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The paper indicates the coal mines as the source of the permanent emission of low-concentrated methane, which increases the greenhouse effect. This paper proposes the catalytic oxidation of methane as the solution for the problem of methane utilization when its concentration in air is insufficient for flame combustion. The long-term studies enabled to find the active oxide and metallic catalytic systems for the reaction of methane oxidation. For the utilization of gases with low-concentrated methane it seems to be economically well-justified to use of the low-temperature catalysts, especially palladium catalysts. Depending on technological solutions it can be considered as the method for methane utilization or as an environmentally friendly way for generation of electric and thermal energy.

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PP-II-26

Studying of the Structure and Catalytic Properties of Polyoxometalate such as Keplerate Based Molybdenum Oxide in Reactions of Oxidation of Olefin and Aromatic Compounds

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The cavities of synthesized clusters of Mo_{132} can contain both molecules of water and anions of carboxylic acids (formic, acetic, or monochloroacetic). Several physicochemical methods such as IR, ESR, NMR spectroscopy are needed to analyze the structure of buckyball carcass as well as the composition and the structure of organic molecules inside buckyball's cavities. As precipitations are frequently fine-crystalline the X-ray diffraction method is not always suitable. The clusters of Mo_{132} give ESR signal with g = 1.93 referring to Mo^{5+} ions in structural defects. The shape of this signal depends on, for example, whether acetate or monochloroacetate is a guest molecule. Earlier NMR spectroscopy practically was not applied in studies of keplerate Mo_{132}. These compounds contain proton carboxylic acids in unusual hydrogen-bonded cluster of guest molecules encapsulated as a part of overall "onion-tipe" structure. Acetate polyoxomolybdate has the following features in the ^1H NMR spectrum: 0,81 ($2CH_3$), 1,00 (s), 1,23 (s), 1,99 (CH_3), 2,08 (s), 4,76 (H_2O), 4,77 (H_2O) ppm. The following signals were observed in the ^{13}C NMR spectrum: 19,51, 24,32 (CH_3), 25,76 (CH_3), 60,14, 181,42 (C=O), 182,50, and 183,32 (C=O) ppm. After drying at temperature 100–170°C the samples of keplerate Mo_{132} does not contain molecules of solvent, and chemical shifts in ^1H and ^{13}C NMR spectra relate only to anion carboxylic acids: 1,99 (CH_3), 2,06 (s) [^1H NMR]; 23,33 (CH_3), 179,66 (C=O) [^{13}C NMR].

Simultaneous recording of NMR and ESR spectra of keplerates with unpaired electron is possible, apparently, because of insignificant concentration of defects in Mo_{132} clusters. To evaluate the influence of the carboxylate ligands on the structure of the encapsulated molecules and catalytic properties we also used other carboxylate ligands.

Catalytic properties of the synthesized samples were investigated in modeling reactions of oxidation of turpentine, α-pinene and 2,3,6-тrimethylphenole by oxygen and liquid-phase oxidation of anthracene with hydrogen peroxide. The products of oxidation were analyzed by GC. Polyoxometalate is steady enough in reaction of oxidation of α-pinene (at 50°C, in acetonitrile) at small pressure of oxygen as any visual changes in color were not observed for reaction solution. Polyoxometalate with spherical nanocluster structure $(NH_4)_{42}[Mo^{VI}_{72}\ Mo^{V}_{60}O_{372}\ (HCO_2)_{30}\ (H_2O)_{72}]\cdot 30HCO_2Na\cdot 250H_2O$ was also tested in reactions of oxidation of turpentine. Spherical molybdate complex appeared to be unstable in polar solvent acetonitrile. Apparently, it is caused by replacement of formiate anion with molecules of acetonitrile under the conditions of oxidation. It was shown by measurements of UV spectra and photogalvanic effect that molybdate complex undergo gradual oxidation and destruction by the influence of oxygen of air. At the same time the rate of oxidation of α-pinene without solvent in presence of polyoxomolybdate was low. Bubbling of air (80°C, 2h) during oxidation of 2,3,6-trimethylphenole in the presence of buckyball acetate results in discoloration of the reactionary solution. Catalytic properties of keplerates were further studied in reaction of peroxidic oxidation of anthracene. The decrease of conversion of anthracene in similar conditions proceeded in the following order: $(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}\ (CH_3CO_2)_{30}\ (H_2O)_{72}]\cdot 30CH_3CO_2Na\cdot 250H_2O$ > $(NH_4)_{42}\ [Mo^{VI}_{72}Mo^{V}_{60}O_{372}(ClCH_2CO_2)30(H_2O)_{72}]\cdot 30ClCH_2CO_2Na\cdot 250H_2O$ > $(NH_4)_{42}\ [Mo^{VI}_{72}Fe^{III}_{60}O_{372}\ (CH_3CO_2)\ 30\ (H_2O)_{72}]\cdot 30CH_3CO_2Na\cdot 250H_2O$

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PP-II-27

Copper Supported Catalysts in Methanol Synthesis and Water Gas Shift Reactions

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Copper based catalysts are wide used in many reactions such as synthesis of higher alcohols, methanol steam reforming and water gas shift reaction. Additionally, in literature data one can find a lot of studies where catalysts supported on binary oxide show high activity and stability in many various reactions. The main goal of this work was determination of the correlation between results of catalytic activity and physicochemical properties of copper supported catalyst 60% Cu/support (support = Al_2O_3, ZnO, Cr_2O_3, Fe_2O_3, $CrAl_3O_6$, $FeAlO_3$, $ZnAl_2O_4$) in methanol synthesis and water gas shift reaction. All catalysts were prepared by impregnation method and their physicochemical properties were determined by BET, XRD, TPR-H_2, TPD-CO_2. The activity tests in methanol synthesis were carried out over this series of catalysts in the temperature range from 220 to 460°C at atmospheric and elevated pressure (4MPa) in temperature range 180–260°C. The activity test in water gas shift reaction was performed in a flow quartz reactor at atmospheric pressure and temperature range from 150–450°C. XRD investigation confirmed the formation of different binary oxide ($FeAlO_3$, $CrAl_3O_6$, $ZnAl_2O_4$, Ag_2CrO_4, $CuCr_2O_4$, $CuAl_2O_4$) and mono oxide copper, zinc, iron, and chromium oxides phases for appreciate catalytic system. Introduction of second metal into aluminium structure cause decrease of specific surface area. The results of activity test show that the copper catalysts supported on binary oxide demonstrated higher activity and stability in both reactions in comparison to system supported on monoxide. Additionally, the activity of copper supported catalysts seems to be connected with reducibility and specific surface area of support.

Methanol Oxidation and Dehydrogenation over Pt and Pd: *In situ* XPS and Mass-Spectrometry Study

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Oxidation and dehydrogenation of methanol over Pd(111) and Pt(111) single-crystals were investigated using *in situ* XPS and mass-spectrometry. It was found that for both metals the methanol dehydrogenation proceeds via two routes: dehydrogenation to CO and hydrogen, and decomposition of methanol with C-O bond scission [1-3]. The rate of the second route is several times lower, however, carbon production in this case leads to formation of carbon deposits, which block the surface and hinder the catalytic reactions. Even in the presence of O_2 in the gas phase, the main route of methanol conversion over Pd is dehydrogenation to CO and H_2. Hydrogen is partially oxidized to water, and CO is oxidized to CO_2. The reactions start at temperature above 450 K when surface carbon depositions are removed by oxygen.

In contrast, over Pt in presence of O_2, the main reaction products are CO_2 and water. Reaction also starts above 450 K when the surface carbon deposits are removed. The reaction comes via two stages. At first, methanol dehydrogenates to CO and H_2, and then total oxidation of these intermediates occurs. The difference in product distribution over Pt and Pd in the methanol oxidation is in a good agreement with the fact that Pt is more active in the CO oxidation than Pd. In both cases, the active state in the methanol oxidation is Pt or Pd in the metallic state.

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PP-II-29

Model Catalysts Prepared by 'Wet Chemistry' Methods on Alumina Thin Films for *in situ* STM and XPS Study

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Original model platinum alumina supported catalysts suitable for *in situ* scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) studies were designed. The set of samples – Pt on model plane support Al_2O_3/FeCrAl with rough surface was prepared by 'wet chemistry' adsorption from platinum nitrate (IV) solution with subsequent reduction in H_2. It was shown that our model is very similar to catalysts on porous γ-Al_2O_3 and θ-Al_2O_3.We found that variation of the deposition conditions affects the particles size distribution. So we succeed to control the size of particles from ~1 nm up to 50 nm.

The prepared Pt catalysts were used for thermal stability study. The analysis of STM data shows that the main mechanism of thermal sintering for our model systems is migration of the Pt particles, rather than atomic migration. It was revealed that for model Pt/Al_2O_3 prevalent mechanism is independent both on method of metal deposition and of particles size distribution. STM investigations show that for vacuum deposited systems even short annealing is enough for the dramatic changes in particles size distribution. 'Wet chemistry' systems are more stable than traditional vacuum deposited models. It could be explained by the stronger metal – support interaction for model catalysts prepared from the precursor solutions.

Based on proposed deposition approach we prepared Sn modified model Pt catalyst. It was shown that preparation method provides the direct interaction of Pt with modifier (SnO_2). After annealing of this model in vacuum changes of particles size distribution were not as considerable as in the case of non-modified systems. Stannic dioxide serves as interlayer between platinum particles and alumina thus impeding the migration of particles.

Using original model alumina support we achieved to prepare Pt catalysts by ‘wet chemistry’ methods conventional for practical catalysis and, on other hand, suitable for modern and very powerful *in situ* physical methods STM and XPS. Possibilities of our approach were demonstrated on Pt particles formation and thermal stability studies. And it is evidently that such model catalysts – Pt/Al_2O_3/FeCrAl are very useful for the *in situ* investigations of mechanisms of catalytic reactions up to the atomic scale.

The authors are appreciating the financial support of research by CRDF (grant No NO-008-X1 and The 2006 BRHE Fellowship Program RNP. 2.2.2.3. 10032) and Program of fundamental investigations of RAS # 27 (Project # 51).

PP-II-30

Study of the Heterogeneity of Active Sites of Supported Ziegler-Natta Catalysts at the Ethylene Polymerization

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It is known that supported Ziegler-Natta type catalysts are heterogeneous on the reactivity of active centers (multisite catalysts) and it is the origin of the broad molecular weight distribution (MWD) of polyethylens (PE) produced over these catalysts. The effect of chemical composition of highly active Ziegler-Natta catalysts (support, active component composition (Ti or V), Ti content and electron donor compound) on the heterogeneity of active sites has been studied. We focus the main attention on the analysis of experimental MWD curves of PE, using MWD decovolution technique into Flory components. Effect of polymerization conditions (cocatalyst composition, temperature and various chain transfer agents) on MWD of PE produced was investigated also.

We used in this study four modifications of highly active supported titanium magnesium catalysts (TMC) differing by the content of titanium and the presence of modification additions: the internal donor (dibutylphtalate) and ethoxy-groups in the composition of catalysts, and vanadium magnesium catalysts (VMC).

The great difference between PE produced with Ti-based catalysts and VMC is observed. VMC produces PE with broad and bimodal MWD. Mw/Mn value for PE synthesized with VMC equals 16, in contrast to polydispersity (PD) values 2.8–6.8 for PE produced with TMC. The results of resolution show the difference in the heterogeneity of active sites among Ti-based catalysts: minimum number (three Flory components) of active sites for TMC with the lowest Ti content and TMC containing donor, four active sites for TMC with high Ti content and TMC modified ethoxy-groups, maximum number of active sites (five Flory components) for $TiCl_3$. VMC contains five types of active sites. The possible structures of the surface titanium species are discussed to explain the effect of TMC composition on the heterogeneity.

It was shown that with increasing temperature MW of PE decreases, while the polydispersity value does not change. The character of GPC curves of polyethylene produced at 60 and 80–90ºC is different: at 60ºC the GPC curve is bimodal with pronounced high molecular weight shoulder, at 80–90ºC the GPC curve is monomodal.

