“Mechanisms of Catalytic Reactions”

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

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ABSTRACTS

Volume I

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“Mechanisms of Catalytic Reactions”,

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

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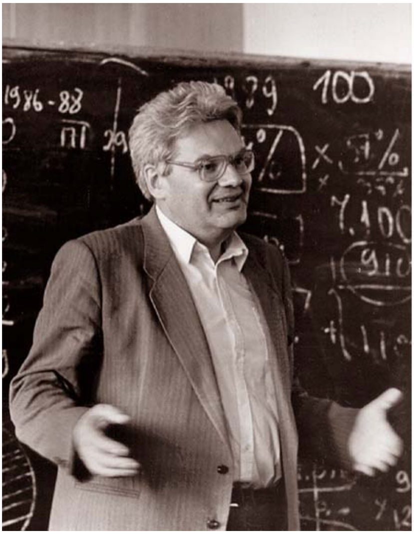
ABSTRACTS

Volume I

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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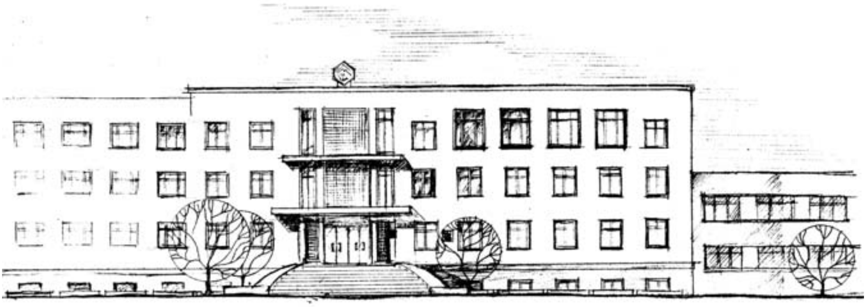

PL-1

Reactivity and Mechanism of Single-Site Olefin Polymerization Catalysts

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Over the last 20 years catalysts based on group 4 complexes with a variety of ligand environments have been found to be extremely active and selective catalysts for the polymerization of olefins to give a wide range of polymer materials with distinctive properties. The development of new activator systems allowed the generation of well-defined catalysts that provided unprecedented insight into the polymerization mechanism. This contribution will summarize key feature of this catalysis, form the role of "super-weakly" anions to the important role that ion aggregation plays in governing ligand fluxionality and polymerization kinetics. Detailed spectroscopic studies have also allowed to identify the reaction products of catalyst precursors with common catalyst co-activators such as tributyl aluminium.

In many instances the species carrying the polymer chain as well as the nature of resting states could be identified. This understanding has led to the development of some of the most active polymerization catalysts ever reported and has provided an intriguing insight into the factors that are responsible for lowering the activation barrier of the chain growth process.

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PL-2

What Did We Learn from NMR of Hydrocarbon Conversion on Solid Acid Catalysts? Advances for the Last 20 Years

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Solid state NMR spectroscopy is considered nowadays as one of the most efficient techniques for characterization of hydrocarbon conversion on solid acid catalysts. It provides *in situ* analysis of the adsorbed hydrocarbon species in a wide temperature range (110-670 K), capable to follow the kinetics of the reaction at 300-573 K and identify reaction intermediates. These facilities of NMR spectroscopy provide the pathway for understanding the mechanisms in heterogeneously catalyzed reactions, which are not only of fundamental interest for refinement of theories in modern physical organic chemistry, but also of practical importance for optimization of existing industrial processes and searching for the new pathways of hydrocarbon conversion.

In this review paper we demonstrate the progress in solid state NMR for characterization of hydrocarbon conversion on solid acid catalysts since the beginning of 1980ties.

First we show how the nature, structure and composition of the adsorbed products of low temperature oligomerization of small olefins were identified, followed the first ^{13}C CP/MAS NMR experiments by Derouane et al.[1] and van den Berg et al.[2]. Further *in situ* analysis of the reaction products at high temperature up to 673 K made it possible to conclude that olefin conversion on solid acid occurs similar to conjunct polymerization process in solution of strong sulfuric acid, producing a mixture of alkanes and alkyl-subsituted cyclopentenyl cations.

Surface isoproxy species as the stable intermediate in hydrocarbon conversion was reliably identified in 1989 [3], followed by unequivocal idenfication of methoxy species by Bosacek [4] and Haw et al. [5] in1993. Identification of alkoxy species by NMR confirmed the eralier quantum chemical estimation of the relative stabilities of the potential intermediates - carbenium ions, alkoxy species, π-complexes: the most stable species among them should be alkoxy species [6]. Surface methoxy species was demonstrated by NMR to act as effective methylating agents when reacted with different probe molecules through C-O bond activation [7].

Alkyl carbenium ions as stable intermediates were not detected so far. However, observation by NMR of the ^{13}C-label scrambling in the adsorbed olefins [8] and alkanes [9,10] at low temperature as well as the reactivity of adsorbed hydrocarbons towards typical traps of carbenium ions, such as CO [11] or CH_3CN [12], provide the evidence for their formation. Recent quantum chemical calculations have found a local minium on potential energy surface for tert-butyl cation [13,14], thus descredited an earlier suggestion that carbenium ions could form on heterogeneous acid catalysts only as the transitions states [15]. Due to presence of carbenium ions in the adsorbed olefin oligomer, its hydrocarbon skeleton is very mobile and oligomer is very reactive species even at room temperature. Olefin oligomer scrambles ^{13}C-label in its hydrocarbon skeleton [11] and readily reacts with typical traps of carbenium ions, e.g., CO or CH_3CN, producing carboxylic acids [16], cyclic carboxonium ions [17], alkylnitrilium cations [12], easily identified by NMR.

With help of NMR it becomes possible to delimit between mono and bimolecular mechanisms of n-butane isomerization on different nature solid catalysts, or to demonstrate bimolecular mechanism for n-butane and mono for n-pentane isomerization on sulfated zirconia or solid heteropolyacid by following the fate of the ^{13}C-label during the reaction.

Capability of NMR to follow the regiospecificity of H/D hydrogen exchange into different fragments of hydrocarbon skeleton in the kinetics measurements in a wide temperature range allowed differentiation among alternative mechanisms of H/D exchange and pathways of C-H bond activation in alkanes. We were able to distinguish between carbenium and carbonium ion mechanisms of CH bond activation in alkanes on pure acidic catalysts and identify strong influence of metal on alkane activation in Zn and Ga modified zeolite catalysts of alkane aromatization. Alkane activation involves metal-alkyl species, which formation was confirmed by NMR [18].

Tracing the isotope label in the course of the reaction with unambiguous indentification of the intermediate and reaction products based on their chemical shifts, the new earlier unknown reactions for heterogeneous catalysts were discovered with NMR. E.g., the process of alkane carbonylation on sulfated zirconia patented by UOP in 2002 was first discoverded with NMR [19].

A reality of the reaction of methane and higher alkane coaromatization has been recently shown with NMR [20]. NMR confirmed not only the occurrence of the reaction but showed how the involvement of methane into the aromatic products occured.

All the findings by NMR in a period of 1989-2009 mentioned above are substantiated through particular examples.

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Surface Science Models in Catalysis: An View at the Atomic Level

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Model systems for heterogeneous catalysts are prepared based on single crystalline oxide films which serve as supports for active components. The latter may be metal nanoparticles or other oxide particles. The systems may be characterized at the atomic level and their structure, morphology, and adsorption behavior may be correlated with reactivity. We will address three case studies:

- Alkene hydrogenation on Pd nanoparticles
- Methanol oxidation on supported vanadia
- Au nanoparticles and their role in catalysis.

PL-4

Ambient Pressure X-Ray Photoelectron Spectroscopy: From *in-situ* to *operando* Studies of Heterogeneous Catalytic Reactions

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The X-ray photoelectron spectroscopy has been recognized as one the best analytical method for probing the composition and electronic structure at solid surfaces and gas-solid interfaces, including catalytic systems. It is based on monitoring of emitted photoelectrons, which imposes limitations on the operation pressures. Additional limitations originate from the necessity of high vacuum conditions for regular operation of X-ray source and electron energy analyzer. As consequence, overwhelming majority of photoelectron spectrometers measures XPS spectra under ultra high vacuum (UHV).

At the same time, there is a principle possibility to measure XPS spectra at high pressures, since the mean free path of photoelectrons in a gas at pressure of ~ 1 mbar is several millimeters. This means that to avoid considerable weakening of the XPS signal, the path of photoelectrons in the high-pressure zone should be as short as possible, and the pressure gap between the high-pressure and vacuum zone as large as possible.

Realization of this approach requires application of the differential pumping which allows minimization of a travel path of photoelectrons in gas phase. The concept of differential pumping for high-pressure XPS was first applied by K. Siegbahn with colleagues in 1969 for investigation of gases at pressures of up to a few tenths of a Torr. In 1979 the construction of the commercialized afterwards XPS system for investigations of solids in gas atmospheres at pressures of up to 1 Torr was reported by R. Joyner and M. Roberts. In this case we can talk about appearance of first *in-situ* XPS spectrometer which allows investigation of heterogeneous catalysts. Some examples from our experience demonstrate variation of chemical states of the catalyst surface under the influence of reaction conditions.

At the same time, simple *in-situ* XPS measurements do not allow elucidation of the structure-activity relationship since the results of ambient pressure surface analysis do not correlate with the catalytic activity data. To remedy this deficiency, catalytic activity data should be measured along with XPS experiments. To perform the activity measurements, the sample should be heated separately from the sample holder and the composition of a gas phase above the sample should be measured with mass-spectrometry or gas-chromatography. Gas-phase XPS also can be used to measure catalytic activity. Conditions for the correct measurement of catalytic activity inside high-pressure cell of XPS spectrometer are analyzed in this lecture. In this case one can say about transition from *in-situ* to *operando* mode. Namely this mode of experiments allows investigation of mechanisms of catalytic reactions.

This approach was used to study such heterogeneous catalytic reactions as ethylene epoxidation over silver and selective oxidation of methanol over copper and vanadia-based catalysts. Both chemical states of the catalysts surfaces and the nature of surface species, as well as their variation under reaction conditions have been analyzed in these experiments. The data are used for discussion about mechanisms of the reactions studied.

PL-5

Hydrogen Activation by Transition Metals

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Supported transition metal clusters and small particles act as catalysts for the hydrogenation and dehydrogenation of hydrocarbons. Using density functional calculations on models of simple and embedded clusters models, we discuss the structural and energetic consequences of hydrogen loading of zeolite supported small transition metal clusters of definite nuclearity, in particular for the cases of Rh_6 and Ir_4 [1–3]. Silver, a widely used oxidation catalyst, was recently shown to catalyze the regioselective hydrogenation of unsaturated aldehydes to unsaturated alcohols. We discuss the activation of molecular hydrogen by silver and the hydrogenation reaction using a slab model density functional approach [4, 5].

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PL-6

Development of Visible-Light-Responsive TiO_2 Thin Film Photocatalysts as an Environmentally-Friendly Material

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Environmentally harmonious, clean and safe chemical technologies and processes to address pollution and climatic change are the subject of much research and discussion. Photocatalysis, in which the abundant and clean energy of solar light could be harnessed, would be a major advance in the development of sustainable, non-hazardous and economic technologies. Development of highly functional TiO_2 photocatalytic materials has been especially promising and, significantly, the photo-induced super-hydrophilic properties of TiO_2 thin films for such applications as self-cleaning and anti-fogging in mirrors and windows have already being realized.

However, unlike natural photosynthesis in green plants, they can make use of only 3-4% of solar light, necessitating the use of a UV light source. Recently, however, we have successfully applied ion-beam techniques such as metal ion-implantation and RF magnetron sputtering deposition to design unique and efficient Ti oxide photocatalytic materials which enable the absorption of visible light of longer than 550 nm. These newly developed Ti oxide-based materials were found to work as efficient and effective environmentally-friendly photocatalytic materials, leading to the efficient use of solar energy for the production of clean H_2 and O_2 from water and other significant reactions.

The plenary lecture presents the development of highly functional TiO_2 thin film photocatalytic materials by applying a RF magnetron sputtering deposition method, enabling the thin films to absorb visible light of longer than 550 nm. The method was found to be one of the most promising approaches in the development of highly functional TiO_2 thin film materials for application in devices for the solar splitting of

H_2O into H_2 and O_2 with their separate evolution as well as to design thin film solid solar cells without the use of any organic dye sensitizers.

In summary, our findings clearly show that these newly developed TiO_2 thin film materials can be considered potential candidates in innovative reactions and processes that can efficiently utilize solar energy.

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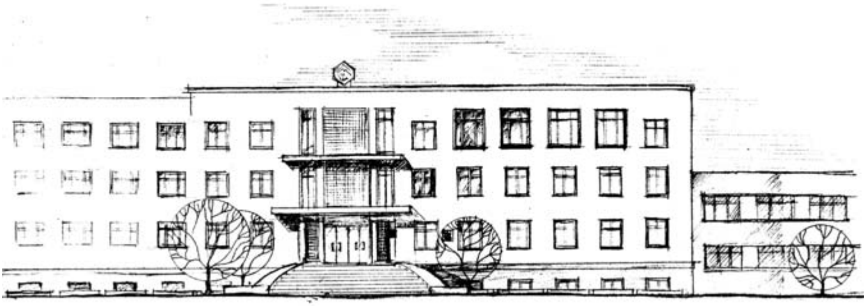
KEYNOTE LECTURES



Molecular Aspects of Light Alkanes Aromatization: Insights from in situ FTIR, NMR and TG-GC-MS

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The results obtained by different in situ techniques, such as FTIR, MAS NMR and thermogravimetric technique coupled with GC and MS (TG-GC-MS) are shown to be complementary for the unravel of the mechanism of methane, ethane and propane transformations over Zn-containing MFI catalysts with different types of active sites: Zn^{2+} cations and zinc oxide species.

^{13}C MAS NMR technique allowed for unambiguous identification of methyl-, ethyl- and n-propylzinc surface species at the onset of alkanes interaction with the catalyst. FTIR and ^{1}H MAS NMR experiments revealed simultaneous observation of ZnOH groups in the case of ZnO-containing catalysts and Si-OH-Al groups over Zn^{2+}/MFI. The results pointed to light alkanes activation via dissociative adsorption.

The dissociative adsorption was shown to be a dead-end surface reaction in the case of methane starting reactant, while in the case of ethane and propane it appeared to be responsible for the initiation of the catalytic cycle leading to dihydrogen and alkenes, which form asymmetric π-complexes with zinc cations. At the later reaction steps, alkenes oligomerize to give charge delocalized carbanionic species stabilized on zinc cations as confirmed by both FTIR and ^{13}C MAS NMR. The role of carbanionic species in consecutive reaction steps is discussed.

Application of TG-GC-MS technique in combination with FTIR spectroscopy revealed that carbanionic species are responsible for soft coke formation at the early stages of the reaction and rapid catalyst deactivation.

Acknowledgments

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KL-2

Active Intermediates of Metallocene and Post-Metallocene Catalyzed Olefin Polymerization

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Metallocene and post-metallocene based single site olefin polymerization catalysts have been one of the most significant achievements in catalytic polymerization. Despite the numerous efforts focused on the catalyst design and the resulting polymer properties, the nature of the catalytically active sites remains mostly hypothetical. In this lecture, our recent studies on the activation pathways and the nature of the active intermediates in several olefin polymerization systems based on metallocene and post-metallocene catalysts will be reported.

First, formation and identification of the active intermediates in three post-titanocene ($(FI)_2TiCl_2$, $(PI)_2TiCl_2$, $(FI)(PI)TiCl_2$) catalytic systems activated with methylaluminoxane (MAO) and $AlMe_3/[CPh_3][B(C_6F_5)_4]$ will be described based on the NMR and EPR data obtained. The main deactivation pathways operating in these systems have been revealed.

In the second part of the talk, recent data on the structure and valence states of the active intermediates formed in catalytic systems based on bis(imino)pyridine iron(II) complexes activated with MAO and $Al(Alk)_3$ will be presented.

It is known that hafnocene complexes are effectively activated with $Al(i\mathrm{Bu})_3/[CPh_3][B(C_6F_5)_4]$ combination, MAO being a rather poor co-catalyst. Our results show that cationic hafnocene hydrides formed in the first case are responsible for the higher ethylene polymerization activity. The structure of the intermediates formed for various hafnocenes with different symmetry upon the activation with MAO and $Al(i\mathrm{Bu})_3/[CPh_3][B(C_6F_5)_4]$ will be discussed.

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KL-3

Selective Heterogeneous Photocatalysis: Achievements and Challenges

Vincenzo AUGUGLIARO, Marianna BELLARDITA,
Agatino DI PAOLA, Elisa GARCÍA-LÓPEZ, Vittorio LODDO,
Giuseppe MARCÌ, Giovanni PALMISANO, Leonardo PALMISANO,
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Applications of heterogeneous photocatalysis as a synthetic route are much less common than typical degradation oxidations, because semiconductor photocatalytic reactions have always been considered as highly unselective processes, especially in water. Nevertheless many selective reactions were carried out by employing not only titanium dioxide, but also other semiconductors [1]. Increasingly stringent environmental limitations for chemical processes are driving researchers to find alternative synthetic routes based on heterogeneous, leach-proof catalysts affording high yields of the wanted product in environmentally benign solvents such as water or (supercritical) carbon dioxide. As recent literature shows, organic chemistry is moving this way as well, bearing in mind that, in many cases, both water-soluble and water-insoluble molecules can react faster in water and, sometimes, higher reaction rates are found with water-insoluble substrates. Some of the few studies on photocatalytic selective reactions in water include hydrocarbon oxidation [2], aromatic hydroxylation [3], naphthalene oxygenation [4], heterocycle functionalisation [5] and cyclisation of amino acids [6]. In particular, selective photooxidation of alcohols to the corresponding aldehydes and ketones was performed either in gas phase or in liquid phase using acetonitrile as solvent. The results obtained by our group by using some home-prepared selective TiO_2 photocatalysts will be presented [7,8].

KL-3

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Increased Selectivity of Pd Based Catalysts in Alkyne Hydrogenation Reactions by the Modification of Their Electronic Structure

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Palladium based catalysts are used for selective hydrogenation of alkynes to alkenes. Modifications of the near-surface region either by the incorporation of carbon on interstitial lattice sites or by the application of Pd intermetallic compounds cause an increased selectivity compared to pure Pd. Under reaction conditions of the total hydrogenation much less carbon is dissolved in the Palladium as shown by in situ photoelectron spectroscopy [1-3]. In situ prompt γ activation analysis studies indicated that unselective hydrogenation proceeds on hydrogen-saturated β-hydride, whereas selective hydrogenation was only possible after decoupling bulk properties from the surface events.

The structurally well-defined intermetallic compound PdGa - highly selective for the selective hydrogenation of acetylene - show a strong modification of the electronic states on the surface of PdGa compared to elemental Pd and a complete isolation of the Pd atoms on the surface of PdGa. In situ investigations proved the high stability of the surface, thus excluding segregation phenomena (common for alloys) or sub-surface chemistry involving C and/or H atoms (known for elemental Pd) [4]. By suppressing the sub-surface chemistry, the electronic modification as well as the site isolation leads to high selectivity and long-term stability of PdGa in the selective hydrogenation of acetylene.

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KL-5

Catalytical Model Systems and Surface Reactivity Studied by High-Resolution, Video-Rate STM

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For decades single-crystal surfaces have been studied under ultrahigh vacuum (UHV) conditions as model systems for elementary surface processes underlying phenomena such as heterogeneous catalysis, epitaxial growth, corrosion etc. This “surface science approach” has contributed substantially to our understanding of the processes involved in especially catalysis, and has in some cases even led to the design of improved catalysts. Recently much attention has also been paid to the so-called gaps between surface science and industrial catalysis. One of these gaps is the pressure gap which arises because of the 13 orders of magnitude pressure difference between UHV base pressures and atmospheric pressure. The other gap is the structural gap relating to the difference in reactivity on single-crystal surfaces as opposed to small nanoclusters.

In this talk I will show how one can use the unique capabilities of Scanning Tunneling Microscopy (STM) to reveal fundamental processes in relation to catalysis. STM has proven to be a fascinating and powerful technique for revealing the atomic scale realm of matter, and the unique aspect of our Aarhus STM has allowed us to record time-resolved, high-resolution STM images, visualized in the form of STM movies (see www.phys.au.dk/spm) [1]. I will show how we can obtain unique new insight into diffusion and transport phenomena associated with surface processes and of nanostructures. We can extract quantitative information on surface diffusion of adatoms and molecules [2-4], diffusion of vacancies and molecules for example water molecules on oxide surfaces [5,6, 7], sintering and diffusion of nanoclusters on oxide surfaces [8], dynamics og de-alloying of nanostructures, diffusion of intermediate species on new nanoclusters [9-11], identification of active sites, determination of new nanostructures with new novel catalytical properties, and I will finally show how our fundamental atomic-scale studies may lead to design of new improved catalysts [12].

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KL-6

Nature of Active Sites and Reactions Pathways in Catalytic Hydrogenation by Transition Metal Catalysts: Insights from DFT Calculations

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The rational design of catalysts requires to understand the nature and structure of the active sites and on the other hand to determine the factors which control the reaction pathways, and hence the reactivity and selectivity, on such sites. Theoretical chemistry and in situ spectroscopy have emerged as important tools to provide insights in the atomic scale phenomena governing heterogeneous catalysis.

The lecture will be centered on selective hydrogenation reactions of poly-unsaturated molecules on transition metal surfaces, from a theoretical chemistry approach, in combination with in situ XPS. We will underline how modifications of the surface can influence the selectivity. In the first example, we will show that Sn, when alloyed with Pt, opens new pathways for butadiene hydrogenation, from a marked weakening of the diolefin-surface interaction. These new pathways are much more selective towards the formation of butene.

The second modification is driven by the reactant itself, by formation a thin carbide-like layer on Pd in alkyne hydrogenation conditions. The stable surface termination is dependent on the gas phase composition: For acetylene, subsurface carbon formation is thermodynamically favored, while this is not the case for ethene. This PdC surface phase has a strong influence on the hydrogenation selectivity

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KL-7

Geometric and Electronic Approaches to Size Effect in Heterogeneous Catalysis

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Catalysis is directly related with the surface properties of a solid catalyst. It is established that catalytic properties are determined not only by such geometric parameters of solid catalysts as their size, specific surface area, pore diameter, and pore-size distribution, but also by the surface morphology. Catalyst surface usually has complex structure that can be described by fractal geometry [1]. Typically, for structure-sensitive reactions a plot of the measured relative rate (r) as a reverse function of particle size (1/d) in log-log coordinates gives a line with slope between 1 and 3 depending on the type of reaction site. That results in an increasing the relative rate with decreasing particle size according to power law scaling. We discuss experiments showing that other types of dependencies between r and d are observed. Namely, relative rate may increase or decrease with decreasing d. Moreover, many experiments show an effect of fractal structure of a catalyst on catalytic reactions [1]. In present study we show two theoretical approaches which describe dependence between r and d. One of them reveals a relation between the fractal dimension of catalyst and the activation energy of heterogeneous catalytic processes. That gives a real picture of the geometrical approach to size effect in heterogeneous catalysis. Another approach is based on the electronic description of the active site illustrating a possibility to observe a quantum-confinement effect in heterogeneous catalysis. Both these approaches are confirmed by our experimental studies of various heterogeneous catalytic reactions, including CO oxidation, hydrogenation of CO, CO_2, organic nitriles, ketones, etc.

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KL-8

Environmental Photocatalysis in Action for Green Chemistry

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Heterogeneous photocatalysis is a recent discipline particularly well adapted to environmental catalysis since it operates at room temperature by replacing catalyst's thermo-activation by photo-activation (or replacing phonons by photons).