Introducing of hydrogen as chain transfer agent at ethylene polymerization proceeds to the great effect both on MW and on PD value as a result of different reactivity of various active sites in the chain transfer reaction with hydrogen.

PP-II-31

NMR Study of Isotopic Labelled Succinic Anhydride

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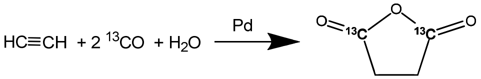
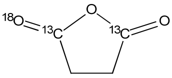
The ^{13}C-labelled succinic anhydride (**I**), which is usable as a precursor in the synthesis of important ^{13}C-enriched acids, was obtained in solutions of palladium complexes by the carbonylation of acetylene with 98% ^{13}C-enriched carbon monoxide in the presence of water. The carbon monoxide which we used contained also 10% of ^{18}O isotope.



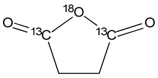
Analysis of ^{13}C NMR spectra (Bruker AVANCE 600) revealed that **I** consisted of isotopomers mixture, which could be divided into two groups: (A) both carbonyl atoms are ^{13}C (theoretical content 96%); and (B) one carbonyl atoms is ^{13}C (theoretical content 4%).

We have identified 15 isotopomers with total mass fraction in the range from 84.7 to 0.035%, for which ^{13}C NMR isotopic shifts were measured. The signals integration allowed to determine the total content of (A) group isotopomers to be no less than 96% which corresponds to calculated value.

The analysis of ^{13}C NMR spectra of isotopomers **Ia–Ib** demonstrated that carboxylate group formation on Pd catalyst was accompanied by the statistical distribution of ^{18}O isotope between two possible positions with regard to double degeneration of isotopomer **Ia** (C=^{18}O/C^{18}OC ratio was 2:1). These data gave us grounds for the discrimination of those hypotheses about the possible mechanism of catalytic process that were not consistent with observed distribution.



Ia



Ib

Consideration of Interrelation “Structure – Property” for Hydrocatalytic Processes

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The big attention is present questions of organic synthesis on the basis of low-molecular compounds of different classes in which some physical and chemical laws are elucidated, in particular "structure - property". However, similar works in the field of petrochemistry and oil refinings practically don’t meet. In the adduced work the opportunity of use of a mix of anthracene and benzothiophene as models of organic mass of coal in catalytic hydrogenation process was investigated. As the catalyst was a mix of ferric (III) oxide, pyrite, the synthesized product and sulfur served in different combinations; solvent was tetralin (m=0.5 g); number of the carried out experiences equally to 12, pressure of hydrogen $P_{H_2}=6\ MPa$, duration of 30 minutes, T=375 K. For the analysis of products of catalytic hydrogenation used chromatography-mass spectrometry method.

At the presence of the present catalysts the yield of methylnaphthalene, dibenzoyl was essentially increases. And at transition from steel to pyrite for dibenzoyl decrease in its yield, and for methylnaphthalene takes place increase. Negative influence of the present catalysts is shown in case of 1, 4-dehydroanthracene, 6, 9-dehydroanthracene. By results of researches the general degree of conversion of a modelling mix amount to 93-95%, it is connected by those oxygen-containing compounds of ferric show high catalytic activity [1].

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PP-II-33

Local Atomic Structure of Nanocrystalline Oxides – Catalyst Supports

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Modern catalytic materials are often characterized by varying degrees of structural disorder. Traditional XRD structure solution reveals the average structure only. However, the local structure (short range arrangement of atoms) of highly dispersed materials often differs from the average one and determines important catalytic properties. Radial distribution function (RDF) of electronic density or atomic pair-density function (PDF) method is effective for studying the local structure. This method is based on the Fourier relationship between intensity of coherent X-ray scattering and RDF of electronic density [1]. Using this technique, one can directly define interatomic distances and coordination numbers of atomic arrangement. To determine features of the local structure of highly dispersed materials in comparison with well crystallized analogues a collation of the experimental RDF and the model one constructed on the basis of known structural data is used [2].

In this work we report some examples of the RDF analysis application: 1) to determine the structure of highly dispersed X-ray amorphous phases; 2) to elucidate changes in local structure of nanomaterials in comparison with well crystallized analogues. Nanocrystalline ceria and zirconia were considered because of their catalytic application. Ceria is widely used as support and promoter in the catalysts of redox processes due to its ability to easy undergo reversible reduction, oxygen storage/release capacity. Highly dispersed low-temperature zirconia is also used as support because of large specific surface area, amphoteric properties and chemical stability.

Ceria samples with different crystallite size (d ~ 5–100 nm) prepared by various techniques were considered. It was shown that degree of disorder of local structure increased with decrease of crystallite size. A reduced coordination numbers of Ce-Ce shells were clearly observed for ceria with d=5nm. Obtained data also revealed the incorporation of residual anionic groups into anionic sublattice of nanocrystalline ceria.

Nanocrystalline yttria-stabilized zirconia samples were prepared via co-precipitation technique and subjected to drying by microwave irradiation and calcination at different temperatures. The changes of local structure with increase of calcination temperature were elucidated. Thus, a study of the low-temperature (300°C) X-ray amorphous sample demonstrated that polynuclear hydroxocomplexes were formed; their atomic short-range order was similar to the zirconia cubic phase. Specific features of the structure were found, one of them was shortening of interatomic distances. The RDF method allowed determining phase composition of nanocrystalline oxide with d~10nm precisely, whereas usual XRD analysis did not.

The work was supported by project № 17 of RAS Presidium fundamental research program № 27 and by the Russian Foundation for Basic Research (project № 09-03-90424-Ukr_f_a).

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PP-II-34

Resting States in Methylalumoxane (MAO)-Activated Zirconocene Catalysts for α-Olefin Polymerization – an *in-situ* UV/vis-Study

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Little experimental evidence has become available so far regarding the complexes occurring as resting states in MAO-activated zirconocene polymerization catalysts under practically relevant reaction conditions. NMR methods, which are most useful otherwise, appear to be less well-suited to estimate the amounts of relevant complex species present in these complex systems. In a recent *in-situ* NMR study, species such as $Me_2Si(ind)_2Zr(\mu\text{-}Me)_2Al(Me)_2^+$, $Me_2Si(ind)_2Zr(\mu\text{-}R)(\mu\text{-}Me)Al(Me)_2^+$ and $Me_2Si(ind)_2ZrMe^{+\cdots}MeMAO^-$ were found to account for 50-60% of the catalyst concentration, with the remaining 40-50% being NMR-silent.

UV/vis spectral methods might provide essential advantages in this regard, as this spectral region lends itself for observation of characteristic metallocene absorption bands [1-3], while not being obscured by monomer, polymer or activator absorbencies. Recently, we have shown that activation reactions of zirconocene catalysts can be reliably followed by changes in their UV/vis-spectra, which are correlated to structural information derived from parallel NMR-spectroscopic analysis [4]. We have thus studied UV/vis changes induced by addition of 1-hexene or propene to $Me_2Si(ind)_2ZrCl_2$/MAO reaction systems, to characterize the complex species formed when these catalysts are actively polymerizing α-olefins. In that way, we have found the NMR-silent species predominating in these catalyst systems to be an aluminum-complexed zirconocene hydride complex of the type $Me_2Si(ind)_2ZrH_2$ ♉ $AlRX_2$.

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The Co Nanoparticles Size Distributions in Co-Supported Fischer–Tropsch Catalysts: the Connection with Selectivity

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In this work a complex of magnetic methods was employed to study the influence of size distribution of Co nanoparticles in 15%Co/Al_2O_3 Fischer–Tropsch (FT) catalysts on paraffins selectivity. The methods used were temperature-programmed reduction and temperature-programmed oxidation with registration magnetization *in situ* and magnetization – magnetic field dependences.

To prepare Co-nanoparticles with different size distributions the following methods were used:

1) variation of calcination temperature (200–500°C);
2) promotion Co/Al_2O_3 catalyst by noble metal (0.1% Pt);
3) addition to CoRu/Al_2O_3 catalyst the 0.05% solution of sucrose.

It was found that increase of size of Co particles leads to higher CH_4 selectivity and, opposite, the smaller selectivity toward C_{5+}. The addition of trace amount of sucrose to CoRu/Al_2O_3 catalyst results in decrease of the average size of Co particles.

PP-II-36

Radiuses and Concentration of Pores in Porous Silicon According to the PAS Method

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Oxidized porous silicon with the metallized surface can be used as the catalysts for reburning exhaust gases [1]. In this connection studies of its porous structure by various methods are interesting. Investigated by the method of positron annihilation spectroscopy (PAS) samples of porous silicon in the sizes 10x20x10 mm^3 with orientations <111> have been cut out from the whole plates of silicon n–type. Two samples designated by us as 164 (the initial monocrystal sample) and PR 86 (the sample of porous silicon received by a method of electrochemical processing in solution HF:$C_2H_5OH = 2:1$) have been chosen for the research at the force of current $J = 20$ mA/sm^2. Parameters of investigated plates of silicon, features of their formation, and basic characteristics of PAS spectra are summarized in Table 1 [2]. Positron annihilation characterized by parabolic component can be explained by positron annihilation on electrons of valent zone of silicon. Wide gauss component (Ig1) is caused by annihilation of positrons and ortopositronium on various channels in a faultless part of crystal volume and on the surface of pores. Narrow gauss component (Ig2) is explained by annihilation disintegration of parapositronium in volume of pores. Average pour size of 2 nm was calculated from intensities and widths of narrow components in PAS spectra and from differences of intensities of wide gauss components between monocrystal sample and the sample of porous silicon [2]. Average concentration of pores is ca. 10^{-14} cm^{-3}. According to these data one may suppose that the most likely effective free centers (areas of positronium capture) are ultramicropores and micropores (ca. 1 nm in size) in microporous layers of silicon.

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PP-II-37

Complexing in US Field

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Complexing kinetics of heterogeneous structures is based on crystallization processes in ultrasound (US) field. The figures below show derivatograms of decomposition process and formation of solid solution from ferric and chromic nitrates at various ratios of initial components. Diagram 1 describes catalysts prepared by mixing method, diagram 2 – by US homogenization. Peaks at T ~ 713K represent the process of formation of solid solution from oxides which is confirmed by X-ray structural analysis results. The table contains data on kinetic characteristics of decomposition process and formation of solid solution for different Fe–Cr catalyst mixtures. Minimum activation energy is related to the samples 4 and 8.

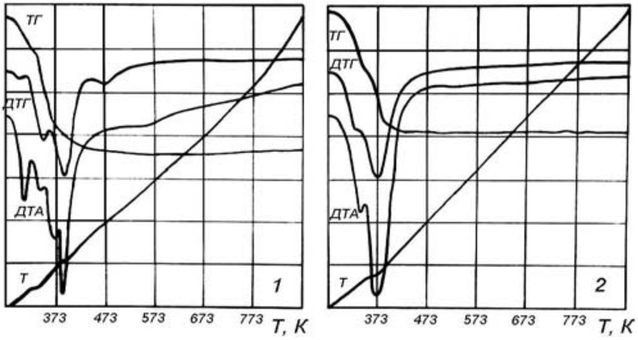
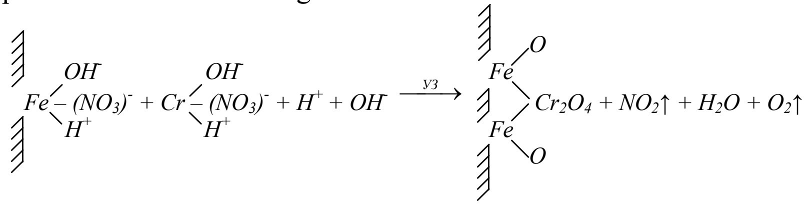


Fig. Derivatograms of Fe–Cr catalysts: 1 – prepared by mixing; 2 - prepared by US homogenization (20% Fe_2O_3 + 80% Cr_2O_3).

From results of X-ray structural and derivatographic analysis it can be seen the catalysts prepared by mixing or by US homogenization are practically identical in phase composition and nature of curves of derivatographic analysis.

Mechanism of formation of mixed catalysts in US field is also closely linked to the kinetics of the decomposition process of the mixture of initial components. Scheme of catalytic complex formation can be represented as the following:



Kinetic characteristics of thermal decomposition of Fe–Cr mixtures prepared by mixing and US homogenization.