Green Chemistry does not concern agricultural chemistry nor its residues but is that which follows the Twelve Principles given in [1].

Fine Chemicals

High initial selectivities (100%) obtained in dry organic media in selective mild oxidation of gaseous or liquid hydrocarbons. For instance, this industrial synthesis presently environmentally-hostilely performed:

$$\text{4-tert-}C_4H_9\text{-}C_6H_4\text{-}CH_3 + 4\ KMnO_4 + 6\ H_2SO_4 \rightarrow$$
$$\text{4-tert–}C_4H_9\text{–}C_6H_4\text{-CHO} + 2\ K_2SO_4 + 4MnSO_4 + 11H_2O,$$

was successfully alternatively obtained in ambient air at room temperature without any waste:

$$\text{4-tert - }C_4H_9\text{-}C_6H_4\ CH_3 + O_2 \rightarrow \text{4-tert - }C_4H_9\text{ - }C_6H_4\text{ – CHO} + H_2O$$

In "thio-photocatalysis", 1-alkenes were 100% converted into 1-thiols or sulfides, when using H_2S or thiols respectively, with CdS or better TiO_2.

Environmental Photocatalysis

Titania becomes a total oxidation catalyst once in water or humid air because of the photogeneration of OH° radicals active (i) in water decontamination with the mineralization of organic pollutants (solvents, pesticides, herbicides, insecticides, fungicides, dyes, etc...) (ii) in air treatment (degradation of VOC's and odors), (iii) in disinfection (killing of bacteria (E.Coli, streptococcus faecalis,…) without re-growth or virus (H5N2, close to that of the avian flu.

Solar Energy: Photocatalysis can advantageously use the UV-A spectrum for outside applications as demonstrated by many campaigns and prototypes in agricultural, water and food industries, especially for removal of odors. The present challenge is the development of the photocatalytic engineering for optimization.

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Photocatalysis: Transformation of Light Energy for Oxidation, Disinfection and Water Splitting

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Gradual exhaustion of the Earth's accumulated energy resources prompts us to use the energy of light for carrying out chemical reactions. Photocatalysis provides a universal approach for such light energy transformation. This presentation gives an overview of recent developments of photocatalysis research at Boreskov Institute of Catalysis.

Major efforts have been directed to development of oxidative photocatalytic destruction over TiO_2-based catalysts. Several new findings include correlations of activity and catalyst specific surface area, diffuse reflectance spectra, deposited platinum oxidation state. A rule for prediction of organic compounds oxidation rate was suggested. Products and kinetics of oxidation of simple organic compounds, organophosphorous and organosulfur compounds [1] were determined. Novel approaches for carrying out gas phase oxidation include addition of gaseous H_2O_2, carrying out reaction over aerosol particles and synergistic combining with electric discharges.

The developed platinized catalyst demonstrated greatly improved activity in destruction of bacteria and viruses deposited from airborne aerosols.

Photocatalytic hydrogen production from water is being developed according to two concepts. The first one is that organic waste compounds serve as electron donors and result in generation of CO_2 and H_2. The second approach generates pure H_2 and O_2 in spatially separated compartments using inorganic redox charge transfer system. This method is most promising for future construction of solar hydrogen generation plants in arid regions.

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KL-10

Homogenous Stable Water Oxidation Catalysts and Noble-Metal Oxo Complexes Realized

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The development of viable water oxidation catalysts is the consensus most difficult step in realizing effective artificial photosynthetic (solar water splitting) systems. In 2008 we reported the first homogeneous water oxidation catalyst, $Rb_8K_2[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]$ (**1**), that is free of organic structure and thus stable to oxidative degradation.[1] The synthesis and properties (structural, electronic and catalytic) of **1** will be described, and a discussion of the challenges and trajectory of this research will be given.

The second topic is terminal late-transition-metal-oxo (LTMO) complexes of the noble metals, Pt, Pd, Au and Ir.[2,3] These complexes have been proposed as intermediates in catalytic technologies ranging from catalytic converters and fuel cell cathodes to "nanogold" and many other important supported catalysts, but they have never been made, despite 40 years of attempts, because of intrinsic instability. We have now made 7 and characterized them using up to 17 techniques.

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Oxidation Catalysis by Polyoxometalates

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Two interesting phenomena made possible by oxidatively stable transition metal substituted polyoxometalates will be addressed:

(1) *Oxidation of alkyl arenes, primary alcohols and vicinal diols catalyzed by* $H_5PV_2Mo_{10}O_{40}$ *by coupled electron transfer oxygen transfer reaction mechanism*[1,2]. These low temperature homogeneous reactions imitate high temperature heterogeneous Mars – van Krevelen type reactions.

(2) *Characterization of Manganese(V)-Oxo Polyoxometalate Intermediates and Their Properties in Oxygen-Transfer Reactions*[3]. Such species may be intermediates in enzymatic and biomimetic catalytic systems. Synthesis, properties, reactivity and DFT calculation of Mn=O-POM will be reported.

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KL-12

Elucidation of the Mechanism and Kinetics of Catalyzed Reactions by Combining Information from Experiments and Theory

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Studies of reaction mechanism have long been pursued in the field of catalysis with the goal of establishing which elementary processes limit catalyst activity and selectivity. For the most part, postulates of reaction mechanism have been based on good chemical intuition supported by as much experimental evidence as possible, a key element being spectroscopic observation of the dynamics of proposed intermediates and their relationship to product formation. Consistency of a proposed mechanism with observed reaction kinetics has also been used to support the plausibility of the mechanism. Recent advances in the prediction of rate coefficients from first principles has provided a further tool for verification of proposed reaction mechanisms and has enabled exploration of the effects of changes in catalyst composition and structure on catalyst activity and selectivity. This talk will illustrate how experiments and theory can be combined in a mutually complementary manner to provide insights into the mechanism and kinetics of catalyzed reactions. To this end, several examples will be presented taken from the fields of homogenous and heterogeneous catalysis. An important point of these examples will be that experimental evidence is needed in order to undertake meaningful theoretical analyses and that the results of theoretical analysis can be used to suggest meaningful experiments. It will also be demonstrated that in some instances experimental observations cannot be interpreted in a meaningful manner without the aid of theoretical analysis.

KL-13

Use of Neutron Beams in Studying Nanoporous Systems Related to Separation or Catalysis

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Nanoporous materials, such as zeolites, have found a wide range of technological applications including adsorption and separation of gases and hydrocarbons, catalysis, ion exchangers, etc. The field of metal-organic-frameworks (MOF) is now intensively investigated. These new materials are very promising since they combine a low framework density, a reasonable stability, and variable pore sizes.

In nanoporous systems, the size of the molecules is comparable to the pore size and anomalous transport behaviours can be found. Neutron scattering techniques have recently provided evidence for several unusual diffusion phenomena often predicted first by simulations: the window effect, the levitation effect, diffusion anisotropy, etc.

In different zeolitic systems, the diffusion coefficients derived in recent years from neutron methods have been found to be larger than those obtained from pulsed-field gradient NMR or from macroscopic methods. Further, the activation energies reported from neutrons are always lower. These discrepancies indicate that real zeolite crystals differ from the idealised views put forward by structural determinations. From the point of view of diffusion, zeolite samples do not represent homogeneous systems. The only explanation which can reconcile the different results is the presence of diffusion barriers within the crystals. The density of defects depends on the synthesis conditions and this affects the separation and catalytic properties of the material.

KL-14

NMR Studies on Catalytically-Important Transition-Metal Complexes

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In our laboratory, we have been investigating the structure (both intra- and supra-molecular) of transition-metal complexes in an attempt to correlate it with their behaviour in catalysis [1]. As far as the determination of the supramolecular structure in solution is concerned, two fundamental pieces of information are needed: 1) the relative orientation of the moieties constituting the supramolecule and 2) the average size of the supramolecule. Intermolecular NOE (Nuclear Overhauser Effect) NMR experiments, based on the detection of dipolar (through the space) coupling between nuclei, are ideal for obtaining information about the relative orientation of the moiety (1) [2]. Diffusion NMR experiments allow the molecular size of the adducts (2) to be estimated [3].

After a brief description of the above-mentioned NMR techniques and the methodologies for obtaining accurate molecular parameters, the results of their application to the investigation of transition metal catalysts are presented. In particular, recent results on catalysts for olefin polymerizations [4] and cationic olefin-gold(I) catalysts (L = PPh_3 and NHCs) [5] are reported.

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KL-15

Understanding Catalysis on a Molecular Scale: A Combined Quantum Chemistry and Spectroscopic Approach

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Production of phenol from benzene is one of today's industrially most important processes. As an alternative to the conventional three-step cumene process which requires liquid inorganic acids and produces acetone in stoichiometric amounts we are investigating an environmentally benign one-step process on copper zeolites using benzene and molecular oxygen as reactants. Based on a combined approach of quantum chemical calculations and various spectroscopic techniques (FTIR, EPR, EXAFS) as well as product analysis it is our aim to obtain a detailed view of the catalytic elementary step on a molecular scale [1]. Once the mechanism is understood it is our intention to tailor various parameters of the zeolite in order to improve selectivity and yield.

It is the main aim of the lecture to illustrate the complementarity of these various techniques.

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KL-16

Novel Catalytic Systems and Mechanisms of Hydrodechlorination Reaction

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Catalytic hydrodechlorination (HDC) is the most promising method for chlorinated wastes utilization: it is suitable to a wide assortment of wastes, fast, often very selective and never results in dioxin formation. It gives also possibility of selective transformation of undesired side-products of industrial processes to more useful ones. The development of new stable and active catalysts is still an important issue. It is possible only on the base of investigation of reaction mechanisms that are depending on reaction conditions and specific substrate or mixture to be processed.

In this report the mechanisms of liquid-phase, gas-phase and multiphase hydrodechlorination reactions will be discussed. As hydrodechlorination is structure-sensitive reaction, the approaches to the construction of the catalysts with optimal structure will be discussed. Modification of both supports and active component helps to provide partially oxidized active center and create the optimal dispersion of metal particles often with optimal inter-particle distances. The main attention will be paid to the reaction mechanisms on the catalytic systems that are listed below.

1. Ultradispersed diamond supported systems, including bimetallic on the base of Co, Fe, Ni and Pd.
2. Ni and Pd containing systems supported on double oxides or heteropolyacids salts modified oxides.
3. Ni and Pd nanosystems with extremely low metal content supported on carbon or oxide supports and prepared by laser electrodispersion technique.
4. Carbon covered Ni and Pd nanoparticles prepared by levitation melting of metal in the presence of hydrocarbon.

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KL-17

Cr_2O_3 as a Catalyst of Dehydrogenation and a Chemisorbent

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Chromic oxide is widely used as a single-component catalyst and as a component of Cr_2O_3/Al_2O_3 and of more complicated catalysts. These catalysts accelerate different redox reactions, such as methanol synthesis, shift-reaction, dehydrogenation of hydrocarbons in the presence of carbon dioxide, oxidative dehydrogenation of isobutene, etc.

We studied the Cr_2O_3 activities in dehydrogenation of C_3H_8 in the presence of CO_2 and in chemisorption of some components (H_2, H_2O, CO_2, O_2) entering into the composition of reacting gas-mixtures characteristic for hydrogenation and dehydrogenation processes. The work is aimed at revealing the Cr_2O_3 chemical state occurring in the course of catalysis, the degree of homogeneity of different surface centers relative to their chemisorption ability, and the reacting-medium effect on the catalytic activity of the substrate.

The measurements of the catalytic activity under flow conditions and the calorimetric and chemisorption measurements of chemisorption and sorption of gases under static conditions were performed. Controlling, in each experiment, of the O, H, and C contents in Cr_2O_3 relative to the standard completely-oxidized state of the samples and full cleaning of CO_2 and H_2O from Cr_2O_3 in the course of the preliminary thermo-vacuum treatment of Cr_2O_3 with its subsequent reoxidation are distinctive features of the experimental procedures.

It is stated that H_2 is capable of chemisorbing at the surface (the molar heat of chemisorption is equal to 310 kJ/mol) and of sorbing into the sample body (the molar heat of sorption is equal to 165 kJ/mol), CO_2 is capable of chemisorbing at the surface (the molar heat of chemisorption is equal to 103 kJ/mol), O_2 is capable of chemisorbing at the reduced surface and of sorbing into the body of the samples containing sorbed H_2 with formation of sorbed hydroxyls, the Cr_2O_3 surface is homogeneous relative to the molar heats of chemisorption of each of the gases under study, and H_2 sorption influences the catalytic activity of Cr_2O_3.

The results confirm G.K. Boreskov's statement that reacting gaseous media influence the activity of catalysts. Our conclusion on surface homogeneity of Cr_2O_3 is in line with the data obtained in the Boreskov Institute of Catalysis and showing that surfaces of the V/Mo, V/Mo/Cu, V/Mo/P, and V/Mo/Cs oxides are homogeneous, with the data obtained in the Karpov Institute of Physical Chemistry and showing that surfaces of some other oxides are homogeneous, and also with numerous data showing that surfaces of different metal catalysts are homogeneous. These available conclusions follow from studies of different gas–substrate systems, for which the molar heats of chemisorption and rates of isotopic exchange between the chemisorbed and gas molecules were measured.

KL-18

Modeling of Gas Transport in a Microporous Solid Using a Slice Selection Procedure. Application to the Diffusion of Benzene in ZSM5

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Mathematical modeling of mass transfer by diffusion in zeolite beds or other solids and the methods for finding the analytical solutions have been extensively studied by several authors. Molecular transport in a bed of zeolite involves two processes: diffusion in the macropores formed by the space between the crystallites (intercrystallite diffusion) and diffusion in the micropores within the crystallites (intracrystallite diffusion). To determine the contribution of each of these processes to the overall diffusion process, one has to know the values of certain parameters, such as the pressure in the gas phase, the dimensions of the crystallite bed, the adsorption isotherms, etc. In the present work we assume that the bed consists of a large number of very thin layers of solid perpendicular to the direction of propagation of the gas.

As an application of the theoretical results we present a study dealing with the penetration of a gas (benzene) in a zeolite catalyst (ZSM5) bed. The proposed experimental method relies on the vertical displacement, step-by-step, of the bed during the adsorption of the gas, the NMR detection using a very thin coil. In this way, the region effectively probed is limited to a very thin slice. Thus we can obtain the variation as a function of time of the concentration of gas absorbed at the level of each slice. This dual approach enables us for the first time to determine the diffusion coefficient profiles at every position in the bed.

These coupled investigations give a better understanding of the diffusion process in this multilayer material.

ORAL PRESENTATIONS

Section I

Mechanisms of homogeneous and heterogeneous catalysis
at the atomic and molecular scale
OP_{20}-I-1 ÷ OP_{20}-I-10, OP_{10}-I-1 ÷ OP_{10}-I-31

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Physical methods for the study of mechanisms of heterogeneous
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Section of the young scientists

Physical methods for the study of nano- and biosystems
in catalysis
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Scientific Bases of Metallocomplex Catalysis of Polymerization Processes by Metal Complexes in Low Oxidation State

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The key event of the last quarter of 20-th century in the field of the catalysis of polymerization processes was the discovery by W. Kaminsky of metallocene catalysts (MCC) which presents a special case of the organometallic complex catalysts revealed by Nobel Prize awarders K. Ziegler and G. Natta in 1954. Usually MCC includes a metallocene derivative of Ti, Zr or Hf in the highest oxidation state and methylaluminoxane $(\text{-O-Al-}(CH_3)\text{-})_{10}$. Cyclopentadienyl ligands fill the coordination sphere of the transition metal and in some cases that provides rigid stereoconfiguration of the active centers of polymerization during whole polymerization process. Just this provides stereospecificity for soluble MCC in the process of propylene polymerization. The discovery of this principle was the stimulus for intensive investigations on the directed designing of metallocene and non-metallocene complexes with rigidly fixed stereoconfiguration of ligands on transition metal atom in highest oxidation state specific for it. MCC and PostMCC (fourth generation catalysts) developed by the present time are characterized by ultrahigh activity, efficiency and productivity. They provides unimodal MWD of obtained polymers and in some cases their high stereoregularity. However, some separate facts mismatched to the basic concept of MCC and Post-MCC were collected during of successful development of metallocene and postmetallocene catalysis.

On the base of literature data and results of methodical researches in IPCP RAS, it has been formulated and experimentally proved insights of new direction of metallocomplex catalysis of the polymerization processes. The new direction of polymerization processes is characterized by following basic features:

- Low oxidation state of transition metal in precursors of the active centers;
- Functioning of the catalysts in polar solvents (e.g. ethers, alkandioles, water);
- Presence of one or two uncoupled electrons on the metal atom;
- Changing of the transition metal oxidation state in catalytic cycles;

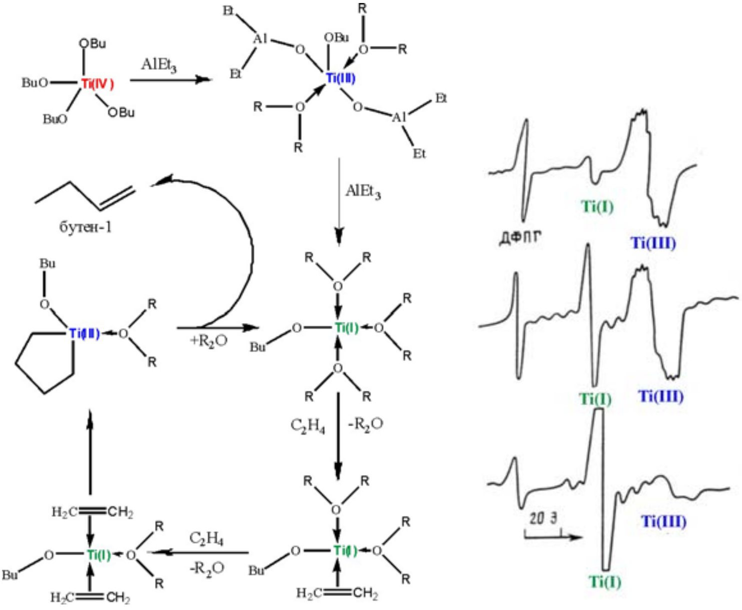
OP$_{20}$-I-1

- Specific mechanisms of the polymerization processes;
- Displaying of the above listed features in some non-polymerization processes (for example, activation of such low-active substrate as nitrogen).

Owing to these features, the catalysts based on the transition metals in low oxidation state also have high activity, efficiency, productivity and selectivity. They can be formed on the base of many transition metals and provide possibility of not only olefin polymerization, but also acetylene, diene and vinyl monomers polymerization.

The example of most studied in details catalysts, which display the listed features are the systems Ti(On-C_4H_9)$_4$ – AlR_3 in ethers (diethyl, dibutyl, di-tretbutil, anisol, phenylethyl, THF) solutions. Under the action of these systems it occurs high-selective dimerization of ethylene to butene-1, as well co-dimerization of ethylene with butadiene and isoprene to the corresponding 1.4-hexadienes, co-dimerization ethylene with methylmetacrylate, and polymerization of acetylene and phenylacetylene and polymerization of butadiene and isoprene.

Proved mechanism of formation and activity of the catalytic sites in above systems in ethylene dimerization process shown on Fig. 1



Evolution of ESR-spectra of products of the reduction of (n-C_4H_9O)$_4$Ti by $AlEt_3$ in diethyl ether at 293 K Al/Ti=10; [(n-C_4H_9O)$_4$Ti] – 69.5 mmol/l Interaction time, min.: I – 15; 2 – 33; 3 – 166

New Prospects of Post-Metallocene Catalysts for Ethylene Polymerisation

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This report presents the analysis of the main features of ethylene polymerization technology using post-metallocene catalysts based on complexes of late transition metals with α-diimine and bis(imino)pyridine ligands as well as phenoxy-imine complexes of transition metals.

The mechanisms of ethylene polymerisation using methylaluminoxane (MAO) activated α-diimine-Ni and Pd complexes and bis(imino)pyridine-Fe and Co complexes are discussed on the basis of the consideration of numerous articles, reviews and patents, including those published by our research group. α-Diimine complexes produce short chain branched polyethylenes while bis(imino)pyridine catalysts provide precisely linear polymers. Possible approaches to control the branching degree by the variation of the ligand structure of the complex are discussed. A potential of the ligand structure optimization to increase the thermal stability of the complexes is revealed and confirmed by quantum chemical calculations.

The results of the studies relating to supported catalysts based on α-diimine and bis(imino)pyridine complexes and “reactor blends” obtained by combining these supported catalyst systems at ethylene polymerisation are analysed.

A particular object of thorough consideration is the prospects for the application of bis(phenoxy-imine) complexes of late transition metals recently discovered by T.Fujita et al.

A detailed analysis of reference data and results of the studies performed by our research group (involving more than 40 phenoxy-imine complexes with various structure) allowed us to make a conclusion regarding an interrelated effect of the substituents in a ligand upon the catalyst activity of the corresponding complexes at ethylene polymerisation. Quantum chemical studies of the structure of bis(phenoxy-imine) complexes using density functional theory revealed the influence of the complex structure features on the energy characteristics of elementary reactions at the polymerization.

The results of the studies of ethylene polymerisation features using a new type of bis(phenoxy-imine) complexes bearing functional groups capable of “self-immobilisation” onto polyethylene yielded in the course of polymerisation are presented. The catalyst complex binding with the polymer is experimentally confirmed and found to provide obtaining ultrahigh molecular polyethylenes with a specific morphology, improved modulus and strength performances without sticking onto the reactor walls.

A new group of bis(phenoxy-imine) complexes with a binuclear structure is synthesised for the first time and shown to possess an advantageous combination of increased thermal stability and high catalyst activity at polymerisation.

OP_{20}-I-3

Aerobic Pd(II)/Cu(II) Catalyzed Oxidation of Olefins under Chloride-Free Non-Acidic Conditions

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Palladium catalyzed oxidations of organic molecules represent a commercially valuable pathway to various oxygenated compounds. The important advantage of these reactions is a possibility to involve molecular oxygen as a final oxidant, which is usually achieved by the reoxidation of reduced palladium species with reversible co-oxidants, $CuCl_2$ being the most convenient one (Wacker catalyst).

We have shown that the $Pd(OAc)_2/Cu(OAc)_2$ system can be used as a more environmentally benign alternative to conventional Wacker catalyst for the aerobic oxidation of terminal olefins to methyl ketones. A significant practical advantage is that the reaction occurs under chloride-free non-acidic conditions and, for this reason, is not complicated by the isomerization of long-chain substrates. Moreover, the catalyst also promotes the unusual oxidation of some polyenes, in which deactivated terminal olefinic bonds remain intact, while sterically encumbered internal olefinic bonds undergo allylic oxidation. A steric possibility for η^2-η^2 -chelation of the terminal and internal double bonds of the polyene molecule on palladium seems to be a crucial factor that determines the reactivity of the internal bond towards oxidation. The presence of the second η^2-coordinated on palladium double bond in these chelates favors the oxidative addition of the olefin, which results in η^3-allyl intermediates and, then, in allylic ethers. The application of the developed system to the oxidation of renewable naturally occurring olefins (linalool [1], nerolidol, dihydromyrcene) resulted in a fist synthesis of various poly-functionalized terpenoids potentially useful as components of synthetic perfumes and pharmaceuticals.