Sample	Final catalyst composition	Order of reaction			Activation energy, kJ/mol	Pre-exponential factor, s^{-1}
		$n = 1{,}26\sqrt{S}$	$n^{\frac{1}{n-1}} = 1-\alpha$	n_{cp}		
1	2	3	4	5	6	7
Mixing method						
1.	80% Fe_2O_3 + 20% Cr_2O_3	0,80	0,71	0,755	41	$1{,}9\cdot10^4$
2.	50% Fe_2O_3 + 50% Cr_2O_3	0,77	0,65	0,710	56	$2{,}3\cdot10^5$
3.	20% Fe_2O_3 + 80% Cr_2O_3	0,61	0,59	0,600	77	$1{,}3\cdot10^6$
4.	90% Fe_2O_3 + 10% Cr_2O_3	0,81	0,62	0,715	37	$3{,}7\cdot10^2$
Ultrasonic homogenization						
5.	80% Fe_2O_3 + 20% Cr_2O_3	0,80	0,64	0,720	39	$1{,}1\cdot10^4$
6.	50% Fe_2O_3 + 50% Cr_2O_3	0,75	0,66	0,705	59	$4{,}1\cdot10^5$
7.	20% Fe_2O_3 + 80% Cr_2O_3	0,60	0,68	0,640	80	$9{,}3\cdot10^6$
8.	90% Fe_2O_3 + 10% Cr_2O_3	0,78	0,62	0,700	34	$2{,}8\cdot10^2$

Physical and chemical studies of Fe–Cr catalysts show well-marked difference in effective radius pore distributions caused by higher degree of dispersion of initial components for the catalyst prepared in US field. By action of the applied acoustic field Fe- and Cr nitrates dissociate to form adsorption active crystallization centers. Dispersion medium ingress into globules is improved by cavitation.

Thus, US homogenization allows formation of active catalytic structure as early as the stage of component mixing.

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PP-II-38

Formation and Stabilization of Monovalent Nickel in the $Ni(COD)_2/BF_3·OEt_2$ Catalytic System

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Previously we demonstrated that in the $Ni(PPh_3)_4/BF_3·OEt_2$ catalytic system, Ni(0) is oxidized quantitatively to Ni(I) to give cationic Ni(I) complexes with phosphine ligands [1].

In order to elucidate the possibility of stabilizing Ni^+ ions in solution without participation of traditional phosphine ligands, we studied the reaction of diamagnetic $Ni(COD)_2$ with $BF_3·OEt_2$ in a toluene solution at room temperature by EPR and IR spectroscopy.

On the addition of $BF_3·OEt_2$ to a solution of $Ni(COD)_2$ an intense signal typical of Ni(I) with $3d^9$ configuration ($g_{\|} = 2.38$, $g_{\perp} = 2.05$) appears in the EPR spectrum. Bands at 1122–1050 and 826 cm^{-1}, which are typical of a tetrahedral ion, appear in the IR spectrum. Thus, in the $Ni(COD)_2/BF_3·OEt_2$ system, Ni(0) is oxidized to Ni(I), the latter being stabilized in the solution, probably, by cyclooctadiene ligands as the $[Ni(COD)_2]BF_4$ complex.

Over a period of 5 to 10 min, the initial paramagnetic complex is converted into a new adduct. The EPR parameters ($g_x = 2.030$, $g_y = 2.048$, $g_z = 2.249$) attest to more covalent character of the metal-carbon bond in the new adduct. Simultaneously bands typical of organometallic bonds appear in the IR spectrum at 577 and 520 cm^{-1}. These spectral data attest to activation of the cyclooctadiene ligand in Ni(I) coordination sphere.

Preliminary studies showed that $Ni(COD)_2/BF_3·OEt_2$ exhibits high activity and high selectivity (up to 99%) in the catalytic cycloisomerization of cycloocta-1,5-diene to bicyclo[3.3.0]oct-2-ene under mild conditions.

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Influence of Preadsorption of Hydrogen on Carbon Oxides Interaction with a Surface of the Hydrogenation Catalysts Containing Fe, Co, Mn and Ni Nano-Particles

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Adsorptive and catalytic properties of mono- and bi-metal systems, containing Fe, Co, Mn, and Ni nano-particles, were investigated in relation of carbon oxides hydrogenation. The average size of particles of a metal phase was 20–40 nm according to electron microscopy. Carbon oxides chemisorption was studied by thermodesorption method. Reactions of hydrogenation were studied in the flow catalytic installation at atmospheric pressure and at temperatures from 150 to 450°C with the subsequent chromatographic analysis of products. Based on received experimental data and calculated values of desorption activation energy it has been established that carbon monoxide is adsorbed linearly and dissociatively on monometallic catalysts followed by interaction of atomic oxygen (formed or existing on the surface) with molecular adsorbed CO. Degree of CO dissociation increases among Ni, Fe, Mn. Carbon dioxide is adsorbed linearly to form carbonate-carboxylate complexes or dissociative with carbon monoxide formation. At joint adsorption there was not observed competition between carbon oxides. Saturation of the surface with hydrogen leads to some increase of desorption temperatures and desorption activation energies and also results in strengthening of the bond with Me. In the presence of hydrogen, which is strongly adsorbed on the surface, the number of d-electrons decreases resulting in weakening of the M–C bond and, accordingly, strengthening of the C–O bond. For the mixture of carbon dioxide and carbon oxide hydrogenation proceed through the stage of dissociative adsorption for both components. The basic products of carbon dioxide hydrogenation were methane, ethane and ethylene. Introduction of carbon monoxide in reaction mixture $CO_2 + H_2$ reduced the yield of methane and ethane, but promoted formation of ethylene.

This can be explained by formation of promoters of a new type on the surface influenced by the reactionary environment. Selectivity toward ethylene on the catalysts containing Fe, Mn, and Fe-Mn is 4–4,5 times higher that one on Ni and Ni-Fe-containing samples. Capable to dissolve, hydrogen give several forms upon adsorption on metals, one of which (HI) is bound with only one atom of metal (Me–H), and the other is strongly coupled with several atoms of metal (HII). The active carbon, formed as a result of dissociative adsorption of carbon oxides, can be hydrogenated to hydrocarbons or give inactive form. The reaction path leading to methane and others alkanes or to ethylene is defined by the ratio of concentrations HII : HI on the surface of active phase, which, in turn, depends on properties of the metal and the size of nano-particles.

PP-II-40

Steady State Isotopic Transient Kinetic Analysis of Catalytic Process of Complete Methane Oxidation

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The catalytic process of complete methane oxidation, which permits to limit emission of pollutions into atmosphere during energy production from natural gas, was investigated by means of the steady state isotopic transient kinetic analysis – SSITKA. This technique allows obtaining *in situ* kinetic information about the reaction mechanism and on the catalyst-surface intermediates [1]. The representative results for the catalytic oxidation of methane are shown in Fig. 1. The delay between Ar and $^{12}CH_4$ (and delay between Kr and $^{13}CH_4$) demonstrates adsorption of methane on the palladium catalyst. The delay between Ar and $^{12}CO_2$ (and delay between Kr and $^{13}CO_2$) is caused by adsorption of intermediates on the catalyst surface. On the basis of these results, kinetic parameters such as surface concentrations of methane and intermediates leading to formation of carbon dioxide as well as their surface life-time on the catalyst surface were determined.

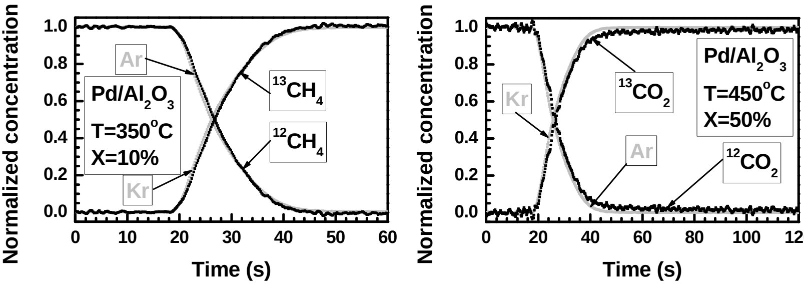

Fig. 1. SSITKA results for methane oxidation over Pd/Al_2O_3.

Acknowledgments. Authors gratefully acknowledges the financial support of this work by the Polish Ministry of Science, Project: UDA-POIG.01.03.01-00-072/08-00.

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PP-II-41

In situ HRTEM Study of Changes of Pd/γ-Al_2O_3 and Pd/CeO_2 Catalysts Induced by e-Beam

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Palladium supported CeO_2 and γ-Al_2O_3 catalysts are widely used in catalytic oxidation reactions. The catalyst deactivation occurs under the action of high temperature due to sintering of active component and support. It is important to study the sintering mechanism for understanding of the thermostable catalyst performance. In this work the investigation of sintering processes was carried out by HRTEM *in situ***.** The catalysts were analysed during the action of electron beam over the specimen directly in the camera of electron microscope.

In the initial calcined Pd/γ-Al_2O_3 samples the encapsulation of metallic particles by disordering shells of support is observed. This leads to formation of core-shell structures. It is noteworthy that Pd particles are not totally covered by the shells leaving small parts of metallic surface opened for exposition with gas reactant. The extreme action of electron beam results in full encapsulation of palladium metallic clusters by alumina shells. It is supposed that this process can be the reason of partial catalyst deactivation during the reactions.

In contrast to Pd/γ-Al_2O_3 the change of Pd/CeO_2 catalysts occurs in a different way. The initial Pd/CeO_2 samples contain metallic palladium nanoparticles stabilized on the ceria surface by epitaxial interaction with the oxide support. The action of electron beam leads to particle parting to small palladium ones with atomic dispersity and their migration over the support surface with formation of small metallic clusters. It is proposed that the solution of palladium inside subsurface layers of the cerium dioxide lattice takes place.

Thus, using model e-beam experiments it is possible to determine the behavior of the Pd catalysts during the temperature treatments. Pd/γ-Al_2O_3 catalysts are characterized by strong change of support, while in Pd/CeO_2 catalysts the main changes are related to palladium.

The work is supported by RFBR (grant № 07-03-12218).

PP-II-42

DRIFT and Quantum Chemical Studies of Methane Adsorption and Activation by Cationic Forms of Mordenite

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DRIFT and quantum-chemical studies of methane adsorption by various cationic (Na, Ca, Mg and Zn) forms of mordenite reveal different vibrational properties of adsorbed methane depending on the exchanged cation. Methane interaction with above cations leads to perturbation and polarization of molecules resulting in a low-frequency shift of the symmetric C–H stretching vibration forbidden in gaseous phase and increasing in intensity of this band for cations in the following sequences: $Na^+ < Ca^{2+} < Mg^{2+} < Zn^{2+}$. At the same time the bands corresponding to the asymmetric vibration are affected to much lesser extent. The strongest polarization by Zn^{2+} cation leads to chemical activation and as the result to heterolytic dissociation of methane at the relatively low temperature 473 K. Thus the redistribution and increasing of C–H stretching bands in intensity provides unique information on selective polarizability of different C–H bonds. The strongly polarized vibrations are closely connected with the heterolytic dissociation of methane, resulting in the formation of acidic hydroxyl groups and methyl fragments.

PP-II-43

An ESR-Study of $MgCl_2$-Supported Ziegler Catalysts Based on Titanium Compounds in Different Oxidation States

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More than 50 years are passed since the Ziegler-Natta catalysts were discovered. During this period an enormous number of articles and patents were devoted to the improvement of the catalyst performance, such as activity and stereoselectivity. But the elucidation of fundamental matters such as the structure of the active sites and its relationship with the catalyst performance has not been reached, even though the nature of the active sites plays a crucial role in determining the catalyst performance.

In this work we have investigated the influence of an oxidation state of titanium on performance of $MgCl_2$-supported catalyst in olefin polymerization.

Titanium compounds, such as Ti(IV)Cl_4, Ti(III)Cl_3•nDBE, [η^6-BenzeneTi(II)Al_2Cl_8] have been obtained for preparation of supported titanium-magnesium catalysts (TMC). Oxidation state of titanium in these compounds was determined with ESR.

TMC have been prepared by adsorption of these compounds on magnesium chloride. ESR-technique has been used to estimate the titanium oxidation state distribution during catalyst preparation and activation with organoaluminium compound (OAC). It has been found that the catalysts $TiCl_4/MgCl_2$-TIBA and $TiCl_3$•nDBE/$MgCl_2$-TIBA have nonuniform titanium oxidation states distribution: there are Ti(IV), Ti(III) and Ti(II) ions on the catalyst surface in the first case and Ti(III) and Ti(II) in the second one. A small part of titanium is represented as isolated ions in different coordination environment. A large one is ESR-silent clustered ions. On the contrary the catalyst [η^6-BenzeneTi(II)Al_2Cl_8]/$MgCl_2$ has uniform titanium oxidation state distribution: the main part of titanium is represented as isolated Ti^{2+} ions.

These catalysts have been investigated in ethylene homopolymerization. It has been found the catalyst [η^6-BenzeneTi(II)Al_2Cl_8]/$MgCl_2$ has high activity in ethylene homopolymerization in absence of organoaluminium cocatalyst. These results allow using this catalyst as suitable model for the elucidation of monomer coordination to titanium and also determination of the contribution of OAC to the broadening of molecular weight distribution of polyolefins.

PP-II-44

The Structure of Supported Tungsten Containing Catalysts of Oxidative Conversion of C_1–C_4 Alkanes

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Catalysts based on 12 series W heteropoly compounds (HPC) supported on Si-containing oxide are investigated and patented for the processes of C_1–C_4 alkane oxidation to alcohols, aldehydes, and C_2–C_4 olefins. Their high activity and thermal stability are established at T = 300–800°C in the following reaction mixtures: O_2, N_2 and water vapor. It is known that bulk HPC undergo destruction on air at 400-500°C. The reason of thermal stability of the supported HPC in high-temperature oxidative processes is not clear. In this contribution the structural transformation of heteropoly acid (HPA) $H_3PW_{12}O_{40}$ in the catalysts (loading 15-20%) were studied as a function of the temperature and the nature of the carrier (O_2, water vapor, complex composition of a reaction mixture – alkane, O_2, N_2, water vapor).

Results of XRD, IRS, TPR methods indicated the preservation of $H_3PW_{12}O_{40}$ structure on the support in a steam-air atmosphere up to 550-650°C (optimum temperature for partial oxidation of CH_4 into CH_3OH and CH_2O). At 600–900°C intermediate precrystal oxide-type phase with uncertain stoichiometry formed, although some features of HPA preserved (W-O-W, W=O). Only at $T \geq 900°C$ (optimum reaction temperatures for oxidation of alkanes into olefins and H_2) the phases of W (VI) appeared. During oxidative dimerization of CH_4 into C_2-hydrocarbons in absorbed layer on $[PW_{12}]/SiO_2$ (Al_2O_3) catalysts (reaction temperature 650–800°C) the HPC phase was observed to renew in situ. It is assumed that the HPC phase, renewed under the conditions of high-temperature oxidative conversion of alkanes, is formed due to interaction of heated water vapor with non-phase fine-dispersive W oxides.

Effect of Reaction Pressure on Performance of Pd/HZSM-5 Catalyst for Selective Hydrogenation of Benzene in Aromatics-Containing Feed

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In this study an effective catalyst for selective benzene hydrogenation in aromatics containing feed has been developed. The catalyst (1 wt.% Pd/HZSM-5) was prepared by incipient wetness impregnation of HZSM-5 zeolite (AlSiPenta, SiO_2/Al_2O_3=24) with an aqueous solution of $[Pd(NH_3)_4](NO_3)_2$ followed by drying at room temperature, calcination in air (500°C, 2h), and reduction in hydrogen (450°C, 1h). The catalyst was tested in selective hydrogenation of C_6H_6 using C_6H_6:C_7H_8:p-C_8H_{10}:C_6H_{14} mixture (1:2:2:4 molar ratio). Experimental conditions were: LHSV = 1 h^{-1}, molar ratio H_2:aromatics = 35:1. The pressure was varied from 1 to 7 atm.

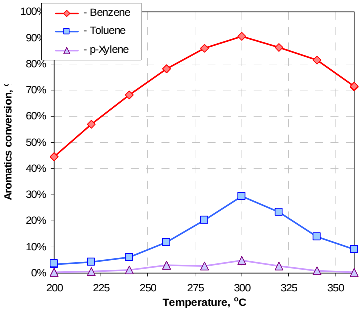

Fig. 1 Temperature dependence of aromatics conversion over **1%Pd/HZSM-5** catalyst in hydrogenation of C_6H_6:C_7H_8: p-C_8H_{10}:n-C_6H_{14} mixture (1:2:2:4 molar ratio).

The performance of Pd/HZSM-5 catalyst at atmospheric pressure is favorable in terms of benzene and xylene conversion ($S_{C6H6\ \mathrm{max}}$ = 65%). However for practical implementation it is necessary to improve the catalyst selectivity and reduce the toluene conversion. Increasing the reaction pressure to 2 atm reduces the toluene conversion and enhances benzene conversion at 250–300°C (Fig.1). Similar trend was observed at 3 atm as well. However, further increase of reaction pressure to 5 atm results in higher toluene conversion. Finally, at

7 atm, both toluene and xylene conversion rapidly increases. The best selectivity in C_6H_6 hydrogenation (~87%) was attained at 2 atm and T_{reac} = 200–240°C.

The radionuclide experiment with ^{14}C labeled benzene provided further insight into reaction mechanism of selective benzene hydrogenation. It was demonstrated that the kinetic factor is predominant over benzene-xylene transalkylation process.

XPS Study of Interaction of Pt/SiO_2 Catalysts with NO_x Mixture: The Nature of Surface Species

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The nature of surface species that are formed in supported metal particles plays a key role in the mechanism of redox catalytic reactions. Supported Pt systems are considered as promising catalysts for various oxidation-reduction processes, including abatement of CO, hydrocarbons and NO_x from automobile exhaust gases.

In the present work we have studied the reactions of NO_x ($NO + O_2$) with the nanodispersed Pt/SiO_2 model catalysts prepared by UHV deposition of platinum on the thin films of SiO_2 grown on the Ta foil surface. TEM analysis of the samples demonstrated uniform size distribution of metal particles with the mean sizes of about 5 nm. According to XPS (Pt4f binding energies and FWHM's of the Pt4f lines), two different states of active component can be produced by the reaction of NO_x with the supported Pt particles, depending on reaction conditions. The first state, which is formed at room temperature, is associated with oxygen atoms dissolved in metal particles. The second state produced as result of the NO_x treatment at elevated temperatures ($\geq 200°C$) is associated with platinum oxide particles, PtO_x. The two surface species differ in their behaviour towards hydrogen. Oxygen atoms dissolved in platinum reacts readily with H_2 even at room temperature. Reduction of platinum oxide particles is found to proceed only after heating of the sample at $\geq 100°C$.

Thus, two different states of active component can be obtained in the reactions of supported metal catalysts with NO_x. These states differ in reactivity towards reducing agents. The role of these species in the mechanism of redox catalytic reactions is discussed.

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PP-II-47

Conversion of Biofermentation Products Using Porous Membrane Catalytic Systems

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Using biofermentation products as feed for the processes of hydrogen generation and other valuable substances is great of interest for the moment. Currently an attention is paying on gas-phase heterogeneous catalytic reactions by using microreactors with the aim of the process intensification. The most prospective trends in this field are the processes of methane conversion into syngas and light olefins as well as the steam reforming of bioproducts such as ethanol, acetic acid, etc. into hydrogen.

For this purpose several types of catalytic ceramic membranes, which are active in this reaction were synthesized. Set of experiments showed that methane conversion occurred intensively already at 250-400°C, which is much lower then in traditional reactor with a loaded catalyst. We believe that this difference is because of improving of heat and mass transfer. In our experiments the catalysts were formed inner of the membrane channels based on metal-contained complexes systems. All studied membranes had nanosize metal oxide catalysts and were characterized by different composition and activity in studied processes.

It was shown that specific productivity of syngas forming reach up to 11500 L/dm^3_{membr} h in the process of dry methane reforming at 650°C. Ethanol and acetic acid practically convert completely into hydrogen-containing gas at 400–500°C with specific productivity 600 $l/dm^3 \cdot h$.

The relationships between composition and structure of membrane-catalytic systems and activity in above mentioned processes dicussed.

Acknowledgements

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DFT-Modeling of the Mechanism of Alkenes Hydroformylation on a Platinum-Lithium Complex with Hydrophosphoryl Ligands

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Catalytic systems for alkene and alkyne functionalization based on Pd and Pt complexes with the hydrophosphoryl ligands are of growing interest. Our previous DFT study of the mechanism of alkene hydroformylation on organoplatinum hydride $HPt[(R_2PO)_2H](PR_3)$ (**1**) (R = H, Me, CF_3) has shown that reversible shifts of proton in the $PR_2OH \cdots O{=}PR_2$-chain inside quasi-chelate ligand $[(R_2PO)_2H]$ proceed in several reaction steps thus providing fine tuning of electron density in the catalytic centre and acting as a molecular switch [1,2]. Here we present the results of catalytic cycle modeling of ethylene hydroformylation on model platinum-lithium hydrides $HPt[(R_2PO)_2Li](PR_3)$ (**2**) and $HPt[(R_2PO)_2Li(H_2O)_2](PR_3)$ (**3**) (R = H) where Li cation is strongly coordinated to both hydrophosphoryl oxygenes. The structures of all stationary points of PES's were calculated on DFT level of theory (PBE, TZ2p basis set for valence electrons, SBK potentials for core electrons) using Hessian analysis and construction of IRC.

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PP-III-2

A Trigger Model of Oscillation Phenomena in the NO+H_2 Reaction on Noble Metal Surfaces

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A set of transition metal single crystal surfaces was analyzed with respect to non-liner phenomena in NO+H_2 reaction and adsorbed layer chemistry in comparison with thermodynamic properties of the adsorbed NH_n species (n=0;1;2;3) calculated by means of semi-empirical Method of Interacting Bonds [1]. The combination reaction of the adsorbed NH species was found to proceed easily on surfaces exhibiting oscillatory behavior in heading reaction, whereas it is substantially endothermic on non-oscillating surfaces. A trigger model of reaction rate oscillations is proposed, where the combination of NH species operates as a temporary reaction route. This pathway is actually cut off until the nitrogen coverage reaches some critical value assuring the necessary conditions for a chain-type NH combination reaction. Then it starts initiating the surface wave propagation and stops immediately on completion the wave leaving the surface nearly clean and ready for the next oscillatory cycle.

Mathematical simulation of the reaction kinetics is performed. Calculations corroborated availability of the sustained reaction rate and respective coverage oscillations within the trigger mechanism at acceptable rate constant values. In contrast to previous oscillation mechanisms no any assumptions such as addition of a buffer step, reaction rate constants dependence on coverage, surface reconstruction, etc. were made in the trigger model. Besides that, the suggested heading makes clear the feedback mechanism and the critical point of regular surface wave initiation. Reliability of calculations, correspondence of the trigger model to relevant experimental data, and possibility of a similar models application to other oscillating reactions are also considered.

Reference:

[1] Cholach, A.; Bulgakov, N; Nieuwenhuys, B. *Surf. Sci.* 2004, *573*, 2, 264.

Modelling of Complicated Oscillations of the Catalytic Reactions Caused by Fluctuations

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In this message we investigate the possibility to describe complicated oscillations with the following elementary mechanism «double trigger»:

1) $A_1+Z+X \rightarrow 2Z$; 2) $Z+X \rightarrow 2X+A_2$

Fluctuations of stage frequencies w_1 and w_2 are considered in the following form:

$$dw_1/dt = (aw_1+w_2)\, z\, (1-z)^2 - w_1 + c;$$

$$dw_2/dt = (bw_1+w_2)\, z^2 (1-z) - w_1 + c,$$

where a, b, c are constants (>0); the concentration of the catalyst centers occupied by intermediate substance X is $x = 1 - z$; rate constants are k_i ($w_i = k_iC_i$), and C_i represent concentration of basic substances A_i.