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OP$_{20}$-I-4

Selective Oxidations with H_2O_2 Catalyzed by di-Titanium Containing 19-Tungstodiarsenate(III)

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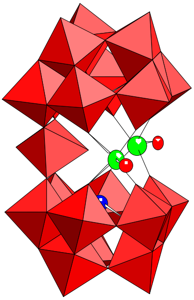
Titanium-containing catalysts, including polyoxometalates (POMs), have attracted increasing attention due to their ability to activate the green oxidant - hydrogen peroxide [1]. The recently synthesized di-titanium containing 19-tungstodiarsenate(III) $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$, comprising two ($B$-$\alpha$-$As^{III}W_9O_{33}$) Keggin moieties linked via an octahedral $WO(H_2O)$ fragment and two unprecedented square-pyramidal $Ti(OH)^{3+}$ groups [2], possesses unique catalytic properties in selective oxidation of organic compounds, such as alkenes, alcohols, diols, and thioethers with aqueous H_2O_2. Under optimal reaction conditions, the selectivity of alkene epoxidation and thioether sulfoxidation is close to 100%. Product and kinetic studies revealed a heterolytic oxidation mechanism involving electrophilic oxygen atom transfer from an active peroxo complex to the organic substrate. This contrasts significantly with the catalytic performance of many other Ti-POMs containing one or more Ti atoms in an octahedral environment, for which homolytic oxidation mechanisms typically operate [1, 2]. The unusual coordination of the Ti atoms in $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$ is believed to be responsible for the unique ability of this compound to catalyze heterolytic oxidation processes using hydrogen peroxide.



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OP$_{20}$-I-5

Fischer-Tropsch-Synthesis Principles

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Self-organization of the Fischer-Tropsch regime and re-assembling of the catalyst under reaction conditions are outlined on the basis of our recent work. Increasing reaction rate and changing selectivity accompany the initial processes.

The multiplicity of product composition refers to distinct elemental reactions - as chain growth, chain branching, desorption as olefin or paraffin and also secondary reactions of olefins for hydrogenation and double bond shift. These are traced with temporal resolution in relation to structural catalyst changes. The rates of these reactions are also dependent on experimental parameters (as temperature and partial pressures of mainly CO, H_2 and H_2O) and are furthermore a function of size (carbon number) of the adsorbed species.

With cobalt as catalyst it has been observed, that the system is very dynamic. Product composition and reaction rate change significantly during self-organization. The cobalt surface is segregated through CO-adsorption to create active cobalt sites of different nature. This is seen as a thermodynamically controlled process.

Spatial constraints on the growth sites increase during self-organization, depressing branching reactions. Secondary reactions of olefins (hydrogenation and double bond shift) decline due to catalyst re-structuring. It is shown how heterogeneous Fischer-Tropsch-synthesis shifts towards homogeneous hydroformylation.

With iron as catalyst, there is less change of selectivity during self-organization, however, activity increases drastically as the iron reacts with CO to form iron carbides, the true Fischer-Tropsch-catalyst. Iron catalyst re-assembling has been traced by XRD and Moessbauer spectroscopy. The initially metallic iron phase of the catalyst disappears completely.

With iron, no olefin secondary reactions may be present; this allows producing α-olefins through Fischer-Tropsch synthesis, propene being a main product compound.

Among the Fischer-Tropsch principles “frustration” of distinct basic reactions is essential.

OP_{20}-I-6

Concept of Acid-Base Catalysis by Metal Sulfides

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There are two acid-base theories in chemistry for homogeneous phases: the Brønsted theory and the Lewis theory. Both are applicable for surface science and heterogeneous catalysis. This paper demonstrates that the mechanism of C – S bond hydrogenolysis reaction with sulfide hydrotreating catalysts can be described in the frame of Lewis acid-base catalysis. The structure of the active component of the sulfide hydrodesulfurization (HDS) catalysts is considered. The active component consists of a single slab of MoS2 (WS2) with Ni or Co atoms being located in its edge plane. The essential element of active component is hydrogen occluded into the MoS2 matrix, which localizes in the center of “empty” trigonal prism of a MoS2 matrix made from six sulfur atoms under Ni (Co) atom at the distance of 1.5 Å. Occluded hydrogen appeared in the active component during the catalyst sulfidation as a result of its oxidative addition to the Ni (Co) atoms. This occluded hydrogen creates an electronic d6 configuration of Ni(IV) or Co(III) atoms, which are the Lewis acid sites with two vacant dz2 and dxy orbitals. Therefore, these active centers can adsorb donor molecules of thiophene. The activation of hydrogen occurs on the couplet sulfur atoms at the edge planes of a single MoS2 (WS2) slab. The driving force of this process is the presence of the S –S chemical bond at the terminal sulfur atoms that restrict an electrically neutral macromolecule of the active component and act as the Lewis basic sites. An excess of electron density is transferred from these atoms to a hydrogen molecule, which results in its homolytic dissociation. The high rate of catalytic transformation is ensured by the fast transfer of electrons and protons along the system of chemical bonds within an electrically neutral macromolecule of the active component.

Experimental Study of Non-Linear Processes in Catalytic $CO+O_2$ and $NO+H_2$ Reactions on Platinum Group Metals: Intermediates and Surface Waves

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In the oscillating regime, the reaction mixture periodically affects the properties of metal surfaces. Mechanisms of oscillatory oxidation reactions are connected with surface reconstructions, with subsurface oxygen formation and associated with the "explosive" nature of interactions between adsorbed species. Isothermal, non-linear dynamic processes of the $CO + O_2$, $NO + H_2$ reactions on Pt, Pd and Ir tips have been studied by FEM/FIM microscope with a lateral resolution of ~ 3–20 Å can also serve as an *in situ* catalytic flow reactor. A very sharp metal tip, ~1000 Å in radius, exposes the surface nanoplanes with different atomic structures. It has been found that the Pt(100) nanoplanes switch reversibly from a catalytically inactive state (hex) into a highly active state (1 × 1) under $CO + O_2$ self-oscillation conditions. The surface of a Pd tip surface is catalytically active in the $CO+O_2$ reaction due to its ability to dissociate O_2 molecules. The FEM study demonstrates the importance of O_{ads} diffusion for the formation of subsurface oxygen O_{sub}, which is an important intermediate species in $CO + O_2$/Pd oscillatory reactions. In the $NO+H_2$ reaction the availability of a vacant site near the NO_{ads} and N_{ads} species may play a central role in the selectivity towards N_2O and N_2. On Ir tips, oscillations in $NO + H_2$ reaction are manifested by regular variations of the emission current as a result of moving waves that spread across the (510), (100) surfaces of the tip.

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OP_{20}-I-8

Alternative Mechanism of Low Temperature Oxidation of CO to CO_2 by Oxygen

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The influence of preparation method on physicochemical properties of supported gold catalysts on Fe_2O_3, TiO_2 and Al_2O_3 were studied. Effect of pretreatment conditions on catalyst activity were examined. The activity tests in CO oxidation by oxygen (or water) were carried out. The influence of hydroxyl groups, potassium additives and chlorine ions on catalytic behavior was investigated. Physiochemical properties of catalysts were determined by BET, XRD, TPR, FTIR, TOF-SIMS, TG-DTA-MS and SEM techniques.

The most active gold/iron oxide catalysts, even below 0 °C appeared those obtained by precipitation-deposition method coprecipitation > > impregnation. Even for a poorly active impregnated Au/Fe_2O_3 catalysts the addition of KOH (up to 10 wt. %) leads to highly active catalytic system which achieve 100% CO conversion at room temperature. The supported gold catalysts dried at 60 °C appeared highly active and stable during seven days test. Thus, alkali ions and high degree of catalyst surface hydroxylation is a prerequisite condition of high catalyst activity especially when catalyst surface is covered with high concentration of potassium. On the bases of our findings an alternative model of CO oxidation reaction in low temperature range is postulated in which the crucial role play peroxide type ions O_2^- or HO_2^- and bicarbonate ions HCO_3^- formed on catalyst surface and engaged in following reaction pathway: $2\ K^+ + 2\ OH^- + O_2 \rightarrow 2\ KHO_2 + 2\ CO \rightarrow 2\ KHCO_3 \rightarrow 2\ K^+ +$ $+\ 2\ OH^- + 2\ CO_2$ The proposed low temperature mechanism is contradictive to commonly accepted relatively high temperature route involving oxygen molecule dissociation as the very first step of CO oxidation: $1/2\ O_2 + 2e^- \rightarrow O^{2-} + CO \rightarrow CO_2 + 2e^-$

Acknowledgements: The support of this work by the Polish Scientific Research Council, PBZ-MEiN Grant 2/2006 is gratefully acknowledged.

OP_{20}-I-9

The Role of α-Sites in the N_2O Decomposition and the Oxidation of Benzene to Phenol over FeZSM-5 Zeolites

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The α-sites are special complexes of bivalent iron stabilized in the micropore space of ZSM-5 matrix. Being inert towards O_2, α-sites are readily oxidized by N_2O:

$$(Fe^{II})_\alpha \quad + \quad N_2O \quad \rightarrow \quad (Fe^{III}–O^-)_\alpha \quad + \quad N_2 \qquad (1)$$

generating α-oxygen species O^- involved, in particular, in selective oxidation of benzene to phenol. Application of various spectroscopic and chemical methods makes it possible to quantify the α-sites, which opens a unique opportunity for molecular scale mechanistic studies of catalytic reactions over FeZSM-5 zeolites.

The nitrous oxide decomposition (NOD) is an ecologically important reaction. In the present work the mechanism of the reaction was studied using a set of FeZSM-5 samples with a wide variation of α-sites concentration. The results were compared with the N_2O oxidation of benzene to phenol (OBP) studied earlier with the same set of samples. In spite of strong differences in turnover frequencies (two orders of magnitude) and activation energies (92 kJ/mol), the reactions were shown to have kindred mechanisms and their rates linearly depend on the α-sites concentration. The mechanism of each reaction consists of two main steps. The first step is a common one and includes the oxidation of α-site by deposition of α-oxygen (eq. 1). The second step is the reduction of the site by α-oxygen removal either with N_2O in the case of NOD reaction, or with benzene in the case of OBP reaction. In both cases the second step is the rate determining one.

Mechanistically, the OBP can be considered as a reduction of N_2O by benzene. One may think that fundamental role of α-sites may hold also for N_2O reduction by other substrates like CO, methane, propane, etc., which are widely used for this purpose.

OP_{20}-I-10

Mechanisms of Paraffins Formation from Ethylcyclohexane on Mono- and Bifunctional Catalysts

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The ethylcyclohexane transformation into paraffins, through ring opening and consecutive cracking of the resulting paraffins, was studied on monofunctional metallic catalysts [1] and bifunctional metallic-acid catalysts [2], under conditions representative of the C8 aromatic cut isomerisation process (hydrogen pressure around 10 bar and temperature of 390° C). This process aims at maximizing para-xylene formation, using a bifunctional catalyst combining a noble metal and a zeolite, on an eventually chlorided support. The C8 aromatic cut is in equilibrium with the corresponding naphtenes, which transformation into paraffins leads to invaluable products. The latter reaction should therefore be minimized. The aim of the present study is to investigate which active sites (of metallic or acid phase) are responsible for the ring opening and consecutive cracking reactions.

The catalysts are composed of highly dispersed platinum (0.3wt% Pt, around 80% dispersion) on either pure alumina for the monofunctional metallic catalyst, or chlorided alumina (1.3wt% Cl) for the bifunctional metal-acid catalyst. In the first stage of the study no zeolite was considered. Bimetallic phases composed of platinum and tin were also prepared. Tin is a namely well known promoter in catalytic reforming process used to minimize the cracking reactions.

The comparison of the products distribution between Pt/Al_2O_3 and Pt/Al_2O_3-Cl catalysts for the same ethylcyclohexane conversion (around 80 %) shows that the C8 paraffins yield is much greater on the bifunctional catalyst, whereas the C1-C7 paraffins distribution is similar. The cracking products are predominantly C1and C2 hydrocarbons, which is typical of hydrogenolysis reactions on metal. When adding tin, ring opening and consecutive cracking reactions decrease significantly, both on the non acidic catalyst and on the chlorided one. The two following hypotheses will thus be discussed for the bifunctional catalyst: (i) ring opening reactions follow a bifunctional mechanism and the subsequent cracking ones are predominantly metallic (unlikely), or (ii) both ring opening and cracking reactions occur on the metallic phase, but the acid phase promotes ethylcyclohexane isomerization and the resultant naphtenes are more easily opened on the metallic phase.

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OP$_{10}$-I-1

Evolution and Interlayer Dynamics of the Active Sites of the Promoted TMS Catalysts under HDS Conditions

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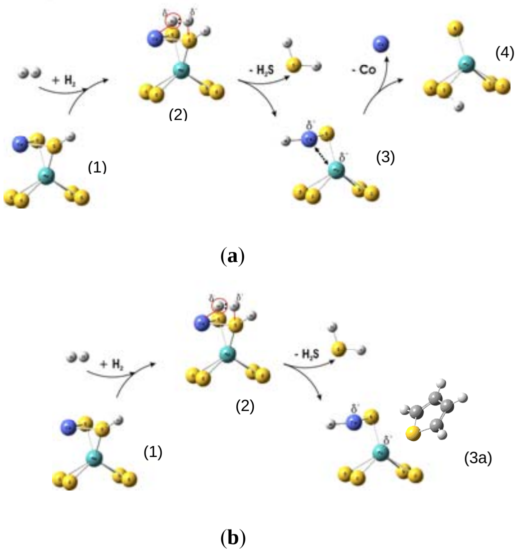
On the basis of the fundamental concepts of catalysis by transition metal sulfides [1–3] a new dynamic model of the promoted Mo-sulfide catalysts functioning under HDS conditions has been developed. The model describes oscillations by sulfur and promoter atoms between the adjacent layers of the slab. The driving forces of such processes is the heterolytic dissociation of the gas phase hydrogen and formation of hydride hydrogen linked to a promoter atom. This hydride hydrogen triggers an electron transfer from a promoter to Mo with the formation of the vacancy. This model correlates with radioisotopic data [4] and an earlier suggested “forcing out” mechanism [5] and gives some new interpretations of the important statements of the electron theory of promotion [2] and the “rim-edge” model [3].



(**a**)

(**b**)

Fig. 1. Single CoMoS cluster transformations under H_2 atmosphere (a) – without thiophene adsorption;
(b) – at thiophene adsorption.
(1) – initial structure of the single CoMoS cluster;
(2) – heterolytic dissociation of H_2 on the SH group and Co atom with formation and following elimination of H_2S;
(3) – repulsion of Co atom form Mo atom and its elimination from the cluster;
(3a) – disappearing of the Co-Mo repulsion as a result of compensation of the positive charge on the Mo atom by electron density of sulfur of the adsorbed thiophene;
(4) – formation of unpromoted single Mo-sulfide cluster.

Thiophene adsorption makes transfer of a promoter to the neighboring slab improbable because the electron density of thiophene sulfur compensates the extra positive charge on the Mo atom appeared after H_2S removal (Fig. 1). When thiophene adsorbs on the vacancy of the CoMoS site the proton linked to Co moves to the SH group of the neighboring layer forming the H_2S which desorbs from this layer and new vacancy is formed. This model explains the reasons of the electron transfer from the atom of promoter to the Mo and different locations of the active sites responsible for hydrogenation and desulfurization on a promoted MoS_2 slab.

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OP_{10}-I-2

Special Features of Catalytic Hydrogenation of Non-Saturated Polymers

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Chemical modification of polymers by catalytic hydrogenation allows solving the problem of sharp increase of their stability and firmness to influence of weather, light, ozone, gasoline, oils, radiation and other aggressive environments.

Despite seeming simplicity of joining of hydrogen to non-saturated bonds of macromolecule, selection of catalysts carrying out this reaction is very complicated. Hydrogenation becomes complicated due to specific features of high-molecular structure.

Our studies of the processes of hydrogenation of non-saturated polymers and oligomers allowed us to study the features of their hydrogenation and to develop the highly effective and selective low-percentage (0.3-2.0%) palladium catalysts for their hydrogenation.

Studying of the effect of the nature of carriers, way of supporting of an active phase, the nature of initial palladium salt, modifying the surface of carriers, and also the influence of thermal treatment in atmosphere of various gases have allowed us to identify that the main role in macromolecules hydrogenation belongs to acidic-alkali properties of carriers and the sizes of their pores providing maximal availability of an active surface to adsorption and activation of macromolecules.

On the basis of experimental data it has been revealed that under optimal conditions the adsorption of macromolecules is a one-step process. Macromolecules in these conditions desorb from the surface practically only after the full saturation of double bond. The catalysts developed by us allow to carry out the hydrogenation process of butadien-nitric and butadien-styrene polymers under very mild conditions (0.1-2.0 МПа, 30-50°C) in 60-120 minutes.

^{1}H NMR, EPR and Catalytic Study of Active Intermediates Formed in the Polymerization Catalysts Based on 2,6-Bis(imino)pyridine Cobalt Complexes

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Highly active catalysts for ethylene polymerization based on tridentate bis(imino)pyridyl complexes of transition metals of the VIII group (late transition metal catalysts) attracted substantial interest in the last 10 years [1,2]. The mechanism of polymerization over these catalysts has been studied using mainly 2,6-bis(imino)pyridine iron (II) [3,4].

In the present research, we report the ^{1}H NMR and EPR study of the intermediates formed upon activation of bis(imino)pyridine cobalt (II) complexes with different substituents in the ligand with MAO, $AlMe_3$ and $Ph_3C[B(C_6F_5)_4]$ and discuss the nature of the active sites of polymerization. Data on the ethylene polymerization activity and the resulting polyethylene properties (MW, MWD) for the different catalyst/activator systems are reported. The obtained results are compared with the data for bis(imino)pyridine iron (II)/activator systems that provide a deeper insight into the catalytic behavior of the intermediates formed in the polymerization catalysts based on bis(imino)pyridine cobalt complexes.

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OP$_{10}$-I-4

Reaction Paths and Resting States in Zirconocene-Based Olefin-Polymerization Catalyst Systems

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Since their discovery about 25 years ago, [1] *ansa*-zirconocene-based olefin-polymerization catalysts have been subjected to numerous thorough studies with regard to their reaction mechanisms. Consequently, substantial experimental evidence supports our present assumptions concerning the nature of the most relevant transition states, which control essential catalyst properties, such as the rates and the selectivity, with which alternative polyolefin enchainment patterns are produced [2].

Surprisingly, however, substantial uncertainty still surrounds the nature of the predominant catalyst species present in a “working” catalyst even for otherwise most well-studied catalyst systems. Studies on related pre-catalyst systems – i.e. on reaction systems containing various zirconocene derivatives in the presence of suitable “cationization” reagents, yet in the absence of olefin monomer – indicate that the particular reactivity of these systems is due to ion pairs of the type $[\{Cp^{x}{}_{2}\}Zr\text{-}Me^{+\cdots}A^{-}]$, were $\{Cp^{x}{}_{2}\}$ stands for a pair of substituted and/or bridged C_5-ring ligands and A^- for a weakly coordinating anion such as $B(C_6F_5)_4^-$ or Me-MAO$^-$ (with MAO being some methylalumoxane cluster) [2]. Pre-catalyst systems containing aluminum alkyls, as parts of the methylalumoxane activator or as “scavengers” together with a perfluorophenyl-borate activator, have been shown to contain, in addition to these cations, also their adducts with $AlMe_3$, i.e. outer-sphere ion pairs of the type $[\{Cp^{x}{}_{2}\}Zr(mu\text{-}Me)_2AlMe_2]^+$ A [3].

Analogous ion pairs, which carry a polymer chain instead of a methyl group, i.e. species of the type $[\{Cp^{x}{}_{2}\}Zr\text{-}polymer^{+\cdots}A^{-}]$, have indeed been observed as resting states, from which polymer chains grow by consecutive olefin insertions into their Zr-polymer bonds [4]. Probable reaction intermediates of the type $[\{Cp^{x}{}_{2}\}Zr\text{-}polymer(olefin)]^+$ A^- might arise by displacement of the anion A^- from such a contact-ion pair or by displacement of $AlMe_3$ from an adduct of the type

$[\{Cp^x{}_2\}Zr(mu\text{-}polymer)(mu\text{-}Me)AlMe_2]^+$ A^-. Alternatively, zirconocene cations $[\{Cp^x{}_2\}Zr\text{-}polymer^+]$, with a beta- or gamma-agostic Zr-alkyl interaction strong enough to relegate the anion A^- to an outer-sphere association [5] and cationic species with a reduced propensity for further olefin insertion, such as those carrying at their Zr center either a secondary polymer residue, resulting from a 2,1-oriented olefin insertion [6] or an allyl-ended polymer chain (formed by beta-H abstraction under release of H_2) [7] have likewise been proposed as resting states in "working" polymerization catalyst systems.

Little experimental evidence is available to date to assess, to which degree one or the other of these alternative entities actually occur as resting states in a polymerization catalyst under realistic conditions, i.e. at or above ambient temperature and in the presence of a large excess of olefin monomer. Under these conditions standard NMR methods, which are most useful otherwise, appear to be of limited utility to estimate in which amounts various complex species are present.

Any fundamental understanding of polymerization kinetics requires, however, that the identity of all catalyst resting states is known, such that their free energies relative to those of relevant reaction intermediates and transition states can be reliably assessed – a necessary prerequisite for any rational analysis of the effects of structural variations on catalyst activities and relative rates of undesirable side reactions, such as those leading to chain-growth termination or chain-end isomerization. Results of recent efforts to acquire reliable information with regard to relative proportions of alternative catalyst resting states by use of suitable spectroscopic techniques will be presented and discussed in this contribution.

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Biomimetic Catalysis of the Lower Olefins Polymerization with Zirconocene and Post-Zirconocene Catalytic Systems

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The kinetics of ethylene and propene polymerization with some zirconocene and post-zirconocene homogeneous catalytic systems shows [1-3] that the reaction mechanism cannot be explained in terms of cation-like active centers (free cations L_2Zr^+R or ion pairs $L_2Zr^+R \cdot RA^-$, where A is Lewis acid). So, the initial rate of monomer uptake w_o testifies that the reaction is of the fourth kinetic order with respect to the monomer concentration (n = 4). In the presence of cation-like active centers this reaction order must be first [4]. The initial rate of the process changes sharply with an increase in the concentration of Zr and passes through a maximum, whereas the reaction order must be n = 0,5 in the case of free cations L_2Zr^+R [4] and n = 1 in the case of ion pairs. It is noteworthy that well-known extremal character of the process rate depending on the [Zr] is unexplainable in terms of cation-like active centers.

A variation in the rate of polymerization with temperature has a bell-like pattern with a maximum at optimal temperature T_{opt}, beyond which the rate falls rapidly [3]. This behavior is inherent to enzymatic catalysis.

The mechanism of the process involving formation of catalyst clusters $[L_2Zr^+R \cdot RA^-]_4$ as active centers and chain growth via the concerted interaction of four cluster-coordinated monomer molecules was suggested [1-3].

Collective interactions that occur in the investigated catalytic systems both at the stage of active centers formation (association of four donor-acceptor complexes $L_2Zr^+R \cdot RA^-$) and at the stage of polymerization (the concerted opening of the four double bonds in activated monomer molecules) explain the behavior of these systems that is unusual for organometallic catalysis. These systems behave like natural biocatalysts – enzymes (a bell-like variation in the rate of reaction with temperature, the simultaneous activation of several substrates by enzyme, and the ability to synthesize stereoregular polymers [5]). These analogues with enzymatic catalysis give us grounds to assign the studied homogeneous systems to the class of biomimetic catalysts [6].

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Reaction Kinetics of the Ethylene Tetramerization Catalyst System $CrCl_3(THF)_3$, $Ph_2PN(^iPr)PPh_2$ and MAO

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Linear alpha olefins (LAOs) are very useful intermediates for the manufacture of many important industrial products. They are mainly produced by metal catalysed ethylene oligomerization processes. An inherent problem is the production of LAO mixtures following a mathematical distribution (Schulz-Flory or Poisson), difficult to separate which often does not match market demand. This is the reason why the interests are focussed to come to more selective processes [1].

We present a kinetic investigation of the well known ethylene tetramerization catalyst system comprising $CrCl_3(THF)_3$, $Ph_2PN(^iPr)PPh_2$ as ligand and MAO as catalyst activator. The main focus of the experimental study lied on the influence of the ligand to chromium molar ratio on the catalyst performance and the selectivity towards 1-octene. It was found that a sub-stoichiometric ligand/Cr - ratio leads to a Schulz-Flory product distribution, while unusual odd-numbered 1-olefins as by-products were formed [2].