The analysis has shown that at $w_2 \in [0.2, 2.2]$ and $c \in [0.8, \infty]$ in area $a \approx a^*$, $b \approx b^*$ the mechanism has two unstable stationary states (SS). Both SS are saddle type with the homoclinic structure and cause complicated oscillations (Fig. 1a). In three-dimensional space there is a rotation of trajectories on the bent toroidal surface similar to "eight" or a Mobius band which have the projection to a phase plane «z–w_1» shown on Fig. 1b.

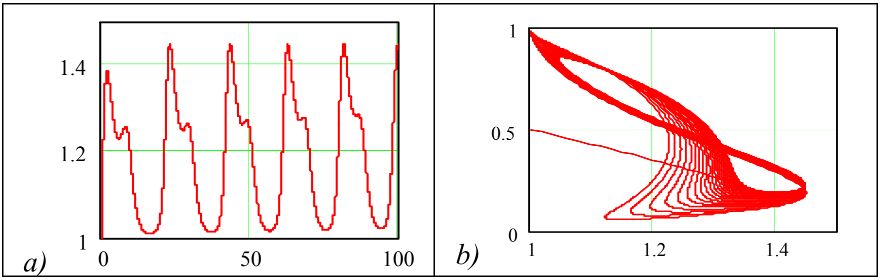

Fig. 1. Unstable states at $a = 1$, $b^* = 0.95$, $c^* = 1$. A nonstationary portrait $w_1(t)$ is shown on (a) and a phase portrait z (w_1) at initial conditions $z_0 = 0.5$, $w_{10} = 1$, $w_{20} = 2$ is shown on (b).

PP-III-4

Thermodynamic Analysis for Alkylation Process Macrokinetic Modeling

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Alkylation of benzene with long-chained olefines is a part of linear alkylbenzene sulfonates production, which are known as widespread surfactants. Computer simulation of catalytic process is an efficient instrument to study different factors influencing quantitative and qualitative characteristics of products in concern of improvement of the existent technologies [1].

The aim of the work at present stage of research was development of formalized reaction network. In order to evaluate reaction running thermodynamic probability quantum-chemical methods could be applied. In particular, semi-empirical PM3 method of Gaussian program package was used. Calculated values of reactions entropy, enthalpy and Gibbs free energy changes were taken into account to choose the most probable mechanism of the reaction and built a macrokinetic model base. Thus, the reaction network was proposed.

The inverse kinetic problem solving for such a multicomponent chemical process as alkylation is complicated due to innumerable variants of hydrocarbons transformations. Therefore, the approach based on thermodynamic data [2] was used for estimation of the kinetic parameters.

References:

[1] Rajeshwer, D.; et al. *International Journal of Chemical Reactor Engineering,* **2006**, *4*, A17.
[2] Martinis, J. *Single event kinetic modeling of solid acid alkylation of isobutane with butenes over proton-exchanged y-zeolites*, Texas A&M University, **2004**.

Higher Hydrocarbons C_9–C_{14} Dehydrogenation Process Thermodynamics Analysis with the Use of Quantum-Chemical Approaches

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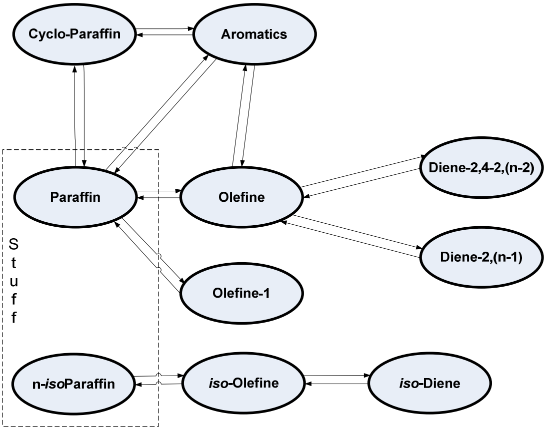
At present time quantum-chemistry and molecular dynamics approaches are generally used in numerical electron and atomic structure modeling of complicated objects. These methods permit calculation of different molecular properties of chemical systems such as energy, nuclear magnetic resonance, spectral, thermochemical and others characteristics [1].

Based on quantum-chemistry calculations the thermodynamic probability was evaluated for the steps of C_9–C_{14} hydrocarbons dehydrogenation process and formalized transformation scheme was proposed.

The Gaussian program package was used with the procedure PM3 of NDDO (Neglect of Diatomic Differential Overlap) method. With such a method only the valent electrons are taken into account to calculate the electron molecular structure. Other electrons in atom are involved as implicit state with the empirical characteristics. The NDDO method neglects the biatomic differential covering of the atomic orbits. These approaches can be used for comparative analysis of any compound properties [2].

It was found that aromatization reaction appears to be the most thermodynamically probable ($\Delta G°_r \approx -300$ kJ/mol). The reactions of dienes formation with cumulative double bonds are not thermodynamically allowed ($\Delta G°_r \approx 9$ kJ/mol). The presence of isomeric paraffins in product is determined by iso-paraffins dehydrogenation process. All other possible reactions are thermodynamically probable and have approximately the same value of isobaric-isothermal potential ($\Delta G°_r \approx -50$ kJ/mol).

To obtaine the formalized reaction scheme the substances were combined into groups of pseudo components according to their reactivity. This reactivity was evaluated on the base of ΔG°_{r}. The chosen formalization level does not block up mathematical description and permits taking into account formation of olefines and dienes with double bond in different positions and transformation of iso-paraffins as raw components.



Formalized scheme for the mechanism of dehydrogenation process

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PP-III-6

Mathematical Model of Ultrasonic Impregnation of Porous Capillary Solid Bodies

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Description of the mechanism of ultrasonic impregnation of heterogeneous catalyst porous structures is based on acoustic effects occurring in liquid on liquid/solid body interface. Heterogeneous catalyst supports have large porous structure, the external surface of which is an oxide formation with many open canals and transport pores. Transition from acoustic flows to high-amplitude vibrations causing disruption of the liquid integrity radically changes the nature of ultrasonic effect on liquid/solid phase interface.

Model of US impregnation mechanism can be represented by the following equation:

$$\frac{\partial C}{\partial t}+\left(\vec{V}\cdot\nabla\right)\cdot C=\text{Д}_{\partial}\Delta C+W_{\partial} \qquad (1)$$

where C – concentration of cavitation cavities; Д_{∂} – coefficient of diffusion in US field; W_{∂} – intensity of cavitation cavern source.

Intensity of cavitation cavern source can be described with the following relation:

$$W_{\partial}=\alpha\frac{E}{W\cdot t\cdot f} \qquad (2)$$

where α – transfer factor of acoustic energy to cavitation energy; E – energy density of acoustic radiation; W – energy of formation of one cavitation cavern; f – US field frequency; t – cavitation cavern lifetime.

Capillary suction rate through pores is proportional to driving pressure ($P_{\text{дв.}}$). US radiation amount of driving pressure is defined by the relation:

$P_{\text{дв.}}= P_{\text{к}} - \rho g \ell \sin\beta + P_{\text{уз.}}$,(3)

where $P_{\text{к}}$ – capillary pressure; ρ – impregnating liquid density; g – acceleration of gravity; ℓ – impregnation depth; β – pore curvature factor; $P_{\text{уз.}}$ – acoustic pressure.

PP-III-6

For one side-open pores impregnation rate is defined by the relation:

$$\frac{d\ell}{dt}=\frac{r^2}{8\mu\ell}\left(P_k+P_0-P_0\frac{\ell_n}{\ell_n-\ell}-\rho g\ell\sin\beta+P_{\text{уз.}}\right), \qquad (4)$$

where $\frac{d\ell}{dt}$ – linear impregnation rate; P_0 – initial gas pressure in pore; ℓ_n, r – pore length and radius; μ – liquid viscosity.

Diffusion rate of active components in solution is described by Fick equation:

$$\frac{dG}{dt}=-D_{\text{э}}S\frac{dC}{d\ell}, \qquad (5)$$

where $\frac{dC}{d\ell}$ – component concentration gradient in perpendicular direction to grain surface; S – grain outer surface; $D_{\text{э}}$ – effective diffusion coefficient.

Effective diffusion coefficient during US impregnation is defined by the equation:

$$D_{\text{уз.}} = \alpha D_{\text{э}}, \qquad (6)$$

where $\alpha=\frac{\phi\Phi}{R}$; $D_{\text{э}}$ – effective coefficient of component molecular diffusion in impregnating solution; φ – porosity; Φ – form factor; R – pore mid-radius.

To estimate the cavern growth rate as a result of unidirectional diffusion equation (1) is used provided $Д_{\partial}\Delta C$ >>$W_{\text{э}}$. In this case the diffusion flow is described with equations:

$$\frac{\partial C}{\partial t}+\left(\vec{V}\cdot\nabla\right)\cdot C=Д_{\text{э}}\Delta C \qquad (7)$$

$$C(t)=C_0\left(1+\varepsilon\sin\omega t\right) \qquad (8)$$

$$R(t)=R_0\left(1+\xi\sin\omega t\right) \qquad (9)$$

$$I=24\pi D_{\text{э}}C_pR\xi^2 \qquad (10)$$

References:

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Quantum Chemical Insight on H_2S Oxidation over the Surface of Active Carbon: An Impact of Spin Catalysis

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Hydrosulphide (H_2S) and lower mercaptanes are known atmospheric pollutants. H_2S fixation is an actual and practically important task. The method of H_2S oxidation by molecular oxygen in aqueous solution of quinones (Q) is one of the most frequently used. Alternative way is a catalytic oxidation on active carbon (AC) surface. According to the current opinion in carbon chemistry the nature of elementary acts in both processes is similar, since ACs contain quinoid surface groups (Q-groups). Thus, the generalised reaction of H_2S oxidation implies reaction with Q-groups.

A series of arguments are provided to support the following 2-stage mechanism of the process:

$Q + H_2S \rightarrow HQ + S;$

$HQ + O_2 \rightarrow Q + H_2O,$

where Q can be either quinone or Q-groups on the surface of AC. The Q and Q-groups are regenerated in the process and, therefore, the overall process may be treated as catalytic one. The elementary acts of this process are not catalytic in a classical paradigm, however, these acts are the subject of spin catalysis. These elementary reactions are spin-dependent and should be sensitive to presence of spin catalysts or intermediate spin-active species. The quantum chemical simulation was performed for the reaction of H_2S with quinones and with model carbonic cluster mimicking an active centre on the surface of active carbon. Energetic parameters of elementary reactions were calculated. An impact of multiplicity state of the system on the pass of reactions was proposed. The quantum chemical calculations demonstrated the formation of elementary sulphur and polysulphides. One can also assume that the oxidative catalysis of the lower mercaptanes passes in analog ous way.

PP-III-8

Carbon and Hydrogen Coadsorption in the Subsurface Region of Pd Catalysts: A Density Functional Study

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Palladium is one of the most important hydrogenation catalysts. In particular, it is used for the removal of acetylene from ethylene feedstocks. On an ideal catalyst, acetylene would be hydrogenated to ethylene while ethylene remains intact. However, experiments show that the selectivity of this process is reduced in the presence of subsurface hydrogen because ethylene is also hydrogenated. Although it is not clear in what way subsurface hydrogen affects that reaction it should be suppressed in an efficient catalytic system. Recently carbon deposition was shown to prevent the participation of bulk-dissolved hydrogen in the reaction, thus improving the selectivity for ethylene as product [1,2]. To explore the mechanism of carbon-hydrogen interactions in the subsurface region we carried out density functional calculations on periodic slab models of Pd(111) [3].

On Pd(111) at low coverage separately adsorbed carbon atoms are calculated to be more stable than dimer (C_2) and trimer (C_3) species. Penetration of carbon atoms from the surface to octahedral subsurface (oss) interstitial sites is energetically favorable in agreement with a previous computational study on Pd nanoclusters [4]. According to the energetics and the activation barriers calculated, at coverage of about half a monolayer of carbon, the formation of C_2 and C_3 species, which are precursors of a graphene phase, becomes competitive to the diffusion of carbon monomers to oss sites. Our calculations also showed that carbon easily replaces hydrogen in oss sites and strongly destabilizes hydrogen located in neighboring tetrahedral subsurface sites. These results suggest that even small amounts of carbon on Pd catalyst may significantly suppress hydrogen dissolution in the subsurface region.