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OP_{10}-I-7

Mechanism of Zr Catalysis in Reactions of Organoaluminium Compounds with Alkenes

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The work is devoted to a fundamental study on mechanism of action of Zr π-complexes (L_2ZrCl_2) as catalysts in reactions of organoaluminium compounds (OACs) with alkenes, namely, in the processes of olefins hydro-, carbo- and cycloalumination. The influence of the OACs nature, Zr π-ligand environment, solvent type, temperature and reagents ratio on reaction chemo- and stereoselectivity has been studied for the first time. The conditions for realization of definite pathways were found.

The structure and reactivity of intermediates, which are formed in the systems OACs-L_2ZrCl_2-alkene, have been investigated by the means of dynamic NMR spectroscopy, encounter synthesis and kinetic studies; and the key complexes responsible for the hydro-, carbo- and cyclometallation pathways were determined.

The quantum-chemical calculations of geometric and energetic parameters of intermediates and transition states of the processes of interligand exchange, β-C-H-activation and alkene coordination were carried out.

On the basis of experimental and theoretical investigations, a generalized model of olefin hydro-, carbo- and cyclometallation, catalyzed with Zr π-complexes is suggested.

Relationship between n-Alkane Chain Length and Turnover Frequency in Alkane Combustion over Pt/Al_2O_3

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In this study we analyze an impact of the size of n-alkane molecule (chain length) on turnover frequency (TOF) in total oxidation over a series of 1%Pt/Al_2O_3 catalysts. The catalysts contain Pt nanoparticles of different size ranging from 1 to 14 nm (TEM data). Aqueous impregnating solutions of oligomeric μ-hydroxo Pt(IV) complexes were used as active component precursors providing size-controlled formation of supported platinum nanoparticles. The catalyst were calcined, reduced in flowing H_2 at 350 °C, and tested at atmospheric pressure in the total oxidation of two n-alkanes of different length: C_2H_6 and n-C_6H_{14}.

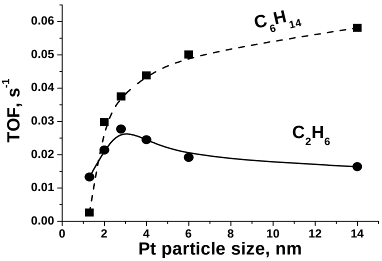

Fig. 1 Effect of Pt particle size on TOF in total oxidation of short-chain (ethane) and long-chain (n-hexane) alkanes

TOF (counting on surface Pt amount from H_2 chemosorbtion) remains relatively constant within the whole range of Pt particle size in the total oxidation of a small molecule (C_2H_6) at 390 °C except for a feebly marked maximum at Pt particle size about 3 nm with the TOF enhancing only by ~ 2 times (see Fig. 1), and the overall activity steadily decreases with decreasing Pt dispersion. However with increasing length of alkane molecule TOF becomes emplicity dependent on Pt particle size. For n-hexane oxidation TOF increases by more than order of magnitude at 170 °C (Fig. 1). Presumably, oxidation of long-chain alkanes as hexane requires multi-atom surface active sites (for multi-point adsorption, or formation of relevant transition state).

As a result, the maximum overall activity in total oxidation of short-chain alkanes is observed over Pt/Al_2O_3 with maximum Pt dispersion. On the other hand, catalysts with larger Pt particles (3-5 nm) demonstrate better efficiency in oxidation of long-chain alkanes.

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Mechanism of the One-Pot *R*-1-Phenylethyl Acetate Synthesis over Chemo-Bio Catalysts

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Cascade reactions are of great interest, especially in the synthesis of pharmaceuticals with the aim of reducing the number of reaction steps to be performed in separate reactors [1]. There is a challenge to combine different types of catalysts, i.e. supported metals and biocatalysts, in one reactor, since the optimal reaction conditions for each catalyst are different. Furthermore, catalysts can affect each other and thus their interrelation could be difficult to understand on the molecular level. The model reaction in this study is one-pot synthesis of *R*-1-phenylethylacetate (*R*-PEAC) starting from acetophenone (AP) hydrogenation over Pd/Al_2O_3 followed by kinetic resolution of the formed (*R,S*)-1-phenylethanol over enzyme (Fig. 1) [2]. Additionally, a third catalyst, used for racemisation of *S*-1-phenylethanol (*S*-PE) would be needed for enabling the dynamic kinetic resolution. In the current work hydrogenation of acetophenone together with kinetic resolution of alcohols to form *R*-1-phenylethanol was studied. The aim was to investigate in detail, which reactions occur. Ethyl benzene is the main side product, which can be formed via dehydration of secondary alcohol followed by rapid hydrogenation of styrene to ethylbenzene (EB) or alternatively via debenzylation of both *R*-1-phenylethylacetate, since Pd is known to be active in debenzylation.

OP_{10}-I-9

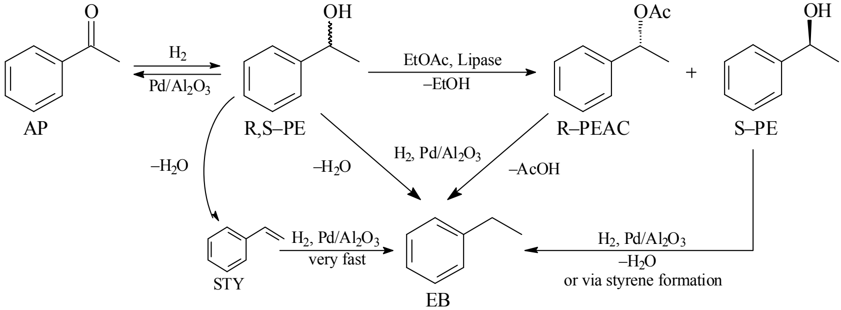

Fig. 1. The proposed reaction scheme for the synthesis of *R*-1-phenylethyl acetate from acetophenone hydrogenation.

Acetophenone was hydrogenated over 5 wt.% Pd/Al_2O_3 in a glass reactor under 1 bar hydrogen at 70°C using ethyl acetate as an acyl donor. An immobilized lipase, Novozym 425 was used as a catalyst for acylation of the formed (*R,S*)-1-phenylethanol. The reaction products were analyzed by GC and confirmed by MS. The catalyst was characterized by CO-chemisortpon, XRD, TEM, nitrogen adsorption and pyridine adsorption.

The kinetic studies were performed using both acetophenone and S-1-phenylethanol as reactants to reveal the reaction mechanisms. Based on the experimental data the main reaction pathway of EB formation includes hydrogenolysis of (*R,S*)-PEs and deacetylation of *R*-PEAC, however, dehydration of (*R,S*)-PEs leading to the styrene formation followed by fast hydrogenation to EB must not be ruled out.

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The Mechanism of Methane and Higher Alkane Co-Aromatization on Zn- and Ga- Modified Zeolite BEA

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Non-oxidative co-aromatization of methane with light hydrocarbons on zeolites modified with gallium or zinc is a perspective process for the utilization of methane. The lack of the isotope tracing confirmations for this reaction, as well as the absence of the experimentally valid insight into the reaction mechanism, provoked considerable doubts as to the possibility of such methane-involved aromatization at all.

In the present study, using solid-state NMR and GC-MS analysis, we report that the transfer of ^{13}C-labelled carbon atoms from $^{13}CH_4$ into the molecules of aromatic products of the methane and propane co-conversion does occur on high-silica zeolites BEA, modified with gallium (Ga/H-BEA) or zinc (Zn/H-BEA). We have demonstrated that the main pathway of methane-to-aromatic conversion represents the alkylation of aromatic compounds, formed from propane, by methane molecules. Further transfer of the ^{13}C-label of methane-^{13}C from methyl group to aromatic ring occurs through the scrambling of the carbon atoms in methylbenzenes via ring expansion/contraction mechanism.

The less efficiency of Ga/H-BEA in the reaction of methane aromatization can be presumably rationalized in terms of changing the mechanism of the alkylation stage: from the electrophilic substitution by $Zn–O–CH_3$ species on Zn/H-BEA towards the unfavorable reaction of nucleophilic substitution by $Ga–CH_3$ groups on Ga/H-BEA.

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OP_{10}-I-11

Control of the Mechanism of Cu^0 Active Site Action Via Composition and Structure of Oxide Catalyst's Precursor

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The control of the catalytic properties of Cu-based oxide catalysts on the stage of their preparation is a complicated and actual problem. Cu metal formed in the course of reductive activation provides the activity of Cu-based catalysts in the reactions occurring in the reductive reaction medium, such as methanol synthesis and dehydrogenation, WGSR and some hydrogenation reactions. However the specific activity and often selectivity of Cu metal in great extent depend on the composition and the way of the catalyst's preparation. In the present study the nature of this dependence is discussed on an example of Cu-based oxide catalysts, obtained by thermal decomposition of Cu- and Cu-Zn-hydroxosilicates of chrysocolla and zincsilite structure, respectively, as well as Cu-Zn, Cu-Al(Cr), and Cu-Zn-Al(Cr) hydroxocarbonates of hydrotalcite and hydrozincite structure.

It has been shown that nanosized Cu metal particles formed in the course of reductive activation provide the activity of Cu-based catalysts in methanol synthesis and dehydrogenation, WGSR and hydrogenation reactions. Their specific activity and the products of reaction depend on the phase and chemical composition of the catalyst. Physico-chemical characterization allows concluding that the mechanism of the acting of active site is determined by the decoration with support oxide clusters, such as ZnO_x SiO_x, AlO_x or their combination. Adsorptive and catalytic properties of Cu^0 particles depend on the decoration, since decoration influences their electronic properties. The extent of Cu^0 particles decoration and its influence on adsorptive and catalytic properties is determined by the nature of precursor. As Si^{4+} and Al^{3+} cations can't accept electrons, the partial positive charge on Cu^0 particle compensation occurs, probably, with OH^- substituting oxygen anions in anion sublattice.

The obtained results evidence, that the directional synthesis of the catalysts for the reactions realizing in the reductive conditions is a solvable problem.

OP_{10}-I-12

O_2 Isotopic Exchange in the Presence of O^- Species on the FeZSM-5

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Oxygen anion radicals O^- play an important role in various physicochemical processes, including those taking place on solid surfaces, where their behavior is especially difficult to follow. This work presents detailed study on the role of O^- radicals adsorbed on FeZSM-5 surface in the reaction of O_2 isotopic exchange carried out in a wide range of temperatures (198-513 K). High concentration of O^- (called the alpha-oxygen) which by two order exceed its concentration on another systems allowed made it possible to identify two exchange mechanisms, R_0 and R_1, operating in the presence of O_α.

The R_1 mechanism ($E = 3.5$ kcal/mol) dominates in the high-temperature region (323-513K) and can be represented by the follow equation:

$$^{18}O_2 + {}^{16}O_\alpha^- \rightarrow [O_3^-]_\alpha \rightarrow {}^{16}O^{18}O + {}^{18}O_\alpha^-$$

This mechanism is convincingly supported by several arguments: the first reaction order with respect to O_2 and O_α; the ESR observation of O_3^- species (in other systems); and, according to the isotopic exchange theory, by a twofold excess of the rate of homoexchange over the rate of heteroexchange.

The R_0 exchange ($E = 0.2$ kcal/mol) is a new reaction channel that appears at cryogenic temperatures and leads to isotope redistribution only between O_2 molecules, not affecting the isotopic composition of O_α. This exchange mechanism is not quite clear. The necessity of O_α presence without its direct involvement in the exchange process seems to be quite surprising. The reaction may proceed via a hypothetical complex $[O_5^-]_\alpha$, which allows cleavage and redistribution of chemical bonds between two O_2 molecules adsorbed on the α-oxygen. The cleavage and redistribution of so strong bonds at cryogenic temperatures with nearly zero activation energy are an intriguing phenomenon worthy of further study.

OP_{10}-I-13

Catalytic Oxidation of Methane

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Methane is 21 times more effective than carbon dioxide as the greenhouse gas. It means that decrease of methane emission by 1 ton has the same effect as the 21 tons reduction of carbon dioxide emission[1]. The effective decrease of emission regarding to carbon dioxide as the product of the combustion reaction is 18.25 tones of CO_2 per 1 tone of CH_4.

The data announced by the State Institute of Geology indicate that annually more than 70% of methane leaves the mines with ventilation air, which can not be caught in the installations utilizing methane, and which create methane-air mixtures with different methane concentration.

On Polish market there is a lack of engineering solutions for low-concentrated methane utilization, similar to that developed by MEGTEC Systems (De Pere, Wisconsin, USA), CANTEM (Canadian Mineral and Technologies, Canada) or by Exploration CSIRO & Mining and Energy Developments Limited (Australia) and which were already successfully used in some coal mines in the United States, Australia, Canada, Sweden and China.

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.

Acknowledgments

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OP_{10}-I-14

Kinetic Description of Catalytic Processes: A New Approach

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The usual procedure for deduction of the kinetic equations (KEqs) considering the reverse reactions is based on the notion on the stoichiometric numbers of rate-determining steps (SNRDSs) (ν). However, for any reaction, the available ν-values are different and the theoretical basis for the SNRDS notion is questionable.

We propose a general approach that uses no notion on the SNRDS. An example is the CH_3OH synthesis (MS) at Zn/Cu. The chemadphases (Z (free ZnO), ZH_2, $ZCOH_2$, ZO, ZH_2CO_2, and ZCO_2) existing at the ZnO-surface, catalyzing the MS, and the RDS nature were revealed earlier (V.E. Ostrovskii, *Catal. Today*, 77 (2002) 141). The new approach allows for improving the KEq obtained there. The RDS is

$$H_2 + Z\,CO_2 \leftrightarrow Z\,H_2CO_2, \qquad (1)$$

and the rate is given by Eq (2), were the θ_{ZCO_2} and $\theta_{ZH_2CO_2}$ should be specified:

$$r = r_+ - r_- = k_{+3}\,P_{H_2}\,\theta_{ZCO_2} - k_{-3}\,\theta_{ZH_2CO_2}. \qquad (2)$$

Let the gross-reaction (GrR) be written by a stoichiometric Eq (SEq) with an arbitrary set of stoichiometric coefficients and the RDS be known. According to the RDS definition, the RDS subtraction from the GrR should give an equilibrium equation (EquEq). To obtain this EquEq, we should specify the numerical factor (matching coefficient, η) by which we should multiply the RDS Eq before its subtraction from the GrR SEq. We show that η has a unique value and requires no experiments to specify it; the specification procedure for any GrR–RDS pair of Eqs will be given. Eqs (3), (4), (5) are the arbitrary SEq, the RDS Eq with the corresponding η-value ($\eta = 3$), which is found analytically, and the EquEq, respectively.

$$\begin{array}{ll} \_\,CO_2 + 3\,H_2 = CH_3OH + H_2O & (3) \\ \underline{3\,ZCO_2 + 3\,H_2 \leftrightarrow 3\,ZH_2CO_2} & (4) \\ CO_2 + 3\,ZH_2CO_2 \equiv CH_3OH + H_2O + 3ZCO_2. & (5) \end{array}$$

We use the set, where four Eqs (the chemadphases number minus two) ((6), (7), (9), and (10)) connect arbitrarily all chemadphases with each other and with the reactants and where (11) is obtained by subtraction of ((6)+(7)+(9)+(10)) from (5):

$CO_2 + Z \equiv ZCO_2$ (6)
$H_2 + Z \equiv ZH_2$ (7)
$ZCO_2 + H_2 \leftrightarrow ZH_2CO_2$ ($\eta = 3$) (8)
$ZH_2CO_2 + Z \equiv ZO + ZH_2CO$ (9)
$CH_3OH + 2\ ZO \equiv H_2 + H_2O + CO_2 + 2Z$ (10)
$CO_2 + 2\ ZH_2CO_2 + ZH_2 + ZH_2CO \equiv 2\ CH_3OH + 2\ ZCO_2 + ZO + Z.$ (11)

Solution of the (6)–(11) set relative to θ_{ZCO2} and θ_{ZH2CO2} and substitution of the corresponding expressions into (2) give the KEq considering the reverse reaction.

Successful applications of this approach to description of available data on the MS and methanol destruction at 0.1–15 MPa and 450–650 K will be presented. This new approach responds to the original notion on the catalysis nature proposed in the paper cited above. Its applications to other reactions will be also considered.

Investigation of Palladium States on Pd/γ-Al_2O_3 in the Oscillation Regime of CO Oxidation

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The study of the polycrystalline Pd and Pd/γ-Al_2O_3 calcined at 800, 1000 and 1200°C in CO oxidation shows that chaotic self-oscillation (S-O) behavior was appeared during sample cooling after achievement of maximum CO conversion. It was shown that S-O is observed both at decreasing temperature and at isothermal conditions. It was established that the calcination temperature of the catalysts appreciably influences on the S-O behavior and changes the temperature region of oscillation performance. Appearance of the S-O is accompanied by the changes of Pd particles morphology and the oxidation state of palladium. The comparative investigation of the polycrystalline Pd was carried out for modelling of the morphology and the oxidation state of palladium in the S-O conditions.

It was shown that the strong surface roughness and formation of PdO particles was observed after sample treatment by reaction mixture in S-O regime. In the course of S-O the reversible transition $PdO \leftrightarrow Pd^o$ with formation of palladium metallic nanoclusters on the surface of the PdO particles takes place. The similar results were obtained for Pd/γ-Al_2O_3 catalysts. On the basis of the experimental data the scheme of CO oxidation in S-O regime is proposed. The difference of proposed scheme from classic model TSM is the formation of metallic nanoclusters covering the surface of PdO particles.

1) $CO + [Pd] \leftrightarrow [Pd]CO$, 4) $[Pd]O \rightarrow [PdO]$,
2) $O_2 + 2[Pd] \rightarrow 2[Pd]O$, 5) $CO + [PdO] \leftrightarrow CO[PdO]$,
3) $[Pd]CO + [Pd]O \rightarrow 2[Pd] + CO_2$, 6) $CO[PdO] \rightarrow CO_2 + [Pd]$.

OP_{10}-I-16

Mechanism of Self-Oscillations in CO Oxidation on Nanosized Pd

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Experimental studies of CO oxidation on the Pd/Al_2O_3 catalysts demonstrate self-oscillations of the reaction rate. At the oscillation region, the Pd nanoparticles on the surface consist of a mixture of metallic and PdO phases. It is established that metallic phase forms some small islands on the surface of PdO nanoparticles. The reversible transition between the Pd phases occurs depending on the reaction conditions. It is proposed that this plays a key role in the oscillation behavior of reaction.

To describe the self-oscillations of the CO oxidation reaction rate we consider the following kinetic mechanism:

1) $CO + [Pd] \leftrightarrow [Pd]CO$,
2) $O_2 + 2[Pd] \rightarrow 2[Pd]O$,
3) $[Pd]CO + [Pd]O \rightarrow 2[Pd] + CO_2$,
4) $[Pd]O + [Pd]_V \leftrightarrow [Pd] + [Pd]_VO$,
5) $[Pd]_VO \leftrightarrow [PdO]$,
6) $[Pd]O \rightarrow [PdO]$,
7) $CO + [PdO] \leftrightarrow [PdO]CO$,
8) $[PdO]CO \rightarrow CO_2 + [Pd]$,

where [Pd] and $[Pd]_V$ are active sites on the surface and in the volume of the metallic phase and [PdO] are sites of the particle, correspondently. There are two routes of CO_2 formation, including the Langmuir-Hinshelwood mechanism on the metallic and oxidized surfaces (stages 1, 2, 3 and 7, 8 respectively). The transition of one Pd phase to another occurs through the different oxygen states (stages 4, 5, and 6).

The kinetic model based on this scheme takes also into consideration that the number of active sites on the surface and in the volume of the particle vary under reaction conditions, while the number of all active sites is fixed. The model describes qualitatively the shape of the reaction rate self-oscillations with small periods observed in the experiment.

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Impact of the Zeolite Structure in the Formation of the Active Sites towards N_2O Decomposition Reaction

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Direct catalytic decomposition of N_2O over metal-substituted zeolites is an attractive and economical option to reduce nitrous oxide emission. Although a consensus has been developed concerning catalytic performance of these materials, the identification of their active sites remains a matter of debate.

Here we report the study of N_2O decomposition over various Cu- and Fe-containing zeolites aiming to find a correlation between the structure of the active sites and catalytic performance. The zeolitic catalysts were prepared starting from Y, Beta, ZSM-5, mordenite zeolites *via* ion exchange procedure [1,2,3], by direct incorporation of Fe^{3+} cation into MFI's framework upon synthesis, as well as by means of the atomic layer deposition of metal acetylacetonates. All materials were characterized by ICP, EPR, XRD, UV-Vis DRS and TPR with H_2.

The impact of the support composition, its topology, location and distribution of the metal-containing species, and also pre-treatment on the catalyst's behavior is discussed. For the active sites formed by both Cu and Fe, their easy and reversible redox transformation is the matter of importance to ensure high catalytic activity towards the reaction.

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OP$_{10}$-I-18

Thermal Desorption of Hydrogen from Ni-Cu-Cr Catalyst on (θ+α)-Al_2O_3, Modified by Cerium

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It was shown that 8,9% Ni-Cu-Cr (1:3:0,1)/2%Ce / (θ+α)-Al_2O_3 catalyst contains nanoparticles (20-100Å) of Ni and Cu oxides, or their mixtures, crystal CeO_2, and aluminates of Ni(Cu)-Al_2O_4 with particle size 100-200Å and other phases (Ce_6O_{11}, $CuCrO_2$, $NiCeO_4$, Cr_5O_{12}) during genesis after heating at 873 K by XRD, TEM and TPR methods. After the further heating there is crystallization of CeO_2, transformation θ→α Al_2O_3, above 1073 K - the content and size of Ni(Cu)Al_2O_4 (400-500Å) particles increase. In structure of catalyst heated at 1173 K after reduction in H_2 at 1173 K the content of aluminates considerably decreases, the content of metallic Ni and Cu increases, there is polycrystalline film $Cu_{3.8}Ni$ (size up to 40-100Å), and also there are translucent particles Ce_6O_{11} (50-60Å).

The results of interaction of hydrogen with 8,9% Ni-Cu-Cr (1:3:0,1)/2%Ce / (θ+α)-Al_2O_3 with using of thermal desorption method are presented. The investigation of the interaction of H_2 with Ni-Cu-Cr catalyst on modified by 2 % cerium (θ+α)-Al_2O_3 by thermal desorption method has shown, that 3 hydrogen forms are formed at 673 K: H_{2ads}, H_{ads} and H-dissolved, differing in desorption temperature and $T_{мах}$ of peaks. Increase of adsorption temperature from 673 K up to 1173 K promotes formation on surface H_{2ads} (E_{des} = 14,4 kcal/mol, the desorption order = 1, H:Ni = 1,6-1,88), H_{ads} and increase in dissolution of hydrogen in Ni lattice and its alloy with copper (E_{des} = 32,9 kcal/mol, the desorption order = 2, H:Ni = 2,0).

Obtained data can be used for an explanation of the mechanism as hydrogenation of organic substances due to the adsorbed forms of hydrogen, and decomposition, selective oxidation of CH_4 and others alkanes into H_2, synthesis-gas because of capability of catalyst to eliminate hydrogen from hydrocarbons and dissolve it in the structure.

Effect of the Mobility of Lattice Oxygen of the Oxide Catalyst on the Reaction Rate in CH_4 Dry Reforming

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Lattice oxygen mobility could be important for stable performance of Pt-supported catalysts for CH_4 dry reforming [1] and other reactions of syngas production from methane due to participation of the near surface oxygen-containing species in the formation of active oxidized Pt centers on the catalyst surface. To estimate the influence of this factor on the methane transformation, experimental studies and modeling of transient behavior of CH_4 dry reforming have been performed.