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PP-III-9

Spin Effects in Catalytic Reactions in Solution

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The influence of electron and nuclear spins on enzymatic processes and photocatalytic reactions in solution will be considered. The detailed description of the elementary steps of the catalytic cycle of horseradish peroxidase (HRP) is made possible by the analysis of experimentally observed kinetic magnetic field effects in the NADH oxidation catalyzed by HRP suggesting that the primary step of the catalytic cycle is the single electron transfer with the formation of NADH•+ radical cation and ferroperoxidase intermediate (Per2+). As a result, the proposed new mechanism allows us to specify the role of the electron spin states for the integrity of the HRP catalytic cycle.

The phenomenon of spin catalysis of radical chemical reactions has been observed in 1994 by Buchachenko and Turro with coworkers. It manifests itself as the increasing of the recombination probability in RP under the influence of paramagnetic particles. This report demonstrates the influence of so called “third spin” on the spin evolution in the radical pairs and biradicals in photoinduced processes. The investigations of the effects of mutial influence of spins in the multispins systems are very popular now because of their theoretical and practical importance.

PP-III-10

DFT Simulation of Al,Zr-Intermediates Formation in the Alkene Hydroalumination by Dimeric Form of $ClAlBu^{i}_{2}$, Catalyzed with Cp_2ZrCl_2

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The mechanism of Al,Zr-intermediates formation in the alkene hydroalumination with $ClAlBu^{i}_{2}$, catalyzed by Cp_2ZrCl_2 has been studied by the means of DFT calculations (*PRIRODA-06*, PBE/3z). The participation of associated forms of organoaluminim compounds (diisobuthylaluminium chloride) is considered in the reaction models. We examined the process of key intermediate Zr,Al-complexes formation in the reaction of Cp_2ZrCl_2 and $ClAlBu^{i}_{2}$ and showed thermodynamically profitable pathway. The free energy of stages (a-l), which are presented in scheme below, are determined at T = 203 K.

a. $Cp_2ZrCl_2 + (ClAlBu^{i}_{2})_2 \rightarrow Cp_2ZrCl_2 \bullet (ClAlBu^{i}_{2})_2$; $\Delta_R G° = 9.8$
b. $Cp_2ZrCl_2 \bullet (ClAlBu^{i}_{2})_2 \rightarrow Cp_2ZrBu^{i}Cl + ClAlBu^{i}_{2} \bullet Cl_2AlBu^{i}$; $\Delta_R G° = 0.9$
c. $Cp_2ZrBu^{i}Cl \rightarrow Cp_2ZrHCl + CH_2{=}C(CH_3)_2$; $\Delta_R G° = 3.1$
d. $Cp_2ZrHCl + (ClAlBu^{i}_{2})_2 \rightarrow Cp_2ZrHCl \bullet (ClAlBu^{i}_{2})_2$; $\Delta_R G° = 8.3$
e. $Cp_2ZrHCl \bullet (ClAlBu^{i}_{2})_2 \rightarrow Cp2ZrBu^{i}H + ClAlBu^{i}_{2} \bullet Cl_2AlBu^{i}$; $\Delta_R G° = 7.8$
f. $Cp_2ZrBu^{i}H \rightarrow Cp_2ZrH_2 + CH_2{=}C(CH_3)_2$; $\Delta_R G° = 7.2$
g. $Cp_2ZrH_2 + (ClAlBu^{i}_{2})_2 \rightarrow Cp_2ZrH_2 \bullet (ClAlBu^{i}_{2})_2$; $\Delta_R G° = -6.3$
h. $2\ Cp_2ZrH_2 \bullet (ClAlBu^{i}_{2})_2 \rightarrow [Cp_2ZrH_2 \bullet (ClAlBu^{i}_{2})]_2$; $\Delta_R G° = 2.1$
i. $[Cp_2ZrH_2 \bullet (ClAlBu^{i}_{2})_2]_2 \rightarrow [Cp_2ZrH_2 \bullet ClAlBu^{i}_{2}]_2 \bullet ClAlBu^{i}_{2} + ClAlBu^{i}_{2}$;
$\Delta_R G° = 0.6$
k. $[Cp_2ZrH_2 \bullet ClAlBu^{i}_{2}]_2 \bullet ClAlBu^{i}_{2} \rightarrow [Cp_2ZrH_2 \bullet ClAlBu^{i}_{2}]_2 + ClAlBu^{i}_{2}$;
$\Delta_R G° = 0.4$
$2\ ClAlBu^{i}_{2} \rightarrow (ClAlBu^{i}_{2})_2$ $\Delta_R G° = -16.0$
l. $[Cp_2ZrH_2 \bullet ClAlBu^{i}_{2}]_2 \leftrightarrow 2\ Cp_2ZrH_2 \bullet ClAlBu^{i}_{2}$; $\Delta_R G° = -2.7$

It was shown that reaction of Cp_2ZrCl_2 with dimeric form of diisobuthylaluminium chloride is more profitable than reaction with monomeric form, which is generated in the endothermic dissociation of initial $(ClAlBu^{i}_2)_2$ ($\Delta_R G°$ = 16.0 kcal/mol, $\Delta_R H°$ = 24.3 kcal/mol).

Acknowledgements:

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PP-III-11

Kinetic Model of Transformations in the Cp_2ZrCl_2 – $AlMe_3$ System

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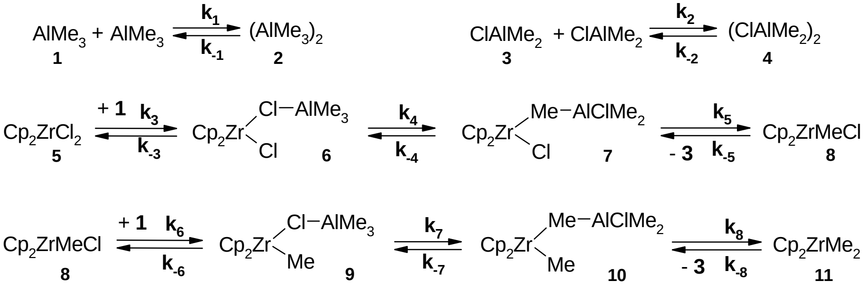
Rate constants of elementary stages for reaction $Cp_2ZrCl_2 + AlMe_3$ have been calculated with Eyring equation by using the results of quantum-chemical data [1] (*PRIRODA*-06, RI-MP2/L2 // PBE/L2, scalar-relativistic Hamiltonian, T = 298K).



Equilibrium Constants (K) and Constants of rates (k)

	1	2	3	4
K_n	4.6e+08	4.8e+12	1.3e+02	3.4e-02
k_n	1.6e+12	1.5e+14	1.6e+14	6.4e+04
k_{-n}	3.5e+03	3.1e+01	1.2e+12	1.9e+06
	5	6	7	8
K_n	1.1e-01	2.8e+03	2.1e-07	4.6e-03
k_n	2.6e+11	1.5e+14	9.2e-01	6.9e+11
k_{-n}	2.3e+12	5.4e+10	4.3e+06	1.5e+14

Equilibrium concentrations ($c_0[Cp_2ZrCl_2] = 0.03$ mol/l]):

$c_{Zr} : c_{Al}$	**5**	**6**	**7**	**8**	**9**	**10**	**11**
1:1	2.0e-03	3.9e-07	1.3e-08	2.8e-02	1.1e-04	2.4e-11	2.1e-06
1:3	3.9e-04	4.2e-07	1.4e-08	2.9e-02	6.5e-04	1.4e-10	1.2e-05
1:60	6.6e-05	3.9e-07	1.3e-08	2.7e-02	3.3e-03	7.0e-10	5.7e-05

Accoding to obtained data compounds **8**, **9**, **5**, **11** predominated in solution at equllibrium conditions.

Acknowledgements:

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Mechanism of Gold Cluster's Oxidation: DFT Study

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As one of the key factors to understand the gold catalytic activity, the adsorption behavior of oxygen molecules on Au clusters has been studied. Despite extensive investigations of model gold cluster, the mechanism of molecular oxygen activation in these reactions is unclear.

The interaction of O and O_2 with symmetrical tetrahedral Au_{20} and distorted $[Au_{20}]$ clusters has been studied using the density functional theory with PBE functional and gold pseudopotential with relativistic corrections included. Oxygen atom may be bonded with apex or facet Au atom (33.7 and 15.6 kcal/mol), and with two adjacent Au atoms of edge (46.6 and 62.7 kcal/mol). Calculated binding energies agree with experimental results [1]. From a temperature-programmed desorption experiment of O adsorption on Au(111) surface the Au-O bond strength is estimated to be about 56 kcal/mol with an upper limit of 64 kcal/mol.

It was found that the dissociative adsorption is more favorable (two Au-O-Au bonds, 34.9 kcal/mol) than molecular adsorption (Au-O-O bond, 19.3 kcal/mol) for O_2 chemisorption. For distorted $[Au_{20}]$ cluster the additional forms of O coordination appear, including μ_3-O form.

The simulation of methane oxidation with Au_{20} as a catalyst was carried out. According to the calculation, Au_{20} cluster may serve as a catalyst to methanol producing from methane under conditions of formation of surface bound O atoms.

Acknowledgements

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PP-III-13

Development of Multiplet Theory of Catalysis

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Multiplet theory of catalysis created by A.A. Balandin was used by its author for explanation and classification of reactions with participation of enzymes. According to Balandin, index group is composed of four or six atoms and these reactions are referred to doublet or triplet types, as a rule.

Our development of this theory is reduced to that the index group defined by Balandin is not surely limited by number of atoms and distances between them but it is always composed of fixed number of oriented triatomic combinations. Corresponding to analysis of steric interactions between substrates and surfaces of enzymes, mathematical tools are developed.

An essence of the developed approach includes the following. Atoms in a substrate molecule are classified to internal, external and boundary ones (this classification was suggested by N.S. Zefirov, V.N. Drozd et al.). Then matrix of vectors between all pairs of atom is created and oriented triatomic combinations are also classified to internal and external ones by means of vector analysis.

The set of oriented triatomic combinations can be considered as third generation of chemical formulas (after composition and structural formulas) for organic substances. They describe not only composition (composition formulas) and topology (structural formulas), but full geometry of molecules. The same sets make it possible to describe the structure of hard surfaces in heterogeneous catalysis and to reduce multiplets to finite quantity of triatomic combinations, for example, a triplet – to one combination, a multiplet from six atoms – to four combinations, and so on. Thereby, enough similar, by chemical composition, surfaces can be compared and distinguished, and multiplets can be classified in more detail. It is noted that our formulas differ for both conformers and enantiomers of molecules.

PP-III-14

Thermodynamic Modeling of the Catalytic System Fe_2O_3 – Mn_xO_y for Ammonia Oxidizing

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For a long time oxidization of ammonia in industry was carried out on a platinum catalyst with rhodium and palladium addition. But this catalyst is expensive, scarce, and, most important, gives permanent losses at application. All these reasons have put a task to search new catalysts, which possess high activity and selectivity and are economic.

Today the catalyst on the base of system Fe_2O_3 – Mn_xO_y is 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 results.

In room temperatures hydrated manganese nitrate is dehydrated, decomposed and reduced in according with the reaction:

$$Mn(NO_3)_2 = MnO_2 + 2O_2 + N_2$$

and stay stable up to 793 K.

In the range of temperatures from 793 to 1374 K Mn(IV) oxide is reduced and transformed to Mn(II) oxide in according with the reaction:

$$4MnO_2 = 2Mn_2O_3 + O_2$$

The further oxidation with formation of manganese oxide Mn_3O_4 occurs under higher temperatures:

$$6Mn_2O_3 = 4Mn_3O_4 + 3O_2$$

At 1461 K the mixed oxide of manganese Mn_3O_4 interacts with the oxide of iron(III) with the formation of manganese ferrite and free oxygen (as above):

$$Fe_2O_3 + 2Mn_3O_4 = 6MnFe_2O_4 + O_2$$

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.

PP-III-15

Lewis Acids Catalysis of Curtius Rearrangement

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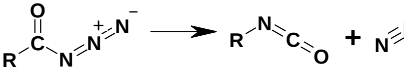
The Curtius thermal rearrangement of acyl azides is one of the classical reactions in organic chemistry. It is one of the few methods of synthesis of phosgene free isocyanates which are the main monomers in polyurethane chemistry.



The reaction usually proceeds at high temperature and is accelerated by Lewis acids. In previous study authors found that the thermal Curtius rearrangement of arylacyl azides proceeds by one step mechanism starting from *syn*-conformer of acyl azide which is more stable than *anti*-conformer [1, 2]. The mechanism of catalysis by Lewis acids was established in this work by DFT (PBE/TZ2P) calculations of PES. The objects of investigation were *syn*-$PhC(O)N_3$–L, where L are Lewis acids (BF_3, $AlCl_3$, $SbCl_5$).

Six types of stable complexes for each Lewis acid (L) with composition 1:1 and 1:2 and transition states corresponding to their transformation into the products were found. The effective activation energies of catalytic processes (see Table, energies in kcal/mol) are significantly lower than Ea of uncatalytic reaction (34.5 kcal/mol). The increased reactivity of complexes in the rearrangement is related to deviation of azide group from the benzene ring plane as the result of complexation with Lewis acids ("induced ortho-effect").

	E_a	E_{eff}	E_a	E_{eff}	E_a	E_{eff}
	L = BF_3		L = $AlCl_3$		L = $SbCl_5$	
I	27.2	22.8	27.0	2.3	27.24	18.9
II	29.0	23.1	27.8	3.0	28.3	20.0
III	32.7	31.0	28.3	15.2	30.8	29.9
IV	35.3	33.8	40.2	29.2	35.6	34.3
V	26.2	20.5	21.9	-9.5	NE*	NE
VI	27.5	21.1	23.4	-6.7	NE	NE

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Oxidative Destruction of Carboxylic Acids during Homogeneous Catalytic Oxidation of Methane

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On basis of biomimetic approach we earlier designed efficient rhodium–iodide–copper (iron) chloride catalytic systems for methane oxidative functionalization by O_2/CO and studied the reaction mechanism [1]. It was found that lower aggressive media CD_3COOD – D_2O can be used for methane oxidation. We studied this reaction by ^{1}H NMR in order to analyze CD_3COOCH_3, CH_3OD, HCOOD, CH_3COOD. By competitive oxidation of CH_4 and CD_4 in CH_3COOH - H_2O we found unexpectedly high value (> 50) for the KIE. Acetic acid appears to be exposed to oxidative destruction into methyl acetate. In deuterated medium we could not observe the reaction by ^{1}H NMR. Propionic acid is converted into $C_2H_5COOCH_3$ + CH_3OH, $C_2H_5COOC_2H_5$ + C_2H_5OH, and CH_3COOH. Possible mechanisms are discussed.

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PP-IV-2

Photolysis in the Bromination of Liquid-Phase Acetone Solutions

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Stirred actinometric solutions of Potassium ferrioxalate, K_3 [Fe $(C_2O_4)_3$]$3H_2O$ sensitive to light (435.8nm), responded consistently to radiation conditions. Instrumentation has been developed that allowed for monitoring the course of photobromination of acetone – dependent chemical reaction in solution under the studied wavelength. The radiation absorbed by solutions investigated was monitored by measuring the change in standardized aqueous solutions of bromoacetone contained in cells identical with those where photolysis of ferrioxalate actinometer was carried out .This chemical method of measuring the radiation absorbed by systems photolyzed, was found to yield results that generally agree with those methods where physical instrumentation was used to measure radiation.

This work studies in detail, the performance of the system. The quantum yield (QY) of the bromine-bromoacetone chemical actinometer was found to be 45.97. The photo product- bromoacetone was determined from the increase in absorbance. The dynamics of acetone photobromination was also investigated. The reaction orders were obtained and the rate law has been formulated. Unlike in other cases of autocatalysis and acid base catalysis, it was observed that [Br_2] influenced the rate law in photolysis.

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New Approach to the Synthesis of Mix Catalysts CeO_2-ZrO_2-SiO_2 Using Beta-Cyclodextrin

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One of the perspective ways to produce catalysts with high surface area is a template synthesis. Recently it was proposed to use cyclodextrins (macrocyclic oligosugars) as template molecules [1]. This method permits to obtain SiO_2 with high surface area with uniform distribution of worm-like pores. In our work we used this new method for the first time to obtain mix catalysts ZrO_2-SiO_2 and ZrO_2-CeO_2-SiO_2. ZrO_2-CeO_2 is one of the most effective supports for the tree-way catalysts but at the same time the problem of its synthesis in finely dispersed state is not solved yet.

First, tetraethyl orthosilicate (TEOS) as silica source was prehydrolyzed in the presence of 0.1 M HCl solution. The solution of beta-cyclodextrin and urea with appropriate amounts of $ZrOCl_2 \cdot 8H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ was added dropwise into prehydrolyzed silica gel with vigorous stirring. After stirring for several hours, the colloid solution was kept for 2 weeks to allow the gel to form and age. After thermal decomposition the samples were annealed at 500 or 800 °C (3 h). So the samples with 10 and 40 wt. % ZrO_2 and with 10, 40, 60, and 80 wt. % $Zr_{0.5}Ce_{0.5}O_2$ were obtained.

It was determined by XRD method that all samples involve SiO_2 and t- or c-$Zr_xCe_{1-x}O_2$ phases. According to SEM technique particles of the samples with and without CeO_2 have different morphology. Catalytic activity of the sample 60 wt. % $Zr_{0.5}Ce_{0.5}O_2/SiO_2$ was studied using partial methanol oxidation as test reaction. 20% conversion of methanol was observed at 312 °C; calculated activation energy is 163±2 kJ/mol.

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PP-IV-4

Physicochemical Properties of TiO_2/SiO_2 Photocatalysts

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The problems connected with an increase in the concentration of carbon dioxide in the atmosphere and growing demand for different organic compounds causes increasing interest in the investigations of CO_2 conversion process. The reactions leading to useful products, such as hydrocarbons, alcohols, etc. in the relatively mild conditions are the most promising. These requirements are fulfilled by photocatalytic processes with using TiO_2 as a photocatalyst. However, the literature data shows that typical photocatalysts exhibits relatively low activity. It appears that the activity of TiO_2 can be improved by the use of supports with high surface area or by activation of the catalyst by small quantities of noble metals, such as platinum, palladium or ruthenium.

The aim of this work was to investigate the physicochemical properties of TiO_2/SiO_2 photocatalysts used in the conversion of carbon dioxide.

The catalysts consisted of 5, 10, and 15% TiO_2 supported on SiO_2 were prepared by an impregnation method using Ti-tetra(iso-propoxide). Decomposition process of the catalyst precursor was investigated using quadrupole mass spectrometer. Moreover, the temperature programmed measurements were performed. XRD method made it possible to determine phase composition of the catalyst and dimension of TiO_2 crystallites. A chemical composition of the surface of the catalysts was also analyzed by SEM-EDS and TOF-SIMS techniques.

Acknowledgement

This work was supported by the Polish Ministry of Science and Higher Education (Project Nr N N205 272535).

PP-IV-5

Novel Optically Pure Derivatives of Diterpenes as Ligands for Catalysts of Asymmetric Reactions

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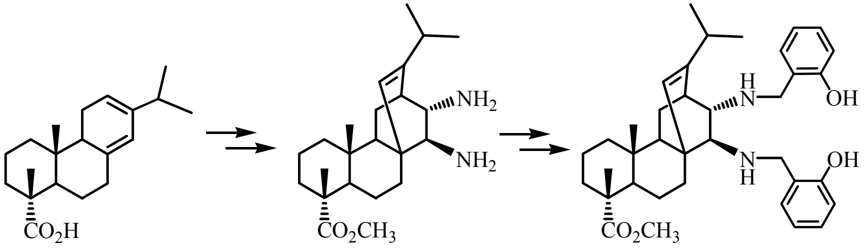
In recent years homogeneous enantioselective metallocomplex catalysis has achieved impressive results in the field of the synthesis of organic compounds of high optical purity. Use of natural terpenoids as a convenient chiral pool for the synthesis of optically active elementorganic compounds is the prospective approach to the creation of wide spectrum of available chiral ligands for the catalysts of asymmetric reactions [1].

Synthesis of chiral 1,2-diamine (**2**) was developed on the basis of enantiospecific transformations of the adduct of levopimaric acid (**1**) with fumaric acid. Starting from the diamine (**2**), chiral aminophenol (**3**) was prepared.



1 **2** **3**

The synthesized new chiral nitrogen containing compounds were used as ligands for metallocomplex catalysts of asymmetric reduction and oxidation.

References:

[1] Tolstikov, A.G.; Khlebnikova, T.B.; Tolstikova, O.V.; Tolstikov, G.A. *Russian Chemical Reviews* **2003**, *72*, 803.

PP-IV-6

TiO_2/C as an Effective System for the Photocatalytic Purification of Water and Air

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The rate of photocatalytic oxidation (PCO) of organic substances is strongly dependent on its concentration especially in the low concentrations range where the PCO rate (W) is in direct proportion to concentration (C). Such behaviour could be easily demonstrated by the Langmuir-Hinshelwood approach:

$$W = {k_r \cdot K_{ads} \cdot C} \Big/ {\left(1 + K_{ads} \cdot C\right)}.$$

On the other hand this equation indicate that the PCO rate is also directly proportional to rate (k_r) and adsorption (K_{ads}) constants. Rate constant values achieved almost highest values due to extensive work of many researches especially in the gas phase PCO [1]. At the same time the adsorption properties of TiO_2 based photocatalysts could be significantly improved due to its modification. TiO_2 deposition on activated carbon (AC) is one of the promising methods [2].

In the current work the TiO_2/C samples were synthesized by the thermal hydrolysis method in the presence of AC particles. These samples demonstrated the high adsorption capacity and activity comparable with commercial TiO_2. The specific activity of TiO_2/C samples (80% TiO_2 and 20% AC) in the reaction of acetone vapour PCO was even higher than for pure TiO_2.

The synthesized samples were tested in the experimental air and water cleaning reactors and demonstrated fast removal of pollutants with its subsequent complete mineralization.

References:

[1] Carp, O.; Huisman, C.L.; Reller, A. *Progress. in Solid State Chem.* **2004**, *32*, 33.
[2] Liu, S.X.; Chen, X.Y.; Chen, X. *J. Hazard. Mat.* **2007**, *143*, 257.

Photocatalytic Denitrification over Ag and Cu Doped TiO_2

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From an environmental standpoint, one of the most acceptable methods for removal of nitrates, which cause health hazards, is to convert them into N_2. Recently developed photocatalytic nitrate reduction using TiO_2 supported Ag nanoparticles [1] is promising approach due to chemical stability, nontoxicity, and low cost of the catalyst. Relation between preparation procedure, metal content, type of hole scavenger, and photocatalytic behavior of Ag/TiO_2 and Cu/TiO_2 catalysts towards nitrate reduction was studied.

The catalysts were prepared using different modifications of TiO_2 by a triblock copolymer induced reduction of $[Ag(NH_3)_2]^+$ in ethanol in presents of Pluronic P123 and Pluronic F127 surfactants under ambient light illumination of varied duration [2]. The silver and copper content was varied between 0.5–2.5 wt. %. The catalysts were characterized by means of ICP, analyses, XRD, UV-Vis DRS and H_2 thermo-programmed reduction (TPR). Photocatalytic reaction was carried out as described in Ref. [1] with initial concentration of nitrate anions 23 $mg\,N\,l^{-1}$ (calculated by nitrogen weight). The use of formic acid as sacrificial electron donor greatly improved both the reaction rate and the selectivity for nitrogen avoiding formation of undesirable nitrite and ammonium ions. The highest catalytic activity was observed for the catalysts derived from TiO_2 with mixed anatase-rutile composition.