Active component 1.4 wt.%$Pt/Pr_{0.3}(Ce_{0.5}Zr_{0.5})_{0.7}O_2$ was supported as thin layer on a separate triangular corundum channel placed in the quartz reactor [2]. The experiments were carried out at 4−15 ms contact times in the range of temperature of 600−900 °C using CH_4 and CO_2 in N_2 feed after catalyst pretreatment in O_2. The response data revealed the characteristic modes in accordance with the reaction steps on catalyst surface as well as oxygen consumption from the active component layer.

A mathematical model was developed for such catalytic systems with a due regard for the effect of the near surface oxygen diffusivity that helps to stabilize Pt centers partially oxidized and increases the rate of methane conversion on these centers. A number of computational runs allowed the rates both of lattice oxygen mobility and main stages of the reaction mechanism to be evaluated on the base of experimental data.

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OP$_{10}$-I-20

Modification of ZSM-5 with SiO_2 / La_2O_3 and Its Catalysis for Toluene Alkylation with Methanol

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The modified ZSM-5 was used to the shape-selective catalysis for toluene alkylation with methanol to produce *para*-xylene. A variety of modification methods have been adopted to improve the catalytic selectivity of ZSM-5 for toluene alkylation or disproportionation reaction, such as impregnation of metallic or non-metallic compounds, chemical vapor deposition of silica (SiO_2-CVD) and pre-coking, etc [1,2].

In this work, modification of ZSM-5 acidity and structure was conducted by chemical liquid deposition of silica (SiO_2-CLD) polymethylsiloxane as a modifier and La_2O_3 impregnation. During alkylation of toluene with methanol to xylene over the modified ZSM-5, *para*-xylene selectivity is over 90 %, with 24 % conversion of toluene and a good stability after modification of loading 6.7 wt% SiO_2 and 4.5 wt% La_2O_3. A variety of characterizations, including absorbed pyridine Infrared Spectroscopy (Py-IR), Temperature Programmed Desorption of ammonia (NH_3-TPD), X-ray Diffraction (XRD) and Physical Adsorption and probe-molecule reactions etc, indicate that *para*-xylene selectivity of the modified ZSM-5 grows up with increasing extent of SiO_2-CLD modification due to the passivation of the acidic sites on the external surface. On the contrary, the reactivity decreases with increasing extent of SiO_2-CLD modification, and toluene conversion drops with time on-stream due to coking over ZSM-5. However, the coke deactivation of the modified ZSM-5 may be improved by La_2O_3 modification effectively, as La_2O_3 supported over ZSM-5 reduces the strength of the acidic sites over ZSM-5.

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Preferential CO Oxidation Reaction over Copper-Ceria Catalyst

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Preferential CO oxidation (PrOx) is one of the promising methods for CO removal from hydrogen-rich gas mixtures produced by hydrocarbons conversion processes. Wall coated microchannel catalytic reactors are favorable candidates for PrOx due to high heat and mass transfer rates achieved. The present work aims at a systematic study of the preferential CO oxidation reaction in hydrogen-rich gas mixtures over a 5 wt% Cu/CeO_{2-x} catalyst in a microchannel reactor, in the presence of CO_2 and H_2O, to optimize the reaction conditions to reach CO concentrations below 10 ppm.

Catalytic experiments have been performed that allowed determining the apparent activation energy of the reactions of CO and H_2 oxidation, the reaction orders with respect to O_2 and CO. It was observed that the hydrogen consumption in the absence and in the presence of CO remained the same when the oxygen conversion was incomplete. In other words, the presence of CO does not influence the H_2 oxidation rate in the oxygen excess. Results of numerical modeling of the preferential CO oxidation reaction over Cu/CeO_{2-x} catalysts using estimated kinetic parameters adequately described the observed catalytic dependences and can be used for microchannel reactor design. The active centers of the Cu/CeO_{2-x} catalysts were found to be the two- and three-dimensional copper clusters distributed over the ceria surface. They are situated predominantly on the certain ceria faces. Compared to other transition metals, copper is known by its ability to embed easily into ceria lattice owing to similar ionic radii, thus generating oxygen vacancies and increasing oxygen mobility in the catalyst.

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OP_{10}-I-22

CO Removal from H_2-Rich Gas Mixtures by Temperature Staged Selective Methanation

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Selective CO methanation in the presence of CO_2 is one of the promising methods for CO removal from hydrogen-rich gas mixtures produced by hydrocarbon conversion processes. Compared to preferential CO oxidation reaction, selective CO methanation is a more feasible process as it uses no oxygen (air); the hydrogen-rich gas is not diluted with nitrogen. The concentration of CO_2 considerably exceeds that of CO in hydrogen-rich gas mixtures produced by hydrocarbon reforming processes. Therefore, there is a need for highly selective catalysts that allow CO conversion, but suppress CO_2 methanation.

The present study was performed with the use of 0.3 wt. % Ru/Al_2O_3 and gas mixtures containing up to 2 mol.% CO. It was found that under conditions of selective methanation over isothermal catalyst bed, the required level of <10ppm CO was achieved in a temperature range 240-250°C with low selectivity (<50%). Activation energies and reaction orders of CO and CO_2 methanation were determined. Mathematical model was developed which described adequately the observed kinetic dependencies. The modeling showed that for achieving <10 ppm CO by selective methanation, it is necessary to create a decreasing temperature profile along the catalysts bed, accompanied by increasing CO conversion. The calculation results were proved by experiment in which the catalyst bed was sectioned and the temperature in each section was controlled individually that allowed generation of decreasing temperature profile along the reactor length. In this experiment, almost 100% selectivity and <10 ppm outlet CO concentration were achieved.

Based on the calculated and experimental results, a 10 m^3 H_2/h reactor with counter- and forward-flows of the reaction mixture and cooling agent were designed.

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DeNOx SCR Catalysts – Mechanism of Deactivation and Alternative Alkali Resistant Catalysts

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Introduction

The use of bio-fuels as alternatives to traditional fossil fuels has attracted much attention recent years since bio-fuels belong to a family of renewable types of energy sources and do not contribute to the greenhouse effect. Selective catalytic reduction (SCR) of NO_x with ammonia as reductant is the most efficient method to eliminate NO_x from flue gases in stationary sources via the reaction $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$.

The traditional SCR catalyst suffers significant deactivation with time due to the presence of relative large amounts of potassium in the fly ash from bio-fuels. A possible solution to this problem is use of highly acidic supports, which would interact with potassium stronger than active metal species [1, 2]. Among potential carriers, sulfated zirconia is of high interest because its acidic and textural properties can be modified by varying preparation conditions [3]. Here we present our latest results concerning the mechanism of deactivation by alkali salts and possible alternative alkali-resistant SCR catalysts .

Experimental

Several catalyst formulations are tested and compared, where the method of metal deposition is carried out by incipient wetness impregnation, IWI. The support is also varied from traditional TiO_2 (anatase) to commercial sulfated ZrO_2. The catalysts are finally doped with potassium via the IWI method to obtain a molar K/V ratio of 0.4.

NH_3-SCR is performed with about 10 mg catalyst (fraction 180-300 μm) in 1000 ppm NO, 1100 ppm NH_3, 3.5% O_2 and 2.5% H_2O, balanced to 300 ml/min with N_2.

Results and discussion

As an example of the catalyst resistance towards potassium poisoning, the SCR catalytic activity of 3 wt% V_2O_5/SO_4^{2-}-ZrO_2 as function of temperature is given along with corresponding K-doped sample in Fig. 1. A 3 wt% V_2O_5- 7wt% WO_3/TiO_2 industrial catalyst is used as reference.

The catalyst supported on sulfated zirconia show initial activity comparable to that of the reference catalyst. After doping with potassium, the sulfated catalyst display good resistance towards poisoning, while the reference catalyst deactivates quite significantly.

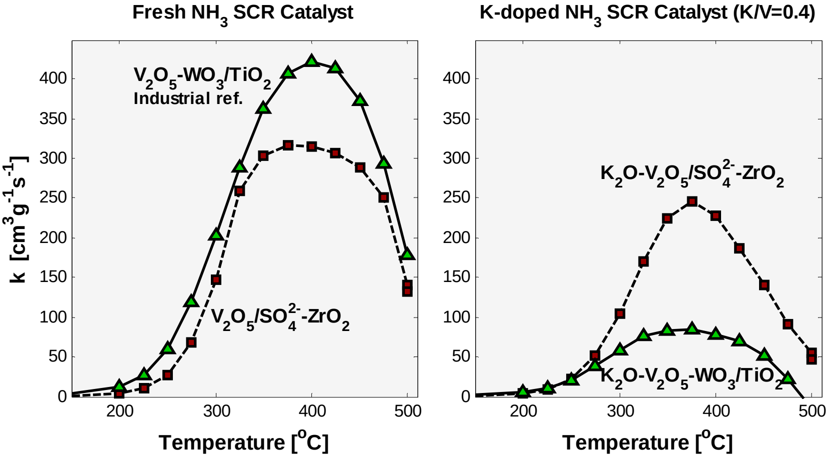

Figure 1. Temperature dependency of the first-order rate constant for the fresh catalysts (left) and the corresponding potassium-doped catalysts (right)

Consequently, SCR catalysts based on sulfated zirconia might be used in power plants utilizing alkali rich biomass, without compromising NO_x emissions due to catalyst deactivation. However, although samples based on sulfated zirconia are much less affected by the poisoning with potassium than traditional catalysts, the deactivation may still possess a problem in long-term use, but their “on stream” lifetime might be significant longer compated to the existing industrial catalyst.

This illustrates the potential of further investigation and optimization of the support material for vanadia-based alkali-resistant SCR catalysts.

Conclusions

Potassium resistance can be altered by optimized with the properties of the support as well as the active sites, presently only to a moderate extent. Hence, potassium resistance remains a key issue for future SCR applications in combination with biomass-based fuels for heat and power generation.

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OP_{10}-I-24

Mechanism of the Reduction of Cu-Zn Mixed Oxide Model Catalyst by Hydrogen

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Cu-Zn (8% at. of Cu) mixed oxide was prepared by decomposition of the corresponding hydroxycarbonate with hydrozincite structure. Similar anion-modified (i.e. containing CO_3^{2-} and OH^- anion admixtures) oxides were studied as models for commercial Cu-Zn-Al catalyst for methanol synthesis by many authors. It was found that reduction of a.m.-$Cu_xZn_{1-x}O$ results in formation of metallic copper particles epitaxially bound to ZnO structure. Exposure of this system to an oxidant results in metallic Cu oxidation and restoration of the initial mixed oxide. In some papers it was supposed that reduction of copper occurs via substitution of protons for copper cations in the defective ZnO structure.

Here, the reduction of a.m.-$Cu_{0.08}Zn_{0.92}O$ was studied by TG-DSC/MS, inelastic neutron scattering (INS), in-situ FTIR/MS at low pressure.

The main findings are the following: 1) kinetics of Cu^{2+} reduction depends a lot on the amount of anionic admixtures, precalcined at 350°C mixed oxide is reduced with E_a = 120-130 kJ/mol, kinetic curves obey Jander law of Cu^{2+} cations diffusion (TG/DSC); 2) precalcined mixed oxide still contains ad-anions; during its reduction, this a.m.-$Cu_{0.08}Zn_{0.92}O$ accumulates significant amount of hydrogen (INS), which form OH^- groups and formates; 3) CO_3^{2-} anions are involved in the reduction process giving gaseous CO_2 and formates on Cu^0 surface (INS, in-situ FTIR); 4) reoxidation of the reduced oxide by O_2 restores the ZnO-like structure (XRD), H-containing species are eliminated from the structure (INS, in-situ FTIR). Basing on these data, the mechanism of $Cu_xZn_{1-x}O$ reduction is discussed.

Different Reaction Mechanisms of Catalytic Wet Peroxide Oxidation over Cu/ZSM-5 Catalysts

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This work is devoted to the investigation of correlation between the structure of the Cu/ZSM-5 active sites and performance of such catalysts as well as their stability to leaching of Cu in the wet peroxide oxidation (CWPO) of different organic pollutants under varied reaction conditions.

The catalyst samples were prepared by different methods: by solid state transformation (SST) and ion exchange (IE) from the protonic form of ZSM-5. The prepared catalysts were characterized by ICP, EPR, XRD, UV-Vis DRS and tested in CWPO of formic acid at pH ca. 3 and organic dyes (*Rhodamine G and Methyl Orange*) at pH ca. 8 using a batch reactor. Essential differences in the catalytic performance were found for CWPO in acid and in subalkali medium. Most active in the formic acid oxidation and stable in acidic media appeared to be catalysts prepared by IE and containing Cu-ions mainly in zeolite channels (as isolated ions and copper-oxide nanoclusters). On the contrary, the SST samples containing CuO nanoparticles showed best catalytic performance in the case of dyes oxidation in subalkali solution. The discrepancy could testify to various reaction mechanisms. Free radical mechanism plausibly works at low pH and Cu-zeolite behaves as Fenton-like catalysts [1]. In alkaline media, a nonradical mechanism demanding presence of two neighbouring Cu-ions is possible [2].

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OP$_{10}$-I-26

Role of Support in the Activity and Selectivity to Nitrogen of Pd-In/Support Catalysts in Reduction of Nitrates

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Nitrates are among the most widespread contaminants of ground and surface waters. The main sources of nitrates are agriculture, plants producing nitrogen compounds and transport. Nitrates are not directly toxic, but they can be transformed into harmful nitrites. Therefore, the removal of nitrates from drinking water is an important and constantly developing field of studies. Catalytic method allows effective removal of nitrates. Supported Pd-In catalysts were not widely investigated, but there is some information in literature about their activity and selectivity in this process [1].

This work presents the studies of activity and selectivity of palladium catalysts promoted with indium and supported on various kinds of carriers in the reduction of nitrate in drinking water. The catalysts containing 5%-wt. of palladium and 0.1÷8%-wt. of indium were prepared from water solutions of $PdNO_3$ and $In(NO_3)_3$ (POCh Gliwice S.A) by aqueous coimpregnation of supports (SiO_2, Al_2O_3, C). 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 was performed for constant initial concentrations of substratum ($C_{0\ NaNO_3} = 1.6\ mmol/dm^3$) in the temperature 293 K.

In addition, the bimetallic Pd-In/Support catalysts were characterized with X-ray diffraction (XRD), Time-of-Flight Secondary Ions Mass Spectrometry (TOF-SIMS), sorption of carbon monoxide and temperature-programmed techniques (TPO, TPR).

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Mechanism of Carbon Dioxide Hydrogenation over Cu-La/Al_2O_3 Catalyst

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Since some natural resources are nonrenewable, the alternative sources and ways for their conversion should be searched. Carbon dioxide is the cheapest and available carbon-based feedstock to be used for the laboratory and industrial syntheses. Creation of the heterogeneous multicomponent catalysts able to activate the CO_2 molecule is one of the prospective ways, which allows synthesizing the various valuable products from carbon dioxide.

In this work, hydrogenation of CO_2 has been studied over the Cu– La/Al_2O_3 catalysts at the various Cu:La ratio.

It has been observed that at T=523 K the CO_2 conversion degree over the Cu–La(1:1)/Al_2O_3 catalyst is 23.8%. Dimethyl ether (DME) in amount of 2.4%, methanol - 84.0% and ethanol -13.6% are produced. Increasing reduction and experiment temperatures to 623 K is accompanied with decreasing CO_2 conversion to 10.9%. Amount of methanol formed is not significantly changed – 84.2%, while the yield of DME is increased to 10.6% and ethanol yield is decreased to 5.2%. The following increase of the temperature up to 773 K leads to increase in CO_2 conversion to 21.1%. Upon these conditions, yield of methanol is 52.0%, ethanol -35.1%, and DME - 12.9%. Besides that water just as carbon oxide and methane in the gas phase is detected.

It has been established that CO_2 conversion and methanol yield depend on ratio of the catalyst composition. At the same conditions (773 K), CO_2 conversion changes in the following order:

Cu– La (9:1)/Al_2O_3<Cu– La (1:1)/Al_2O_3 >Cu– La (1:9)/Al_2O_3

The yield of methanol is 52.0% over the Cu–La(1:1)/Al_2O_3 catalyst. At content of 90 and 10 % of Cu the yield of CH_3OH is lower and is equal to 43.7 and 32.5% respectively.

The electron microscope data show the presence of dispersed and compact areas built of nanoparticles over the catalyst surface. The oxidative forms of copper and lanthanum (CuO, Cu_4O_3, La_2O_3) predominate in initial sample. There are $CuAl_2$ and Al_6Cu_6La – particles too. The spent sample consists of metal particles Al_2La, $CuAl_2$, $AlCu_3$ and oxide particles ($LaAlO_3$, La_2O_3, Cu_2O).

The absorption bands corresponding to linear CO adsorbed on M^{n+} (2190-2160 cm^{-1}) and M^0 – sites (2090, 2040, 2000 cm^{-1}) have been observed by IR study of CO adsorption.

It have been revealed a few adsorption species of hydrogen on the surface of Cu-La/Al_2O_3 catalyst by means of TPD method. They correspond to desorption temperatures T_{des} = 593-623 К, 673-713 К and 673-713 К. The ratio of species and the total quantity of desorbed hydrogen depends on Cu concentration in the bicomponent catalyst. The total quantity of desorbed hydrogen changes in the following sequence:

Cu–La(1:1)/Al_2O_3 (0,271) < Cu–La (9:1)/Al_2O_3 (0,268) <
< Cu–La (1:9)/Al_2O_3 (0,150)

Quantum chemical investigation of suitable models shows possibility of associative and dissociative ($CO_2 \rightarrow CO_{ads} + O_{ads}$) adsorption. This result comes in agreement with IRS-data. At adsorption of $CO_2 + H_2$ at 303-573 К, the following absorption bands have been observed: at 2390-2320 cm^{-1} (CO_{2ads}), 2130 cm^{-1} (M^{n+} CO) and 1600-1250 cm^{-1} (formiate structures).

As a result of comparison of quantum chemical data, experimental data and data available in literature it has been made an assumption that carbon dioxide hydrogenation over Cu– La/Al_2O_3 catalyst proceeds through associatively adsorbed carbon dioxide and oxygenate formation.

Mechanism of Heterogeneously Catalyzed Dehydration of Glycerol over Bifunctional Acidic-Redox Catalysts

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Introduction. Over the last decade, the rapidly increasing production of bio-diesel gives rise to a surplus production and decreasing price of crude glycerol, which has made glycerol as promising low-cost feedstock for the production of fine chemicals [1]. The dehydration or oxidative dehydration of glycerol to produce acroleine or acrylic acid, as an important route for glycerol valorization, could provide a sustainable alternative to the present technology based on C_3-hydrocarbons. Various solid acid catalysts including sulphates, phosphates, zeolites or supported heteropolyacids were tested for the dehydration of glycerol in the gas phase [2-4]. Furthermore, a large amount of by-products (20-45% selectivity) are formed and the catalysts often deactivate rapidly. On the other hand, mixed catalysts containing both acidic and redox active components have a higher long-term stability than merely acidic catalysts. In this investigation, we examine a mechanism of the product formation during the dehydration of glycerol over bifunctional catalysts with acidic and redox activity. Additionally, the deactivation phenomena and the catalytic activity of some supported Al_2O_3-PO_4 doped with oxides of Fe, Cu, Cr, W, Mo or V were studied in the dehydration of glycerol in the presence and absence of oxygen.

Experimental Section. MeO-Al_2O_3-PO_4 catalysts were prepared by a sol-gel and an impregnation method, followed by drying and calcination. All the catalyst precursors, fresh and used catalysts were characterized thoroughly by different analytical techniques such as N_2 sorption, XRD, NH_3-TPD, H_2-TPR, XPS and elemental analysis. The gas phase dehydration of glycerol was carried out at 280°C in a continuously operated fixed-bed reactor.

Results and Discussion. TPD-NH_3 measurements show that MeO-Al_2O_3-PO_4 catalysts have a higher total acid site density than their

MeO-Al_2O_3-analogues. This makes these catalysts appealing for the dehydration reaction demanding higher overall acidity. To study the activity of acidic MeO-Al_2O_3-PO_4 catalysts doped with different metal oxides, model temperature-programmed experiments using DTA methods with MS-detection were carried out. After saturation of the catalyst in 6 vol.% steam of glycerol at 160 °C, the DTA-TG/TPD and DTA-TG/TPO_2 measurements were performed in flowing air and helium at temperatures of 100- 800 °C, respectively. The TG/TPD and TG/TPO_2 experiments provide detailed and fully quantitative information about formation of the dehydration products, i.e., acroleine, acetol, acetaldehyde and water, as well as total oxidations products, i.e., COx, HCOOH, CH_3COOH, after pre-adsorption of glycerol on the catalyst. Fig.1a shows that Al_2O_3-PO_4 catalysts containing W, Mo, Cu possess higher total acidity and are more active towards formation of acroleine. The NH_3-TPD profiles of the used VO_x-, MoO-, CuO- and WO-Al_2O_3-PO_4 catalysts indicate the formation of the “new” and strong Brønsted-acid sites

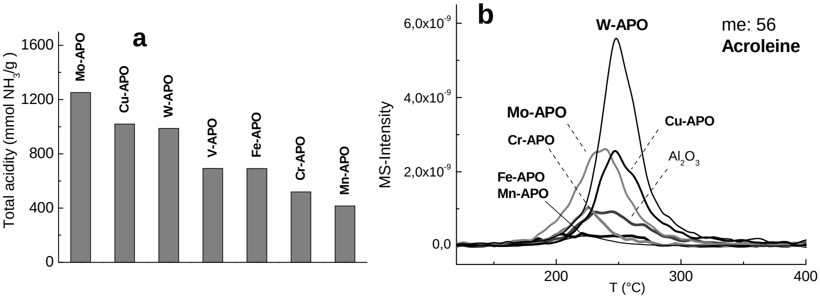

Fig. 1. Total acidity of MeOx-Al_2O_3-PO_4 catalysts (a) and TG/TPD-MS patterns (b) for formation of acroleine over catalysts loaded (saturated) with glycerol steam at 160 °C.

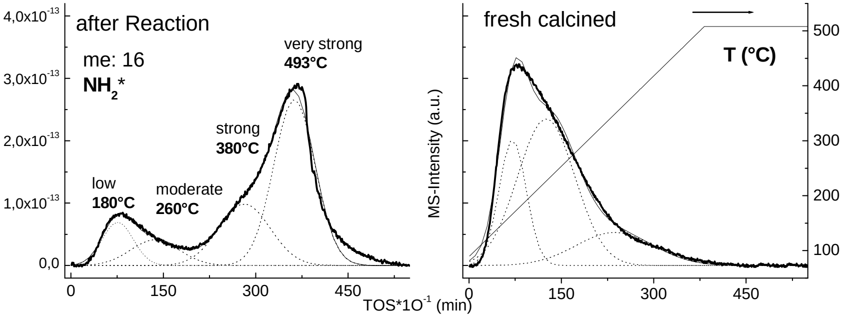

Fig. 2. NH_3-TPD profiles for fresh and used VOx-Al_2O_3-PO_4 catalysts

during dehydration of glycerol in the presence of water (Fig. 2). Consequently, these catalysts exhibit excellent long-term stability over more than 48 h on-stream. The changes in catalyst performance will be discussed in terms of the difference in the acidic properties and the generation of new Brønstedt-acid sites which lead to stable long-term activity and stability of the catalysts. Additionally, it was found that the dehydration reaction is initiated on acidic sites only. The mechanism of the non-oxidative and the oxidative dehydration of glycerol as well as the deactivation phenomena of the catalysts will be discussed.