References:

[1] Zhang, F.; Jin, R.; Chen, J.; Shao, C.; Gao, W.;. Li, L.; Guan, N. *J. Catal.* **2005**, *232*, 424.
[2] Zhang, L.; Yu, J.C. *Catal. Commun.* **2005**, *6*, 684.

PP-IV-8

Design and Application of Fe,Al-Containing Materials for Peroxide Oxidation of Pollutants: Effect of Iron Environment on Textural, Physicochemical and Catalytic Properties

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Recently Fe- and Fe,Al-containing systems based on mesoporous silica materials are an ongoing subject for research as heterogeneous oxidation catalysts due to their Fenton like behaviour ($Fe^{2+}/Fe^{3+}/H_2O_2$). Fe-MMM-2 and Fe,Al-MMM-2 were synthesized via sol-mesophase rout under weak acidic conditions. Fe-MMM-2 synthesis $Na_2Si_2O_5$ and $FeCl_3$ were used as silica and iron precursors, respectively. Fe,Al-MMM-2 was prepared using $Na_2Si_2O_5$ and mixed polyoxocation $[FeAl_{12}O_4(OH)_{24}(H_2O)_{12}]^{7+}$. XRD, low-temperature N_2 adsorption, IR, DR-UV-vis and DRIFT spectroscopic techniques, were used for characterization of the new materials. It has been established that textural, physicochemical, catalytic properties of the catalysts and stability to leaching of metal from the solid depend on (*i*) pH of the synthesis solution; (*ii*) agglomeration and isolation of iron ions; (*iii*) iron and aluminum content in the samples. The catalytic activity in wet full oxidation of pollutants such as phenol and monoazo dye acid chrome dark-blue (ACDB) with hydrogen peroxide strongly depends on the presence of isolated iron species, which are stable to leaching. The increase in iron loading and pH of the synthetic solution leads to iron agglomeration, which, in turn, results in the reduction of the catalytic activity of Fe-MMM-2 and in the increase of iron leaching. It was shown that catalytic activity could be improved by insertion of Al species into the framework of the silicate matrix. Increase of aluminium content in the Fel-MMM-2 increases the acidity of the Fe,Al-MMM-2 catalyst, that plays a significant role in switching the selectivity towards hydroquinone in PhOH oxidation with H_2O_2 ($PhOH/H_2O_2$ 1:2 mol/mol. It is demonstrated that activity of Fe,Al-MMM-2 is higher than that of Fe,Al-pillared clay (Fe,Al-PILC) due to the higher surface acidity and decrease of diffusion limitation.

Non-Equilibrium Catalytic Pyrolysis of *n*-Hexadecane under Microwave Heating

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Microwave (MW) heating has some features which cannot be achieved with conventional heating: it is possible to heat chemical reagents to high temperature in a short period of time; heating is selective; reagents can be heated in a closed system without any thermal or mechanical contact with environment.

Idea of this work is based on possibility to heat selectively a catalyst or sorbent or, what is better, its active component only with the use of microwave technique at comparatively cold ambient medium. In this case we can arrange a fast supply of the heat to catalyst and remove the desired reaction product prior to its secondary conversion to by-products.

Solid particles (catalyst) are heating when absorb microwaves and move inside liquid medium (hydrocarbon) which is “transparent” for MW. Particle surface is the area of contact of hot solid material with more cold liquid. The contact can lead to fast catalytic transformations of molecules of liquid. The products obtained are cooled when moving to the volume of liquid.

In this work, the special set-up based on the one-mode MW cavity and ordinary MW generator (2.45 GHz, 850 W) has been designed and used to perform the catalytic decomposition of $C_{16}H_{34}$ in the presence of different catalysts. The reaction products were analyzed by GLC method. We have found that MW heating of the catalysts stimulates the decomposition of *n*-hexadecane to lighter molecules and in some cases the main products are alpha olefins. That can be explained by “quenching” effect.

PP-I-111

Kinetic Study of Hydrogenation of Nitrate and Nitrite in Water over Bimetallic 5%Pd-2%In/SiO_2 Catalysts

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Nitrate concentrations in natural water are still rising in many parts of the world. Nitrate ions (NO_3^-) are not directly toxic, but they can be transformed into harmful nitrite ions (NO_2^-) in the human body, which cause a blue baby syndrome and are a precursor to carcinogenic nitrosoamine. The increasing rigorousity of the drinking water quality standards (the legal limits established by the EU are 50 mg NO_3^-/dm^3) generates the urgency to develop new technologies for nitrate removal. Nitrates can be removed from water by biochemical and physicochemical methods. Those methods allow effective removal of nitrates but then have several economical and ecological disadvantages. Therefore, increasing attention is being focused on catalytic denitrification using solid catalysts as an alternative technology.

This work presents the studies of activity and selectivity of palladium catalysts promoted with indium in the reduction of nitrate and nitrite in drinking water. The catalyst containing 5%-wt. of palladium and 2%-wt. of indium was prepared from water solutions of $PdNO_3$ and $In(NO_3)_3$ (POCh Gliwice S.A) by aqueous coimpregnation of SiO_2 (Aldrich, 250 m^2/g). Before the catalytic tests, the catalyst samples were calcinated at 773 K for 4h in air atmosphere and reduced in hydrogen atmosphere for 2h at 573 K. Reduction of nitrates and nitrites were performed for different initial concentrations of substratum ($C_{0\ NaNO3}$ = 0.4÷3.2 mmol/dm^3, $C_{0\ NaNO2}$ = 0.5÷4.2 mmol/dm^3) in the temperature range of 293-313 K over Pd-In/Al_2O_3 catalysts. Both the depletion of nitrates and the depletion of nitrites follow approximately a first order decay. In addition, the apparent activation energy for catalytic liquid-phase nitrate reduction and the apparent activation energy for catalytic liquid-phase nitrite reduction in the studied temperature range were found, as well.

PP-I-112

Zirconium Complexes Bearing η^5-5',6',7'-Trihydrospiro[Cycloalkane-1,4'-Indenyl] Ligands and Their Application in Olefin Polymerization

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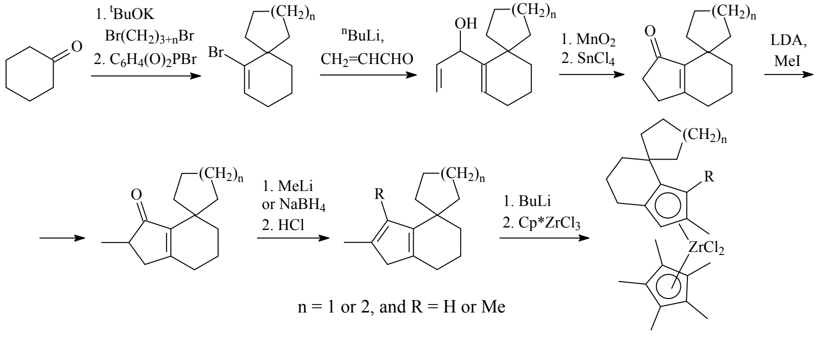
The group 4 metallocenes bearing η^5-4,5,6,7-tetrahydroindenyl ligands ($IndH_4$) are of particular importance for olefin polymerization catalysis, as the respective *ansa*-complexes are known to form catalysts for isotactic polypropylene (*i*PP) synthesis. It is well-known that *ansa*-metallocenes bearing $IndH_4$ ligands are less prone to the epimerization under the effect of light or heat. Therefore, the development of synthesis of η^5-4,5,6,7-tetrahydroindenyl ligands is of great importance. Only scarce examples of the successful synthetic approaches have been already described in the literature.

In our work, we synthesized novel zirconium complexes bearing Me-substituted 5',6',7'-trihydrospiro[cycloalkane-1,4'-indenyl] ligands, i.e. the ligands including a quarternary carbon atom (spiro fragment) in α–position of the saturated ring of $IndH_4$.



n = 1 or 2, and R = H or Me

Ethylene polymerization catalyzed by the obtained complexes activated by methylaluminoxane (1/500 molar ratio of Zr/Al, 10 bar ethylene, 60°C) was studied. These catalysts were found to show moderate activities (up to 700 kg/g*bar*h) and give polyethylene with M_w between 300 and 550 kDaltons. Additionally, kinetics of ethylene polymerization was studied in detail.

PP-I-113

Halogen-Substituted Constrained Geometry Complexes, Their Cross-Coupling Chemistry, and Catalysis of Ethylene/α-Olefin Copolymerization

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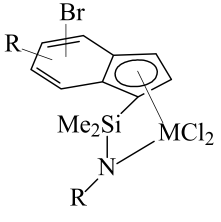
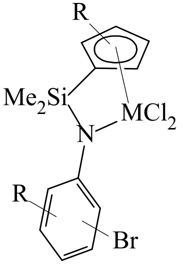
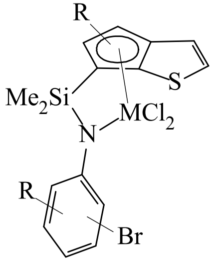
Constrained geometry complexes (CGCs) of the group 4 metals activated by methylalumoxane (MAO) are active ethylene/α-olephine co-polymerization catalysts applied in industrial scale. Since the performance of such catalytic systems depends strongly on ligand structure in CGC, the development of method that allows easy preparation of libraries of CGCs can be useful for screening of CGC-based catalytic systems.

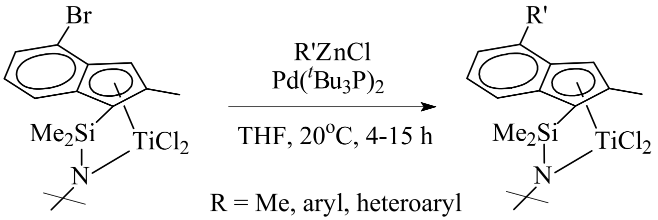
In this work the Negishi cross-coupling protocol applied to halogen-substituted CGCs and arylzinc chlorides was investigated. First, the halogen-substituted CGCs of the following families were successfully synthesized and unambiguously characterized:







These complexes were shown to undergo Negishi-type cross-coupling reaction with methyl, aryl- and heteroarylzinc chlorides in the presence of the palladium catalyst giving series of the respectively substituted CGCs, e.g.:



Finally, these complexes activated by MAO were found to be active ethylene/octene-1 co-polymerization catalysts giving polymers with up to 35% content of octene-1 co-monomer. Mechanism of olefin co-polymerization using these catalysts is discussed in detail.

PP-I-114

The Combustion of Toluene over Perovskite –Type Oxides $La_{1-x}Sr_xCoO_3$

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A series of nanosized perovskite-type oxides, $La_{1-x}Sr_xCoO_3$ (x = 0,1-0,4), was synthesized by citric method. The samples were characterized by XRD, IR and SEM. The XRD results show that all samples have principal phase with rhombohedral perovskite structure and particles size of 30-50 nm. The catalytic performance of these nanoperovskites has been evaluated in the total combustion of 1000 ppm of toluene in air. The result obtained shows the highest activity for the sample $La_{0,9}Sr_{0,1}CoO_3$.

PP-I-115

Synthesis and Modification of MCM-48 Mesoporous Material as Catalysts of n-Butane Conversion Reaction

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Mesoporous material MCM-48 *(Ia3d)* has been synthesized using a commercially available triblock copolymer ($EO_{20}PO_{70}EO_{20}$)–butanol mixture in aqueous solution. Transitional metal oxides (V_2O_5 and TiO_2) supported on mesoporous materials (MCM-48) have redox properties such as V_2O_5/MCM-48, TiO_2/MCM-48, V_2O_5-TiO_2/MCM-48 catalysts. The above catalysts were characterised by XRD, TG-DTA, TEM, BET and showed that obtained samples with surface area of $730 m^2g^{-1}$, pore size diameter of $54 A^o$ and highly ordered structure. The structures of mesoporous material supported metal oxides were not changed. Catalytic activities of these materials were evaluated by the oxidative dehydrogenation reaction of n-butane to butene. Catalytic activity of V_2O_5/MCM-48 was higher than that of TiO_2/MCM-48 and catalytic activity of TiO_2-V_2O_5/MCM-48 was highest with conversion up to 20% and selectivity of 87%.

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ABSTRACTS

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