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OP_{10}-I-29

Elucidation of Pd Species Required for Effective Fatty Acids Deoxygenation of Palmitic and Stearic Acids

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Fatty acids and their esters are potential raw materials for producing green biodiesel. In this work HRTEM, TPR and CO TPD measurements were applied to elucidate Pd species required for efficient fatty acids deoxygenation of palmitic and stearic acids.

1 wt.% Pd/C catalysts with different metal dispersion 18 (A), 47 (B), 65 (C) and 72 (D)% were prepared [1], characterized and tested in selective deoxygenation of stearic and palmitic acid into heptadecane and pentadecane mixture. The catalyst activity decreased as follows: (B)>(C)>(D)>(A). Note that the catalysts C and D with different activity have almost the same particle size (HRTEM and CO chemisorption). TPR analysis of catalyst samples detected several Pd ox-species: at 20-25°C, 70–80°C and 195–240°C. CO TPD data for the fresh and spent catalysts indicate both linear bonded CO at about 80–90°C and bridged one at about 175–200°C which according to [2] are associated respectively with Pd(111) and with sum of Pd(100) and Pd(111) faces. The calculated ratio between Pd(100) to Pd(111) decreases as follows: D (0.33)>C (0.30)>A (0.20) indicating that the higher number of Pd(100) provides the higher catalytic activity of Pd catalyst in fatty acid deoxygenation [3].

Acknowledgements

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Transient Kinetics of Toluene Oxidation in Anaerobic Conditions

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Cyclic reduction and re-oxidation of the catalyst is one of the ways to reach an improved performance in catalytic partial oxidation reactions. The physical basis for it lays in an ability to regulate the ratio between the adsorbed species interacting on the catalyst surface. This operation is industrially used in the DuPont process of butane oxidation to maleic anhydride over a vanadium-phosphorous catalyst [1]. The reason to apply this cycle was to improve the selectivity by a decrease of the concentration of surface oxygen, which is thought to be responsible for total oxidation. The common objectives of the use of periodic operation in catalytic reactors are to provide an increased conversion, selectivity, and reduced deactivation [2]. An important mechanistic information could be extracted from the transient behavior of the reaction after a fast change of the composition of reaction mixture over the catalyst. Modelling of the transient phenomena allows obtaining valuable kinetic constants, which often could not be determined from the steady-state experiments.

The aim of this work is to investigate the step of the interaction of toluene oxidation into benzaldehyde on vanadia/titania catalyst in anaerobic (without presence the oxygen in gas phase) conditions. This step is important for the vapor phase oxidation of toluene, which proceeds through the Mars and Van Krevelen mechanism [3].

The catalyst was prepared via a well-known grafting technique by the vapor deposition of $VOCl_3$ on the surface of TiO_2 (Aldrich). The BET specific surface area was equal to 9 m^2/g, the amount of vanadium was found to be 0.57 wt. % that corresponds to 0.75 of a monolayer (ML) [4]. It is important that this catalyst contained only about a monolayer of the surface vanadia species and did not contain any bulk crystalline V_2O_5.

An experimental set-up used for the transient response study has been described in [5]. The catalyst (1 g) was loaded into a fixed bed reactor of i.d. 6 mm. Before each experiment, the catalyst was pretreated in an oxidative atmosphere (20 vol. % O_2 in Ar) at 673 K for 30 min. Then the flow was switched to Ar and the catalyst was cooled to the reaction temperature. The reaction was carried out with a 2 vol. % toluene/Ar mixture (1 ml/s). The products were analyzed with a quadrupole mass spectrometer and a gas chromatograph .

Two types of transient response techniques were used: response to a step-input and response to a pulse-input. During the step-input experiments interaction of toluene with pre-oxidised catalysts was performed for 20 min. During the pulse-input experiments, the same toluene/Ar mixture contacted with the catalyst shortly for 2.5 s and then the flow was switched back to pure Ar until no gaseous products were observed by the mass-spectrometer. This cycle was repeated several times. The total amount of toluene, which passed the catalyst during the single pulse, was small and corresponded to 0.12 molecule nm^{-2}.

On the base of experimental data the kinetic model of the interaction of toluene with the pre-oxidized catalyst has been developed under assumption that the catalyst surface contains two types of oxygen sites responsible for total and partial oxidation. The model includes 5 steps.

The kinetic constants and activation energies of the kinetic model were determined. The model satisfactorily describes the transient behavior of toluene and reaction products.

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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 ($^1O_2$) chemistry has been an attractive topic of intensive research over the years [1]. Recently a new efficient source of singlet-oxygen generation has been reported: decomposition of dioxiranes catalyzed by anionic nucleophiles, where quantitative yield of $^1O_2$ has been recorded by means of infrared chemiluminescence (IR-CL) [2]. Herein we report on 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 [2, 3]. Kinetics of the reaction has been studied by IR-CL method. Activation parameters of the process were determined. It was shown the catalytic decomposition of the DMD into $^1O_2$ 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.

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OP_{20}-II-1

A Novel Approach in the Study of Activation of Chemical Bonds in Adsorbed Hydrocarbons Resulting from Their Polarization by Active Sites of Acid Catalysts

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The general way of activation of chemical bonds in heterogeneous acid catalysis consists in their polarization by active sites. The reaction coordinates are then represented by vibrational excitation of polarized chemical bands, which can be estimated from increasing intensities of the corresponding IR bands because the intensities depend on the change of the dipole moment during vibration. In our previous works such approach was used for the study of activation of light hydrocarbons on zeolites and oxide catalysts by DRIFT [1-4].

In the present study we present new results devoted to the further development of this new approach for adsorption and catalytic transformation of light hydrocarbons on catalysts. By DRIFT and transmission IR spectroscopy the relative and absolute intensities of small hydrocarbons adsorbed by cation-exchanged zeolites (mordenite and faujasites) were analyzed. The obtained results indicate high absolute intensities of IR bands from polarized chemical bands and anisotropy of polarization of different vibrational modes.

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The Mechanism of NO Activation on Cu-ZSM-5 Catalysts

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Investigation of the electronic state transformation of copper cations in Cu-ZSM-5 during NO, CO and hydrocarbon adsorption are very important for understanding of their high catalytic activity in NO decomposition and deNOx with hydrocarbons [1-3].

Current communication is devoted to DR-UV-Vis study of NO activation on Cu-ZSM-5 catalysts as function of Cu/Al (0.05 – 1.4) and Si/Al (17-45) ratio, catalyst pretreatment, NO pressure and temperature.

Based on the UV-Vis data, the low-temperature NO activation has been supposed to occur with participation of Cu^+ cations of the chain structures through the electron transfer to adsorbed cis-dimer NO. The amount of chemisorbed NO has been found to increase with the growth of the Cu/Al ratio and reach a maximum at Cu/Al ~ 75-100% independent of the Si/Al ratio and pH of the copper acetate solution used for the Cu-ZSM-5 synthesis.

Using DFT method, we examined the interaction of ONNO with molecular cluster $(HO)_3Al$-O-Cu-O-Cu modeling the catalytic active site in Cu-ZSM-5. The calculations showed that the stabilization of the nitric oxide dimer in cis-form is more energy-wise favorable on Cu^+ cation of copper oxide chain than isolated Cu^+ cation [4]. The high calculated electron affinity (E_a = -1.3 eV) of the ONNO dimer and significant strengthening of the N-N bond (N-N≈1.4 Å) in the anion radical confirms the experimental data on the formation of surface anion π-radical on electron donor sites, $[Cu^{2+}\text{-cis-}(N_2O_4)^-]$. The transformation of the latter to transition state having asymmetrical structure results in its low-temperature decomposition and formation of reaction product.

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OP_{20}-II-3

Thiophene Conversion on Acidic Zeolites as Studied by Multi-Technique Microspectroscopy

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An interest in catalytic and adsorption processes for removing sulfur-containing compounds from hydrocarbon streams is driven by stringent environmental specifications for fuels. One of the proposed pathways of removing organosulfur compounds is a selective adsorption using porous solids, in particular, acidic zeolites. A number of studies have addressed the adsorption and surface reactions of thiophene on zeolites; however, no consensus regarding the conversion mechanism has been achieved. Here we present a combined microspectroscopic study [1] of thiophene interaction with H-ZSM-5 zeolite crystals. First, aluminium concentration and acid site strength were mapped with soft X-ray microspectroscopy and synchrotron-based infrared microscopy with probe molecules, respectively. UV-Vis and fluorescence microspectroscopy show that carbocationic thiophene oligomers are formed in the straight channels of ZSM-5. Oligomer chain length varies across the crystals, as was shown previously for the case of styrene [1]. Formation of an intermediate species in which thiophene sulfur is coordinated to two framework oxygen atom is evident from sulfur K-edge XANES spectra. IR spectra indicate that the thiophene ring remain intact during the reaction. Based on the combined data the mechanism of the thiophene conversion on acid zeolites is proposed. This study demonstrates the general applicability of the multi-technique microspectroscopic approach in heterogeneous catalysis.

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Ceria-Zirconia Supported Gold Catalysts for Low Temperature CO Oxidation

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The relation between the physico-chemical properties and the catalytic performance of $Au/Ce_{1-x}Zr_xO_2$ (x = 0, 0.25, 0.5, 0.75, 1) catalysts in CO oxidation reaction has been investigated. Gold was deposited by the direct anionic exchange (DAE) method. Factors influencing the structure and catalytic activity of $Au/Ce_{1-x}Zr_xO_2$ catalysts were discussed. The role of the support in the creation of catalytic performance of supported Au nanoparticles in CO oxidation was significant. A direct correlation between activity and catalysts reducibility was observed. Ceria, which is susceptible to the reduction at the lowest temperature, in the presence of highly dispersed Au nanoparticles, appears to be responsible for the activity of the studied catalysts. The ability to preserve high activity in stoichiometric and lean in O_2 gas mixtures suggests the participation of the support not only in providing centres for oxygen activation but also as a buffer in releasing-uptaking oxygen through redox processes realized by Ce^{4+}/Ce^{3+} redox couple. Moisture contained in the reactant mixture influences the reaction in the significant extent.

The advantages of the catalysts under study suggest the potential possibility of their practical application e.g., in closed-cycle CO_2 lasers, purification of breathing air in closed spaces, safety masks and as a material for gas sensors for detection of trace amounts of CO in air.

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OP$_{20}$-II-5

Application of *in situ* Mössbauer Spectroscopy for the Study of Tin-Modified Pt and Au Catalysts Used in Low Temperature CO Oxidation

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Low temperature CO oxidation over SiO_2 and Al_2O_3 supported Sn-modified Pt and Au catalysts prepared by an organometallic method have been investigated using Thermal Programmed Oxidation technique. In situ ^{119}Sn Mössbauer spectroscopy has been used to follow compositional and structural changes of these catalysts during the catalytic run. All results indicated that the origin of the promoting effect of tin is rather complex.

The results of Mössbauer spectroscopy over SiO_2 and Al_2O_3 supported alloy type Sn-Pt catalysts with different Sn/Pt ratios showed that under condition of CO oxidation the PtSn alloy phases are oxidized and strongly reconstructed. It has been demonstrated that alloy phases are transformed to Sn^{4+} oxide species and PtSn alloys with decreased tin content. The results show that the *in situ* formed, highly mobile *"Sn^{n+}-Pt" ensemble sites* are responsible for high activity.

Analysis of in situ Mössbauer spectra obtained over Au/SnO_x-Al_2O_3 catalysts shows that after activation in H_2 at 350°C all the three oxidation states of tin (Sn^{4+}, Sn^{2+} and Sn^0– in AuSn alloy) coexist. Upon reduction/oxidation cycle, almost 80 % of tin may take part in the reversible interconversions of Sn^{4+} to Sn^{2+} and to AuSn alloy. The activity measurements suggested that the atomic closeness of Au nanoparticles and Sn species may play important role in the activation of O_2. Moreover, results indicate that the high activity can also be attributed to the stabilization of well-dispersed Au particles by surface Sn^{n+} ions.

An *Operando* XPS-MS-GC Study of the Oscillations in the Propane Oxidation over Nickel

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One of the most interesting and unusual phenomena of catalysis is the rate self-oscillations [1,2]. To date, approximately 70 oscillating heterogeneous catalytic systems are known. Although several systems, like oscillations in CO, H_2 and CH_4 oxidation over transition metals have been described extensively in the literature, the origin of these oscillations remain obscure. Here we present first results of an *operando* study of the oscillations in the propane oxidation over Ni in the mbar pressure range. We used time-resolved X-ray photoelectron spectroscopy (XPS) *in situ*, i.e., while oscillations take place, simultaneously with mass-spectrometry (MS) and gas-chromatography (GC) for monitoring gas-phase components. *In situ* XPS is one of the most useful tools to investigate both the surface composition and the nature of adsorbed species. When the *in situ* XPS is coupled with mass-spectrometry or/and GC, it becomes a particularly effective *operando* technique, which makes it possible to correlate the surface properties with the catalytic performance.

The use of this *operando* technique allowed us to show that the main routes during oscillations are total and partial oxidations, while the rate of propane dehydrogenation is negligible. The self-oscillations in the propane oxidation over Ni originate due to the periodic oxidation and reduction of the catalyst surface. The details of the mechanism of oscillations are also discussed.

The work was partly supported by SB RAS (Integration project № 107).

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OP_{20}-II-7

Reductive Dehydration of Alcohols into Aliphatic Hydrocarbons over Nanostructured Polymetallic Catalysts

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Recently it was found the reaction of aliphatic alcohols' C_2-C_5 conversion into alkanes' fraction with number of carbon atoms up to C_{20} over catalytic composition consists of intermetallic hydride $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.36}$ and industrial aluminaplatinum catalyst (AP-64). This reaction was named as Reductive Dehydration of Alcohols[1]:

$$nC_2H_5OH + H_2 \longrightarrow C_{2n}H_{4n+2} + n\,H_2O; \quad n>1$$

The reaction is carried out in inert gas atmosphere, with temperature about 300-400 °C and presser approximately 5 MPa. The yield of aliphatic hydrocarbons was 25-30% and content of isoalkanes was 60 mass. %. But during of reaction the intermetallic hydride loss mechanical stability. This is main reason that impedes practical usage of such catalytical systems.

Catalysts based on γ-alumina oxide and nanostructured metal oxides of II, VI – VIII groups of Mendeleev's table were developed. Heterometallic acetate and alcoxide complexes were used as precursors for catalysts preparation. Over these new original catalysts ethanol converts into aliphatic hydrocarbons fraction up to C_{10}, that mainly contains alkanes and olefines with even number of carbon atoms [2]. It was shown that in the presence of these polymetallic catalysts cross-coupling reaction of carbon skeleton of ethanol and other aliphatic alcohols carrying out intensively. At total conversion of alocohols mix is 85-95% the yield of alkane-olefin fraction C_4 – C_{10+} is 30 -45% contained 50 mass.% of branched hydrocarbons.

It was shown principal ability to regulate selectivity in formation of alkanes and olefins by way active catalytic components change.

It was found that alkanes and olifines can be forming via ethylene and acetaldehyde as intermediates in cross-coupling reaction. In this context hydrocarbons fraction yield depends from technological process organization and considerably rises in circulation mode in compare with flow one of carrying out of catalytic experiments.

It was shown that diethyl ether that forms during parallel etherification reaction is an alternative substrate converts into hydrocarbons.

By using of X-Ray diffraction and molecules-probes thermodesorption it is discussed the relationships between active sites' structure and acidic-base properties of catalytic surface with the selectivity in aliphatic hydrocarbons forming.

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OP_{20}-II-8

Dehydroalkylation of Benzene with Propane and Dehydrogenation of Propane over Me-ReO_x/Al_2O_3 Contacts

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In this report the activity and catalytic role of ReO_x structure in low temperature (453 - 573 K) dehydroalkylation of benzene with propane and dehydrogenation of propane over Me-ReO_x/Al_2O_3, where Me = Pt, Ni or Co are discussed. ESR/GC-MS, including in situ study, DSC, IR-spectroscopy, H-D exchange reaction are used to identify the catalytic active centers and the reaction with their participation. Five kinds of the paramagnetic centers are identified by ESR for Re-Al oxide samples with different oxidative-reductive treatment. The first center is characterized by the superhyperfine structure due to interaction of non-coupled electron with magnetic nucleus $^{185,187}Re$, with a spin I=5/2, belonging to paramagnetic Re^{6+} ions having square -pyramidal structures of local environment and Re=O bond. The second center is observed at sharp freezing of sample subjected to high-temperature evacuation from 773 K to 77 K. Intensive narrow signal with g=2.001 and H=25Gs in EPR spectra measured at 77 K is observed along with a signal from the first center. This center belongs to anion vacancies with an electron. The third center having single signal with $g_{eff.}$=2,02 and H=80 Gs belongs to Re particles. This signal is observed only for samples treated in H_2 atmosphere at 773 K during 5 hours. The fourth signal is observed after adsorption of molecular oxygen at room temperature over the samples pretreated in H_2 at 773 K. This signal belongs to O_2^- ion - radical connected with surface Al^{3+} ion. The fifth centers belong to nitrogen oxides NO and NO_2. NO is observed for reduced and NO_2 for oxidized samples. Absence of appreciable magnetic interaction between the observed centers allows asserting that they are at a distance from each other.

It has been established, that rhenium catalysts, being inactive in reaction of H/D exchange, gains an activity in this reaction after high-temperature evacuation (773 K, 1 hour) and the subsequent interaction with propane at the same temperature. The formation of catalytic active centers of H-D exchange is characterized by the induction period with duration which is determined by duration of high-temperature evacuation. Reaction of H/D exchange on bimetallic samples has shown a presence of synergetic effect caused by interference of active components. Presence of Pt leads to formation of active centers which catalyze the H/D exchange at lower (523 K) temperature. The nature of the active centers of low-temperature H/D exchange reactions and the mechanism of their formation are discussed. It is assumed that the defective structure, formed at high-temperature evacuation of oxide samples precedes formation of catalytic active centers of low-temperature H/D exchange in these reactions. Thus, one may conclude that the centers of low-temperature exchange are a product of high-temperature interaction of hydrocarbon with coordinately non-saturated rhenium ions of lower oxidation state.

Activity of rhenium catalysts essentially depends on duration of preliminary high-temperature evacuation during which an accumulation of coordinately non-saturated rhenium ions in lower oxidation state occurs, high-temperature contact of which with methane results in formation of the centers, catalyzing the low-temperature exchange reaction.

The influence of the presence of the Ni, Co, Pt on reaction ability of ReOx structure is observed. It was shown that the bimetallic catalysts are considerably more active than mono-metallic in these reactions. The reactions of dehydrogenation of propane and dehydroalkylation of benzene are realized at lower temperatures on bimetallic catalysts due to formation of structures such as –O-Pt-O-ReOx after high temperature calcination and $(\text{-O-Pt}^{+}\cup\text{ReO}_3)$ after high temperature evacuation and formation of Pt particles, CHx and ReOx structures after reaction with hydrocarbon. Three types of nanostructured Pt particles are identified and it was shown that reaction ability of the ReO_x species changes dramatically for the systems with different dispersity. The samples with large (> 1,5–2,0 nm) and small (< 1,5–2,0 nm) metal particles have different catalytic activity with respect to H/D exchange reaction. The rate of reaction per Pt atom was the same on the catalysts investigated for particles > 1,5–2,0 nm and considerably lower than the rate of reaction on samples with smaller Pt clusters.

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OP_{20}-II-9

Chlorine Atomic Structures on Ag(111): Low Temperature STM Study and DFT Calculation

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Here, we present for the first-time low temperature (5 K) STM study of Cl/Ag(111) system. We report observation of the new atomic structures. Chlorine adsorption was done at 150 K and 300 K. At initial stage of adsorption we observed decoration of the step edges by chlorine atoms. At further dosing, chlorine atoms occupy the atomic terraces. It is of great interest that chlorine atoms do not form islands with close-packed structure. On the contrary, they are organized in the zig-zag chains, with atoms occupying fcc and hcp sites. Finally, at coverage of 1/3 ML a well ordered structure (√3×√3)R30 is observed in the STM images. Increase of chlorine coverage above 1/3 ML gives rise to compression of the chlorine lattice. On the first stage, compression is local. We observed “stars” surrounded by undisturbed (√3×√3)R30° structure. On the second stage of compression, the “stars” are replaced by the striped domain wall network separating linear domains with (√3×√3)R30° structure (Fig.1). The six-spot diffraction pattern (Fig.1b) directly corresponds to LEED pattern characteristic to the striped domain wall system. The coverage of 0.38 ML is characterized by the complete disappearance of the “stars” and formation of the straight domain-wall lines separated by the average distance ≈ 23 Å. At coverage exceeding 0.38 ML a new structural phase was detected. The nucleation occurs in the form of the small 15-25 Å islands (Fig.1a). Local structure of this phase can be described by the (3×3) unit cell (Fig.1c). As chlorine adsorbed, the new islands of the (3×3) phase appear on the surface. Note, that one can distinguish nine different antiphase domains of the (3×3) structure on the (111) surface. The array of the antiphase domains is known to cause the split of the spots in LEED. In present case, one should observe splitting around (3×3) positions in the reciprocal space. As a whole, the structure appears to be incommensurate with respect to the substrate. That is why the magnitude of splitting measured in LEED pattern can not be simply expressed via the basic vectors of the substrate. The atomic structure of the (3×3) phase has been determined with DFT calculations. Further chlorine dosing leads to formation of small (10-15 Å) clusters on top of the (3×3) phase.

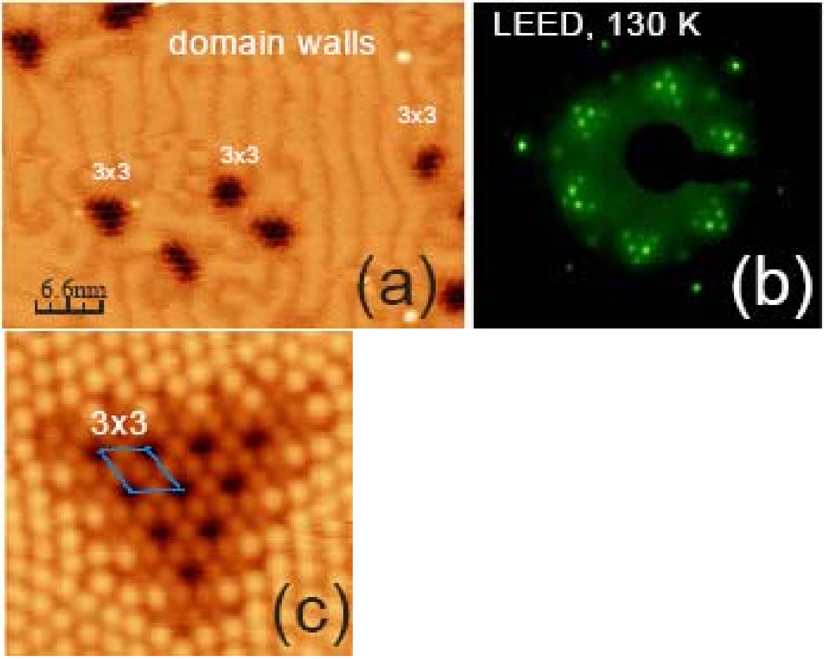

Fig. 1 (a) Co-existence of striped domain walls and (3×3) phase. (b) LEED pattern corresponding to (a), (c) An atomic-resolution STM image of the single (3×3) island. Unit cell is indicated.

OP$_{20}$-II-10

Hydrogen Production by Ethanol Reforming. The Role of Rh-Pd Nanoclusters Anchored to Ceria for the Unusual Catalytic Stability

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H_2 generation using renewable sources, to power fuel cells is receiving considerable attention in search for a sustainable energy-future system. We have developed a catalyst active and stable for the steam reforming of ethanol and water gas shift reaction. The catalyst is composed of nano-clusters of Rh and Pd deposited on CeO_2 nano-particles. Rh is necessary to break the sp^3 C-H of the terminal CH_3 group further facilitating the carbon-carbon bond dissociation. Reasons for the high catalytic activity and stability will be discussed in light of surface and bulk characterization and study of the surface reactions.

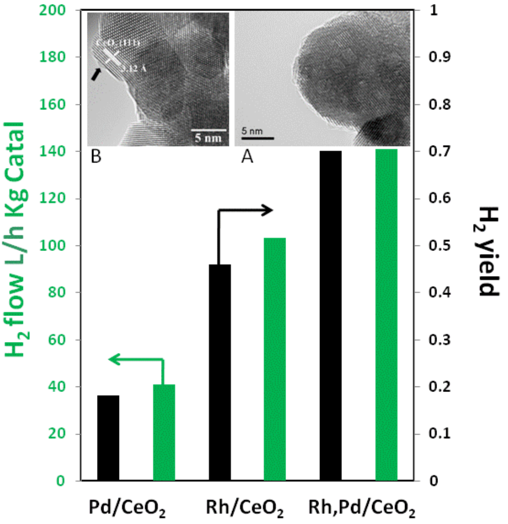

Figure: Catalytic activity and H_2 yield for Rh,Pd/CeO_2 catalyst. *Inset A* (TEM) used catalyst containing large reconstructed regions formed during the initial periods of the reaction. These reconstructions are linked to the process of reduction of the metal cations during the reaction. *Inset B* (HRTEM): presence of very small particles of the transition metals (Rh and/or Pd), with no other particles present.

OP_{20}-II-11

The Thermal Stability and Reducibility of Chromium-Aluminum Catalytic Systems

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Chromium containing catalysts are widely used in many catalytic reactions such as dehydrogenation of hydrocarbon, VOX oxidation, partial oxidation of methane, methanol synthesis and many others. Despite of extensive research efforts the reduction process calls many controversies. Due to this reason we would like to check the reduction behavior of chromia-alumina supported catalysts as well as chromium aluminum binary oxide systems in presence and absence of metallic phase in such systems.

The mono and bi oxide supports were co precipitated from following precursors: $Cr(NO_3)_3\ 9H_2O$ and $Al(NO_3)_3\ 9H_2O$. Samples were dried and calcined in air at 400° C for 4h. The obtained Al_2O_3–Cr_2O_3 support contained Cr and Al in molar ratio from 1:10 up to 10:1 given the chemical formula $Cr_xAl_{2-x}O_3$. The supports were impregnated. Physicochemical properties were determined by: BET, TOF-SIMS, SEM-EDS, and TG-DTA analysis. The reducibility were studied by TPR_{H2} and XRD “in situ” techniques .The main conclusions followed from our work are following:

1. The presence of Cr_2O_5 as intermediate step of CrO_3 reduction was experimentally proved.
2. Reduction of chromia in chromium–aluminum system takes according the scheme : $CrO_3 > Cr_2O_5 > Cr_2O_3$.
3. Presence of metallic phase independently on its kind (Cu, Ni, Ru) causes the significant shift of TPR profile in lower temperature region due to appropriate chromate formation.
4. The formation of metastable CrO oxide during the reduction process in the presence of metal phase was experimentally proved.

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OP_{10}-II-1

Studies of Deactivation-Regeneration Process of Hydrodechlorination Catalysts Using Time-of-Flight Secondary Ion Mass Spectrometry

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One of the most promising methods of the elimination of chlorinated organic compounds is catalytic hydrodechlorination. It allows converting toxic chlorides into the corresponding hydrocarbon molecules without production of other undesirable chemical compounds such as dioxins. The literature data shows that palladium catalyst is the most active in this reaction. However, it undergoes relatively fast deactivation. Therefore, it is necessary to undertake an attempt to work out an effective method of its regeneration.

It appears that time-of-flight secondary ion mass spectrometry (ToF-SIMS) can be very useful technique in such a type of investigations. Owing to the application of ToF-SIMS the changes in the surface composition of the catalyst in deactivation and regeneration steps can be determined. The advantages of this technique result from high sensitivity of secondary ion mass spectrometers, possibility of a detection of not only elemental but also molecular ions and the fact that ToF-SIMS can give information from upper layer of the investigated material.

The aim of this work was to determine the changes in the surface properties of Pd/support catalysts used in hydrodechlorination of CCl_4 during deactivation and regeneration steps. ToF-SIMS results showed that the regeneration (in the O_2/Ar atmosphere) of hydrodechlorination catalysts caused a considerable decrease in the amount of chlorine and Pd-Cl species on the surface of previously deactivated samples. Their concentration was only slightly higher than in the case of as-prepared samples. Of course, this type of treatment made it also possible to uncover Pd active species coated by carbon deposit.

In situ XPS and Mass-Spectrometry Study of Deactivation of Palladium Catalysts in the Propylene Oxidation

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The combustion reaction between C_3H_6 and O_2 (1:1, 1:10, 1:100) on the Pd(110) and Pd(551) single-crystals was studied by in situ XPS and TPR in the mbar pressure range. The main reaction products were CO_2 and H_2O. The activity in propylene oxidation shows the explicit hysteresis: during a heating it significantly increases at 560, 500 and 485 K for $R=P(O_2)/P(C_3H_6)=1, 10, 100$ correspondingly, whereas a quick decrease in the activity was observed at 425 K during the cooling ramp. By using XPS it was found, that the lower activity part of the hysteresis corresponds to formation of a PdC_x phase. This phase forms over the Pd surface due to carbon layer formation and partial carbon dissolution in the subsurface region. This leads to catalyst deactivation in temperature range from 273 K to T_c=560, 500 and 485 K for R=1, 10, 100. During the heating at T_c the carbon clean-off reaction by oxygen proceeds and the O_{ads} appears on the surface. This temperature region is characterized by the highest reaction rate. In the cooling branch from 675 K to 425 K the formation of the surface palladium oxide takes place, which prevents the carbon deposition even at 425 K. It was found that the increasing of the partial P_{O2} leads to decreasing of the reaction rate. This phenomenon is explained by the inhibiting effect of oxygen adsorption and formation of the surface oxide. Thus, we conclude, that the formation of the surface oxide or PdC_x phase results in decreasing of the reaction rate: presence of oxygen-free metal surface, where propylene can adsorb and dissociate, is necessary for high catalytic activity.

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OP_{10}-II-3

In situ FTIR Study of CO and O_2 Interaction with Pd/CeO_2 Catalysts

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Palladium and cerium oxides are the basic components of industrial emission control catalysts playing almost indispensable role in deep oxidation of CO at low temperatures (T<150°C). It was assumed that the activity of these catalysts depends not only on the size and morphology of the metal particles, but also on the chemical nature of metal-oxygen species and synergetic metal-ceria action in catalytic CO oxidation.

The state of active sites of series Pd supported catalysts (with 0.5-5% Pd) on CeO_2 with different quantity of point and structural defects was investigated by FTIR spectroscopy of adsorbed CO, XPS, UV-Vis DO and HRTEM. Two surface phases where palladium in metallic flat clusters and in ionic state (in phase like $Pd_xCeO_{2-\delta}$ contained weakly bonded oxygen) were found in active catalysts.

The temperature programmed reaction with CO or H_2 and *in situ* FTIR spectroscopy of the adsorbed CO and $CO+O_2$ at 77-300 K were used to study the Red-Ox properties of Pd/CeO_2 catalysts. According to FTIRS data the CO and O_2 interact reversibly with active surface of catalysts at 300 K. CO reduces Pd^{x+} sites in $Pd_xCeO_{2-\delta}$ phase with formation of metallic clusters (reaction 1 and 2) while O_2 oxidizes dispersed metal particles with Pd^{2+} sites formation (reaction 3). Simultaneously the interaction of adsorbed CO_2 with OH-groups and weakly bonded oxygen of CeO_2 with accumulation of the surface carbonates and hydrocarbonates occurs. It was established that the Pd concentration and defect structure of support influenced on reducing ability of Pd-oxide species in the presence of CO gas phase. The correlation of the reduction rate of Pd-oxide species and low-temperature activity in CO oxidation was observed.

1. $2Pd^{+} O^{2-} + CO_{ads} \rightarrow Pd^{o} + Pd^{2+} O^{2-} + CO_{2\ ads}$
2. $Pd^{2+}O^{2-} + CO_{ads} \rightarrow Pd^{o} + CO_{2\ ads}$
3. $Pd^{o} + CO_{ads} + O_{2\ ads} \rightarrow CO_{2\ gas} + Pd^{2+}O^{2-}$.

In situ NMR Imaging Study of Heterogeneous Catalytic Reactions

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The occurrence of the heterogeneous catalytic reactions is often characterized by the spatial non-uniformity of various parameters. In order to map this non-uniformity, imaging techniques are necessary.

In the current work NMR imaging was applied to follow *in situ* the progress of an exothermic reaction carried out in a trickle bed reactor at elevated temperatures. The spatial distribution of a liquid phase inside an individual catalyst pellet as well as in a catalyst bed under operating conditions was directly visualized. It was found that the occurrence of the exothermic reaction influences very much the distribution of the liquid phase inside the individual catalyst pellet as well as in the catalyst bed. Moreover, under certain conditions the temporal oscillations of the liquid phase content inside the individual catalyst pellet as well as in the catalyst pellet within the catalyst bed bound with the coupling of the heat and mass transfer processes with a chemical reaction were experimentally observed.

The progress of an exothermic reaction under conditions of the periodical supply of a liquid reagent to the catalyst bed was also studied by NMR imaging. The comparison of the distribution of the liquid phase in the catalyst bed at the continuous and forced time-varying supply of the liquid reagent to the trickle bed reactor was done.

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OP_{10}-II-5

An Influence of Pt and Pd Particles Size on Pairwise H_2 Addition Observed on Various Supports in Catalytic Hydrogenation with the Use of Parahydrogen

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The particles size as well as the nature of the support is one of the parameters, which variations lead to crucial change in activity and selectivity of catalytic processes over a metal supported catalysts. A novel technique which allows one to investigate hydrogenation process over such catalysts is an implication of parahydrogen, which leads to enhancement of NMR signal intensity if reaction occurs with pairwise addition of H_2 molecule to substrate called parahydrogen-induced polarization (PHIP) [1]. In the present work we consider Pt and Pd metal catalysts supported on ZrO_2, TiO_2, SiO_2 and Al_2O_3. The particles size was varied from 12 nm to 1 nm and below. It was found that during the propene hydrogenation over Pd catalysts just Pd/TiO_2 demonstrate appearance of PHIP. These data give us an opportunity to talk about synergism in Pd and TiO_2 action during hydrogenations that lead to facilitation of pairwise H_2 addition to propene. It should be noted that PHIP intensity enhances within the Pd/TiO_2 catalyst series with increasing of the Pd particles size from 0.7 to 11.3 nm. To the contrary Pt metal catalysts demonstrate appearance of PHIP within all considered series and its intensity enhancing with the increase of the metal particles size.

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Parahydrogen Induced Polarization (PHIP) as the Tool for the Studies of Heterogeneous Hydrogenation Reaction Mechanisms

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One of the great areas of using PHIP is detection of intermediates and mechanism of hydrogenation reactions. For homogeneous hydrogenations catalyzed by transition metal complexes in solution, the utilization of the nuclear spin isomers of molecular hydrogen has become an established tool for the studies of reaction mechanisms and kinetics. It has been demonstrated recently [1,2] that the creation and observation of parahydrogen induced polarization can be observed in heterogeneous hydrogenation reactions catalyzed by immobilized as well as supported metal catalyst [3]. These experiments serve as a direct verification of the mechanism of heterogeneous hydrogenation reactions involving heterogeneous catalysts. Moreover, this fact can be used for the production of spin polarized fluids for MRI applications [4] as well as for developing novel research tools for mechanistic and kinetic studies of heterogeneous hydrogenation processes.

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OP_{10}-II-7

Application of the Differential Charging Effect for XPS Identification of Surface Species in NSR Catalysts

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NO_x storage-reduction (NSR) catalysts are used for purification of automobile exhausts from nitrogen oxides. The complex multiphase composition of the NSR catalysts makes it difficult to elucidate the roles of each catalyst component in the mechanism of NO_x abatement, in particular, in identification of surface species produced in the reaction course. This work illustrates how this problem can be tackled by XPS provided that the differential charging of separate phases is applied to study of such complex catalytic systems as the NSR catalysts.

Samples of the model NSR catalysts, $Pt/BaCO_3/Al_2O_3$ and $Pt/BaCO_3/CeO_2$, were prepared as thin films on a tantalum foil. XPS spectra were measured ex-situ, after the reactions of the samples with NO_x ($NO+O_2+H_2O$), SO_x ($SO_2+O_2+H_2O$), or reducing ($CO+H_2O$) gas mixtures in temperature range of 100-450°C. The value of the differential charging for each component was evaluated by the binding energy BE(C1s) from amorphous carbon accumulating by the corresponding component during the spectra measurement.

The NO_x treatment of the catalysts caused formation of surface barium nitrate and oxidation of platinum particles supported both on $BaCO_3$ and Al_2O_3 (CeO_2). Interaction of the $Pt/BaCO_3/CeO_2$ with SO_x produced surface sulfates, $BaSO_4$ and $Ce_2(SO_4)_3$, that gave two S2p lines differing by the apparent $S2p_{3/2}$ binding energy due to a difference in the charge accumulated by parent $BaCO_3$ and CeO_2. This difference in $BE(S2p_{3/2})$ values allowed us to determine temperatures of $Ce_2(SO_4)_3$ and $BaSO_4$ decomposition which were ca. 500°C and 600-700°C, respectively.

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The Study of Co-Based Catalysts Activation under Action of Reaction Media of $NaBH_4$ Hydrolysis

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Cobalt-based catalysts, including cobalt salts, cobalt oxide and lithium cobaltite, have shown the best performance in $NaBH_4$ hydrolysis. It has been suggested that cobalt salts and oxides are being reduced in the $NaBH_4$ reaction media to form catalytically-active cobalt boride phases.

We have studied the activity of cobalt oxides prepared by different methods**.** The catalysts samples before and after $NaBH_4$ hydrolysis have been characterized by spectral methods (FTIR, DRS UV-Vis, Raman), TPR with H_2, XRD, electron microscopy, and magnetic susceptibility method.

Borides Co_xB formed as result of interaction of cobalt compounds with $NaBH_4$ are amorphous so it is difficult to analyze both their composition and formation kinetics. But cobalt oxides and Co_xB differ considerably by their magnetic characteristics. That is why the magnetic susceptibility method can give especially important information.

The obtained results show that there is time delay required for activation of catalytic systems under consideration. It was attributed to a period of time necessary to reduce cobalt oxide by the sodium borohydride solution to form active ferromagnetic phase of cobalt borides. It was shown that the activation time, observed $NaBH_4$ hydrolysis rate were correlated with the Co_3O_4 ability to reduction in reaction media with the formation of cobalt borides. The rate of Co_3O_4 reduction and Co_xB composition depend on physicochemical properties and preparation method of tested cobalt oxide sample.

OP_{10}-II-9

Study of the Reaction of Activated Aluminium with *tert*-C_4H_9Cl

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It is known that aluminium activated by liquid In-Ga eutectic interacts with alkyl chlorides [1]. It is supposed that catalytically active complexes like Lewis acids are formed. They can convert alkanes and alkenes even at room temperatures (20 – 30 °C). The interaction of activated aluminium with liquid *tert*-C_4H_9Cl is accompanied by intensive evolution of gaseous substances, changing in liquid medium composition and formation of resinous substance. The purpose of this work is the ascertainment of generation of $[Al_nCl_{3n+1}]^-$ forms by set of methods: ATR FT-IR *in situ*, NMR-spectroscopy ^{27}Al and qualitative analysis of the reaction products by GC/MS.

The appearance of $[Al_nCl_{3n+1}]^-$ ions (where n = 1, 2) and molecular forms $AlCl_3$ and HCl have been established by ATR FT-IR *in situ* at the interface of the solid activated aluminium – liquid *tert*-C_4H_9Cl.
$AlCl_4^-$ ions in liquid medium have been registered by ^{27}Al NMR-spectroscopy. The presence of branched hydrocarbons $C_8 – C_{12}$ in liquid and resinous substance medium was revealed by GC/MS method.

On the basis of obtained results possible stages of catalytic process have been proposed. Taking into account data of article [2], the following scheme of possible way of the branched alkenes formation has been suggested:

$$Al + 3\textit{tert}\text{-}C_4H_9Cl = 3\textit{iso}\text{-}C_4H_8 + AlCl_3 + 1{,}5H_2;$$

$$AlCl_3 + \textit{tert}\text{-}C_4H_9Cl + \textit{iso}\text{-}C_4H_8 = C_8H_{17}^+AlCl_4^-;$$

$$C_8H_{17}^+AlCl_4^- = C_8H_{16} + AlCl_3 + HCl.$$

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Main Features of Active Palladium Catalysts of Low Temperature CO Oxidation

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In this work the detailed analysis of the active component states of Pd/CeO_2 and $Pd/Ce_{1-x}Zr_xO_2$ catalysts of low temperature (LT) CO oxidation is presented. The wide set of supports and catalysts differed by the preparation procedure, calcination temperature and palladium loading were studied. The catalysts were investigated by complex of physical and kinetic methods: XPS, HRTEM, FTIR, UV-Vis, XRD, light-off, TPR-CO, TPR-H_2.

It was established that main peculiarity of the supported Pd/CeO_2 and $Pd/Ce_{1-x}Zr_xO_2$ catalysts is the absence of Pd metallic and oxide nanoparticles. Palladium is finely dispersed up to atomic level due to chemical interaction Pd-CeO_2 forming two main surface interaction phases (SIP). The interaction of the first type stabilizes palladium as Pd^{2+} ions composed of palladium-oxidized SIP as $Pd_xCe_{1-x}O_{2-\delta}$. The second type of interaction stabilizes palladium as a flat metallic Pd clusters formed due to the epitaxial interaction between palladium (111) and CeO_2 (111) surface facets (palladium-reduced SIP). The formation of the Pd-CeO_2 interacting phases is a key factor of high LT activity in CO oxidation because of appearance of new active sites on the catalysts surface. These sites are characterized by the enhanced Red-Ox properties providing efficient catalysis at low temperatures 300-400 K. Using TPR, FTIR and XPS methods the reduction-oxidation processes of active sites have been investigated in detail. The role of zirconium addition to ceria is discussed to explain the improved catalytic performance of $Pd/Ce_{1-x}Zr_xO_2$ systems.

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OP_{10}-II-11

Structural Aspects of Formation of Catalytically Active Nanoparticles on Surface of Various Supports

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Fine metal and oxide particles supported by various oxides are an important class of catalytic systems. The surface of oxide support can strongly affect the degree of dispersion, structure and catalytic properties of supported nanoparticles. Structural characterization is known to play key role in understanding of catalyst structure-activity relationships. The most interest is in the structure of catalytically active nanoparticles. However, traditional routine XRD methods are usually ineffective for this study. The contribution to XRD pattern originating from small fraction of active component is insignificant in most cases. Moreover, diffraction patterns of highly dispersed materials are characterized by strong background and broadened peaks. Radial distribution function (RDF) of electronic density or atomic pair distribution function (PDF) method is effective for studying the local structure (short range atomic arrangement) of nanoparticles. This method is based on the Fourier relationship between intensity of coherent X-ray scattering and RDF of electronic density [1, 2]. Using this technique, one can directly define interatomic distances and coordination numbers of atomic arrangement. To determine features of the local structure of supported nanoparticles as against well crystallized analogues a comparison of the experimental RDF and the model one constructed on the basis of known structural data is used [3].

In this work we report some examples of the RDF analysis application: 1) to determine the structure of highly dispersed active component in supported catalysts 2) to elucidate structural aspects of interaction between the support and active component.

The $Au(Pt)/\gamma\text{-}Al_2O_3$ catalysts with different metal content were considered. RDF data strongly suggested an epitaxial interaction between supported metal Au and Pt particles and the surface of support. Such interaction may be a reason for high thermal stability of supported metallic nanoparticles.

The Cu/ZrO_2 catalysts with tetragonal (t) and monoclinic (m) zirconia were considered. It was shown that Cu/t-ZrO_2 catalysts contained undetectable by usual XRD analysis highly dispersed copper species. RDF analysis revealed that copper (II) oxide chain clusters and chain network were the main copper species, while particles with CuO bulk structure were not formed significantly. Moreover, the obtained data were in agreement with the incorporation of some copper ions into zirconia lattice. RDF data also suggested interaction of active component with zirconia surface in Cu/m-ZrO_2 catalysts, which efficiently stabilized small CuO particles. The model of epitaxial growth of CuO particles on certain planes of m-ZrO_2 was proposed.

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OP_{10}-II-12

A Novel Experimental and Theoretical Approach to the Adsorbed Species Ascertainment

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The conjugate electron excitation effect developed recently from an extended disappearance potential spectra processing is highlighted [1]. It consists of ordinary substrate core level excitation accompanied by electron transition from the valence state of adsorbed particle to vacuum level. This phenomenon is displayed experimentally as a set of spectral satellites localized by the respective ionization potential above the substrate Fermi level. Altogether 10 satellites of that kind are discovered for 6 different adsorbed species of H, O, N, NH_x, CO, and NO on the Pt(100) single crystal surface. The conjugate electron excitation enables to identify the chemical nature of any adsorbed species which valence state structure is exactly responsible for location and distribution of the respective spectral satellites. In particular, it gives a unique opportunity to control experimentally the presence and location of adsorbed hydrogen atoms. The probable mechanism and peculiarities of this effect indicate that it can be considered as a fundamental phenomenon representing the basic regularity of electron-solid interaction.

Adequate quantum chemical calculations are performed for those adsorbed systems which were studied experimentally. A good agreement between experimental and theoretical data enhances reliability of each other, confirms the correctness of theoretical approach and duly data processing, and provides new information on valence states structure of adsorbed species and substrate plasmon vibrations. Obtained results considered altogether evidence for considerable unity of substrate and adsorbate electronic structures as an essential quality of any adsorbed system.

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Stochastic Model of CO Oxidation Reaction over Pd Supported Nanoparticles: Boudart Reverse Spillover

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The model of oscillatory dynamics of the CO + O_2 reaction over the supported Pd nanoparticle has been studied by means of Monte-Carlo technique. Thereto we combine the usual kinetic Monte-Carlo approach to model the CO oxidation reaction over the Pd(110) single crystal [1] and the stochastic model for the imitating the supported nanoparticle with dynamically changing shape and surface morphology [2]. Furthermore, according to Boudart [3] considering the kinetic features of CO oxidation reaction over Pd/Al_2O_3, it is necessary to take into account the contribution of CO_{ads} diffusion over the support onto the active metal particle surface (spillover) giving the additional source of CO_{ads} flux to the particle through its perimeter. This can manifest as size-dependent reactivity of the supported catalysts [4]. Oxygen can adsorb only on the available centers of the palladium particle, preferably on the terraces.

The dependence of the oscillatory dynamics on the size and surface roughening of the supported particle has been studied. The presence of CO_{ads} spillover determines the character of surface waves over the Pd nanoparticle – oxygen wave propagates from the central region of the particle to the perimeter, and the CO_{ads} reverse wave moves from the perimeter, always enriched by CO_{ads}, to the center of the particle.

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OP_{20}-III-2

Kinetics: The Link between DFT Calculations and Industrial Reactor Design, and Catalyst Discovery

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It is shown how recent developments in computational methods has allowed a detailed elucidation of surface reactions, and how this approach has led to several new concepts that are useful for catalyst discovery and industrial reactor design. This approach is based on linking kinetic modelling with DFT calculations, and it has already led to entirely new catalysts with improved activity and catalysts with improved selectivity.

OP_{20}-III-3

Automatic Techniques of Chemical Mechanisms' Analysis

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Mathematical modeling of complex reacting systems has gained importance in the recent years due to the requirements of economical and efficient use of available resources. The most complicated part of the modeling of such systems is obviously the chemical kinetic model. In order to improve agreement of simulated and experimental results one inevitably has to increase the complexity and the dimension of the mathematical model. In this way, chemical reaction mechanisms become not treatable by conventional analytic methods, moreover, very often even the numerical treatment is limited to academic problems only. Accordingly, the need for automatic numerical methods providing with important properties of the mechanisms and their reduced models, which are simple (low dimensional, less complex etc.), but nevertheless, describe quantitatively the underlying catalytic process, has been constantly increased.

The main purpose of the intended talk is to introduce automatic methods of kinetic mechanism analysis and its reduction with emphasis on application to systems of catalytic reactions. Theoretically, the methods are based on two frameworks: invariant system manifolds which are defined in the state space of the reacting system and on a decomposition of motions [1]. These concepts allow constructing low-dimensional approximations of the detailed model describing the so-called short-, long-term and rate limiting dynamics accurately. Practically, numerical analysis [2] can provide us with the actual number of degrees of freedom of the considered system which can be used to simplify significantly the mechanism of catalytic reactions.

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OP_{20}-III-4

Thermodynamic Analysis of Nanoparticle Size Effect on Catalytic Kinetics

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The impact of nanoparticle size effects on the heterogeneous catalytic kinetics will be discussed accounting for changes in chemical potential upon adsorption [1, 2]. Two-step and Christiansen sequence, as well as Langmuir-Hinshelwood mechanisms were considered, showing that for catalytic reactions over nanoparticles not only the rates, but also reaction orders can be different from those obtained for large nanoclusters. Contrary for nonuniform surfaces kinetic regularities could be the same despite differences in the reaction rates depending on the crystal size.

Theoretical considerations will be presented for selectivity dependence in parallel and consecutive reactions on the nanoparticle size when there are changes in chemical potential with adsorption. Comparison with experimental data for Fischer-Tropsch synthesis by cobalt supported on carbon nanofibers, as well as for crotonaldehyde hydrogenation over gold supported on TiO_2 illustrates applicability of the thermodynamic analysis for the explanation of nanoparticle size effect on kinetics.

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Mechanism of Acrolein Hydrogenation on Silver Catalysts: A Density Functional Study

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Supported silver catalysts exhibit a remarkably high selectivity in the industrially important hydrogenation of α,β-unsaturated aldehydes to produce technologically important unsaturated alcohols [1]. However, many aspects of the reaction mechanism remain to be clarified. The first challenging problem represents hydrogen activation on silver-based catalysts because on clean silver, in contrast to metals of the Pt group, dissociation of H_2 is a highly activated, endothermic process. On the basis of high-level density functional (DF) results for periodic slab models, we suggested that oxygen impurities are involved as active sites for hydrogen activation. Dissociation of molecular hydrogen on various surface/subsurface oxygen species was calculated to be exothermic and characterized by lower activation barriers than on clean silver [2].

Furthermore, with acrolein as a representative reactant, we studied the pathways for the hydrogenation of the C=O and C=C bonds of acrolein on clean silver and various types of oxygenated surfaces [3]. On Ag(110) our results imply propanal, the undesirable saturated alcohol, to be the main product. In contrast, for a O_{sub}/Ag(111) substrate which contains subsurface oxygen centers our calculations suggest a very high selectivity for the corresponding unsaturated alcohol, allyl alcohol, although the activity of this system is lower than that of clean silver. At variance with Pt(111), where the selectivity of the hydrogenation to allyl alcohol is strongly reduced by the hindered desorption of the latter [4], allyl alcohol and propanal products are predicted to desorb easily from both Ag(110) and O_{sub}/Ag(111) at common reaction temperatures.

OP$_{20}$-III-5

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Quantum Chemical Study of $RNiXL_2$ Complexes and Their Catalytic Activity in Radical Reactions

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Nickel-catalyzed organic reactions are now widely developed and quite important in organic and polymer synthesis. Recently it was shown that Ni(0) complexes with organic halides (RX) catalyzes vinyl radical polymerization. The mechanism of formation of radicals in this system is discussed in literature. First, the Ni(0) oxidatively adds to RX to form $RNiL_nX$. The latter is proposed to be catalytically active species for polymerization as well as for coupling reactions.

In this work the possibility of generating radicals from $RNiL_nX$ via homolytic dissociation of Ni-C bond was estimated by quantum chemical calculations. Density functional theory with hybrid functional B3LYP and LanL2DZ basis set is used. Various ligands were examined. These are triphenylphosphine (PPh_3), diphenylphosphinoethane (dppe), diphenylphosphinomethane (dppm), diphenylphosphinopropane (dppp), diphenylphosphinobuthane (dppb), bipyridine (dPy), phenantroline (Phen) also X= Cl, Br, I. Calculations were carried out for aryl (C_6H_5, o-, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$) and alkyl (C_5H_{11}) derivatives.

According to the data obtained the homolytic Ni-C bond dissociation under mild conditions is most preferable for $RNiXL_2$ complex with L = PPh_3 and dppe and unfavorable for that with nitrogen ligands – dPy, Phen. The Ni-C bond dissociation energy increases from $RNiIL_2$ to $RNiBrL_2$ and $RNiClL_2$. Surprisingly it was shown that aryl complexes have weaker Ni-C bond than alkyl complexes. In addition, ortho-substituted aryl complexes were found to be more stable than para-substituted analogues.

Thus, on decomposition, the $RNiXL_2$ complexes may generate radicals initiating vinyl polymerization and other reactions. The generation of radicals proceeds more easily for PPh_3 and dppe ligands.

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OP_{20}-III-7

Interaction of Oxygen with Ag_4 Cluster Supported on Defect Silica Surface: an Embedded Cluster Density Functional Study

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The interaction of molecular and atomic oxygen with the silver cluster Ag_4 adsorbed on a nonbridging oxygen, NBO, a point defect of silica surface has been studied by means of hybrid quantum mechanical/molecular mechanical (QM/MM) embedded method covEPE [1,2] implemented in the package of quantum chemical programs PARAGAUSS [3]. The interaction of the molecular oxygen (O_2) with the surface of silver cluster leads to formation of bridging (Ag-O-O-Ag) and terminal (Ag-O-O) groups and is characterized by weak binding energy ($E_b < 1.0$ eV). Atomic oxygen is tighter bonded with the Ag_4 ($E_b \sim 3.0 – 4.0$ eV) and exists in two- and three-coordinated forms. The interaction of oxygen with the silver cluster leads to transfer of electronic density from metal species onto oxygen atoms that is more significant in case of atomic oxygen. Experimentally observable consequences of the oxygen interaction with adsorbed silver cluster, such as core level shifts, have been calculated and shown to correlate with the binding energy E_b.

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OP_{20}-III-8

Structure and Chemical Activity of Transition Metal and Metal Oxide Catalysts: An Insight from Theoretical DFT Studies

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In this talk, we will present the results of DFT calculations on the selected examples to show the ultimate importance of proper modeling of structure and chemical activity of transition metal and metal oxide catalysts to better understand the experimental findings.

First we consider the formation of oxygen vacancy site on rutile TiO_2(110) and its interaction with molecular oxygen. The experimental TPD observation on triply exceeding concentration of O_2 per vacancy site at low temperature saturation coverage can be well explained without making an assumption on the formation of O_4 particle at the vacancy site if one properly address the mechanism of formation of precursor defect sites on rutile TiO_2(110). Next the mechanism of the selective oxidation of methanol into formaldehyde over vanadia supported on silica and titania catalysts will be discussed. An improper use of cluster models mimicking an intrinsic support structure may result in the failure to explain the experimental findings on selective oxidation of methanol into formaldehyde over these modified oxide catalysts. Finally, an attractive bonding interaction not only for bromine and Pt(111) but also for all the three adsorption modes of NO on the Pt(111) surface will be explained. In agreement with experimental observations, the cluster quantum chemical calculations predict that the first peak in the IR spectra appears at ca. 1515 cm^{-1} at the initial stage of low NO coverage, while it would shift to 1707 cm^{-1} at high NO coverage.

Based on these results obtained, some discrepancies with the results of other theoretical studies in literature will be critically pointed out.

OP_{20}-III-9

Isotope Kinetics and Atomic-Molecular Mechanisms of Polyatomic Molecules Exchange

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The first strict *isotopic-kinetic equations* were derived for exchange of diatomic molecules [1-3] and were effectively applied to study behaviour of dioxygen over oxide catalysts [4. 5]. It must be noted that to derive this equations the redistribution of isotopes was suggested to occur due to the “direct” exchange between diatomic molecules and partner. However it was shown this approach is not applicable to polyatomic molecules.

Kinetics of redistribution of polyatomic isotope molecules is uniquely determined by the type of the molecule A_a reversible fragmentation $A_a = \Sigma\nu_i A_{ai}$ ($\Sigma\nu_i \mathbf{a_i} = \mathbf{a}$) during reactions [6]. The fragments A_{ai} are either individual species or parts of a molecule accepted by other species in elementary acts. At an infinite variety of all possible reaction mechanisms in some chemical system, there is a strictly determined number of the *fragmentation variants (types of mechanism).* They are defined by the vectors of stoichiometric coefficients ν_i enumerated by the methods of combinatorial analysis.

Derived strict isotopic-kinetic equations of polyatomic molecules exchange were applied to study activation of methane and ethylene over various catalysts.

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OP_{20}-III-10

Nonlinear Mechanism of Catalytic Reaction and Active Surface Geometry

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In this work, for the first time, bifurcations and the dynamics of reaction–diffusion systems are numerically and qualitatively studied for four classical geometries of the active surface: plate, sphere, cylinder, and torus. It is shown that the conditions for diffusion instability are essentially dependent on the geometry and local curvature of the surface. The dynamics of emerging dissipative structures − non-steady-state clusters and autowaves on the catalyst surface − is numerically studied.

Numerical analysis and analytical studies demonstrated that the geometry of the surface plays an important role in manifestation of critical phenomena in reaction − diffusion systems. The local curvature of the surface on which there are mass transfer and chemical reactions significantly affects the conditions for loss of stability of spatially uniform steady states. On the real surface with local defects, it is in regions with abruptly changing curvature that dissipative structures and oscillations may emerge. Such defects may act as a sort of nuclei of microclusters and autowaves on the active surface.

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OP_{10}-III-1

A Modeling of Parameters of Heterogeneous Reactions on the Basis of Hypothesis About Mechanism of Interaction of Molecules of Substrate with Catalytic Surface

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For modeling of catalytic reactions it was introduced the notion "framework molecular shape" (FMS) which is a set of coordinates of all carbon atoms in a molecule. One can pick out "external" atoms from this set. External atom is the atom that has flatness, which contains it and all other carbon atoms are placed on one side of this flatness. Geometrical figure that is formed by external atoms was called by the authors the visualization of FMS. We also have called C-C bonds placed on edges of visualization of FMS "external bonds".

The hypothesis formulated in this report is that a carbon atom or C-C bond which takes part in catalytic process on catalyst with flat surface must be external. For modeling of these processes we introduce new parameters into the model. These parameters are accessibility's measures of C-C bonds and C atoms. If an atom or a bond is not external, its accessibility's measure is equal to zero. For external atoms and bonds, they are determined by measure of corporal angle in vertex of visualization of FMS for atoms and measure of angle between its sides for bonds; the more the angle the less accessibility.

Modeling of temperature dependencies of product yields of catalytic processes with participation of hydrocarbons were made using of these accessibilities and some other data (e.g., energies of ionization of radicals). The results obtained correlate with experimental data (e.g., data of cracking of n-butane on Pt-Ga/MFI). Modeling of product yields of hypothetic reactions of n-alkanes was carried out in the case of homolytic breaking of C-C bonds with consequent recombination of radicals formed on the flat catalytic surface.

Migration of Hydrogen Atoms on the Gold Cluster's Surface in the Synthesis of Hydrogen Peroxide

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One of the most important with a view to green chemistry reaction catalyzed by gold nanoparticles is the direct synthesis of hydrogen peroxide [1]. Mechanism of this reaction and the hydrogen atoms migration on the gold catalyst's surface has not been determined yet.To understand the mechanism of catalytic reactions quantum chemical methods are frequently used.

The aim of this work is to investigate catalytic oxidation of hydrogen in the presence of Au_8 model catalyst, as well as the migration of hydrogen on the Au_8 cluster, using quantum chemical methods: density functional theory with PBE functional and gold pseudopotential with relativistic corrections included.

The oxygen adsorption on Au_8 cluster with Au_8-O-O complex formation is the first step in catalytic cycle. Then H_2 molecule adsorb dissociatively on Au_8-O-O complex. The first atom of hydrogen migrates to oxygen with HAu_8-O-OH formation. Migration of the second H-atom passes through 4 steps over HAu_8-O-OH intermediates and lead to hydrogen peroxide adsorbed on Au_8.

The energy barriers were calculated for each step. It was shown that the H-migration on gold cluster deals with low energy barriers (not higher than 85 kJ/mol). Moreover the rate constants were calculated. Obtained data were compared with the alternative mechanisms of H_2O_2 synthesis on model Au_3 and Au_2^- clusters (energy barrriers not higher then 36 kJ/mol and 85 kJ/mol correspondingly). All mechanisms of H_2O_2 synthesis known by the present time include adsorption of oxygen at the first step and adsorption of hydrogen at the second.

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OP$_{10}$-III-3

Thermodynamic Approach to Study Phase-Chemical Transformations at Catalysts Preparing and Operation

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Proposed methodology allows to simulate different stages of catalysts preparation and operation, to take into account thus both chemical and phase transitions – with the quantitative account of synthesis target- and by-products leaving reactionary space (i.e. those, on which the system becomes open), catalysts ageing effects, etc.

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

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

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

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

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

The developed method of the iterative solution for (1)–(3) and the procedures, realizing it, have no restrictions neither on componentity, nor on a nature of researched systems. Required thermodynamic functions of substances are received from the special developed databases.

Realization of the method has allowed correctly and effectively to solve the put problems for various classes of catalytic materials.

EPR Studies of C-, N- and Fe^{3+}-Doped TiO_2 Photocatalysts

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C- and N-doped nano-TiO_2 photocatalysts, prepared through hydrolysis of $TiCl_4$ with tetrabutylammonium hydroxide followed by calcination at 400°C or at 350°C, were active in complete mineralization of 4-chloropheneol [1, 2], and Fe^{3+}-doped systems, prepared using flame spray pyrolysis method, were active in photocatalytic mineralisation of oxalic acid [3], under visible light illumination. The samples were illuminated *in situ* at 298, 77 and 5 K with a 100 W halogen lamp in the spectral range between 400 and 1000 nm, and with a 250 W high-pressure mercury lamp. Bare and doped photocatalysts were investigated with EPR, XRD and FTIR spectroscopy before and after reactions.

In the paper, we will report our recent results on features of C-, N- and Fe-doped TiO_2 under UV and visible light illumination at different wavelengths, in comparison with published data. The nature of paramagnetic centers, their dynamics under illumination, and probable mechanisms of photooxidation will be discussed.

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OP$_{20}$-IV-2

Influence of UV Irradiation on the Abies Wood Oxidative Delignification in the Medium "Acetic Acid-Hydrogen Peroxide-TiO$_2$ Catalyst"

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The present paper describes the influence of powdery TiO$_2$ catalyst and UV pre-treatment of the reaction mixture "abies sawdust-CH$_3$COOH-H$_2$O$_2$-TiO$_2$ catalyst" on the oxidative transformation of lignin polymers at different reaction conditions. Industrially produced TiO$_2$ (GOST 9808-84) with an average particles size near 10 μm, phase composition: rutile 92 %, anatase 8 % and BET surface area 3 m^2/g was used as a catalyst. Delignification was carried out in a metal shaking reactor of 200 cm^3 volume. In order to reduce the diffusion limitation, the high liquid to solid ratio (15-20) was used.

The most pronounced intensification of lignin depolymerisation reactions was observed under combined action of TiO$_2$ catalyst and UV pre-treatment of the reaction mixture. The optimum delignification conditions supplying the complete oxidative degradation of abies wood lignin to dissolved products were selected.

The high delignification activity of acetic acid/hydrogen peroxide mixture may be explained by a formation in this medium of the reactive hydroxyl- and peroxyradicals. As it is known, these radical species can accelerate the oxidative destruction of lignin.

In order to establish the possible mechanism of wood delignification the catalytic activity of powdery TiO$_2$ and dissolved H$_2$SO$_4$ catalysts, the composition of reaction products were compared. The unexpectedly high delignification activity of suspended TiO$_2$ catalyst is related probably with its ability to initiate the formation of active radical species from H$_2$O$_2$. They can diffuse through liquid reaction medium to wood particles, resulting in the oxidative destruction of lignin. UV-irradiation accelerates the generation by TiO$_2$ hydroxyl- and peroxyradicals.

Kinetics and Mechanism of Photoassisted NO Reduction by Carbon Monoxide on TiO_2

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Currently photocatalytic methods to purify indoor air from organic and inorganic pollutants are intensively being developed. In most cases titanium dioxide is used as a photocatalyst under UV irradiation. In this study, a new approach to the sensitization of a bulk TiO_2 photocatalyst to visible light is developed [1]. The method is based on the production of a nonstoichiometric TiO_{2-x} with partially reduced surface layer. Electron-donor centers are formed in the TiO_{2-x} able to absorb visible light and to take part in photocatalysis. It is shown that the photoassisted reduction of NO by CO into N_2 and N_2O can occur on the TiO_{2-x} catalyst upon visible light irradiation at ambient temperature. The selectivity of the NO photoreduction into N_2 reaches 90-95%. The photoreaction is accompanied by intense oxygen isotopic exchange between NO and TiO_2. The photocatalyst demonstrates a stable activity upon admission of successive portions of the CO–NO reaction mixture. A multistep reaction scheme is proposed which allows to self-consistently describe all the experimental findings observed. The NO-CO/TiO_2 system was further studied by FTIR and TPD methods. The spectroscopic data prove the proposed reaction mechanism.

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OP_{20}-IV-4

Multi-Electron Water Oxidation in Photosynthesis and Its Functional Chemical Model

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The life on earth is almost entirely solar-powered. During daylight hours, the sun provides several thousand times more power to the surface of the earth than is produced by all of the electrical power stations. Around 50 % of the radiation that reaches the earth's surface, namely the visible region, is useful to photosynthetic organisms [1]. Photosynthetic organisms convert this radiation into chemical energy, in the form carbohydrate and dioxygen.

The overall equation of oxygenic photosynthesis is given in equation 1, where (CH_2O) represents carbohydrate [1]:

$$CO_2 + 2H_2\mathbf{O} \longrightarrow (CH_2O) + \mathbf{O}_2 + H_2O \qquad (1)$$

The atoms of the produced dioxygen molecule are derived entirely from water, which is oxidatively split into dioxygen and four protons by the water oxidation enzyme in the photosystem II (PS II) of photosynthesis.

Investigation of the functional chemical model of the manganese cofactor (Mn-co) of the water oxidation enzyme, namely sulfuric acid solutions of manganese(IV) sulfate, shows that dioxygen molecules are formatted in the coordination sphere of polynuclear clusters Mn_n with $n = 2$, 4 and 8. In coordination spheres of clusters Mn_n with $n = 6$ and 12 instead of dioxygen molecules of ozone have been generated according to equations:

$$Mn^{IV}_6 + 6\ H_2O = 2\ O_3 + Mn^{II}_6 + 12\ H^+ \qquad (2)$$

$$Mn^{IV}_{12} + 12\ H_2O = 4\ O_3 + Mn^{II}_{12} + 24\ H^+ \qquad (3).$$

Analogous six-electron water oxidation to ozone have been discovered in some seaweeds in extremal conditions (namely, water deficit).

Photostimulated six-electron water oxidation to ozone with functional chemical model (Mn clusters with $n = 6$ and 12 in solutions of sulfuric acid) and photoinduced water oxidation to ozone with red and brown seaweeds have been investigated kinetically. Results are presented on an attempt to gather further information on the six-electron water oxidation with functional chemical models (with other transition metal ion) and new types of natural photosynthetic organisms differing from investigated recently red and brown seaweeds. The data obtained reveal that the six-electron water oxidation to ozone can be realized in the chemical model by irradiation with the light and the water oxidases of red seaweed *Callithamnion corymbosum* and brown seaweed *Cystoseira barbata* in addition to basic process of four-electron water oxidation to dioxygen can oxidize water to ozone by six-electron manner.

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OP_{20}-IV-5

Bistability-Monostability Bifurcations: Method of Detection of Trace Amounts of Enzymatic Reactions Inhibitors

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Catalytic and especially enzymatic reactions are inhibited by an excess of their reactants and products. Such inhibitions means that the rate of enzymatic reaction is non-monotonic function of the reactant concentration. This property allows choose conditions for a continuously stirred tank reactor (CSTR) that the enzymatic reaction occurs in bistable regime. The reactant concentration evolves asymptotically either to a low value stationary state or to a high value stationary state in dependence on initial conditions. Addition of small amounts of inhibitors to the enzymatic reaction in CSTR in the low value stationary state follows in disappearance of this stable state accompanied by large increase of the reactant concentration to the high value stationary state. This effect appears provided that the amount of inhibitor is larger than the critical value. In order to detect the critical amount of an inhibitor it is sufficient to register the large increase of the reactant concentration in CSTR.

The advantages of the method are shown on the example of the acetylcholinestarase (AChE) reaction. AChE is inhibited by an excess of its natural reactant - acetylcholine (ACh) [1] and many inhibitors including organophosphorous compounds which are well known anti-cholinesterase agents. The theoretical calculations based on experimental data [2,3] and the last model for the AChE reaction [4] show that it is possible to detect $10^{-10} – 10^{-13}$ moles of anti-cholinesterase agents.

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Biomimetic Oxidation of Alkanes on Homogeneous Rh, Pd, Pt Catalysts: Design and Feasible Mechanisms

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By analogy with biocatalysts action we used two approaches. The first approach consists in the use of reducing agent (RA) and the second one consists in the lowering of RA unproductive consumption. The most proper RAs for chemical systems are H_2 and CO which should be activated. In proton media for such activation the complexes of Rh, Pd, and Pt are suitable. These complexes are known to activate alkanes. In biological systems the direct interaction of RA and O_2 is impossible. One way to decrease the RA unproductive consumption is the use of ligands which are stable to oxidation, e.g., 2,2'-bipy, 1,10-phen. In this case stabilization of Pd and Pt complexes regarding to redox decay occurs. For O_2 activation and conversion into two-electron oxidant it is necessary to use cocatalysts: I (-I, I), Cu (I, II), Fe (II, III), etc. Mechanistic studies for methane oxidation were reported [1]. C_2-C_4 alkanes were found to oxidize across the C–C bonds as well. Feasible mechanisms are considered.

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OP_{10}-IV-1

Biomimetic Catalysis of Archaic Chemoautotrophic CO_2 Fixation Reactions in Hydrothermal Environments

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Conventional model of archaic chemoautotrophic CO_2 fixation is based on reaction sequences, which are self-organized in a network-autocatalytic cycles along the relaxation pathway for redox couples in nonequilibrium reducing hydrothermal environments [1, 2, 3]. In ancient hydrothermal systems the absence of enzymes of CO_2 fixation process was compensated by transition metals mineral catalytic parageneses, which are biomimetically similar to metal-sulfur clusters of some enzymes of CO_2 fixation contemporary pathways. The parageneses thermodynamic analysis was applied, and a number of Ni, Co, Fe, Cu and Zn containing sulfides are investigated for the promotion of a CO_2 fixation model reaction with relevance to local reducing environments of early Earth.

In the stability area (facies of methane-acetate-succinate) of the CO_2 fixation autocatalytic cycles, at both P_{sat} and T = ~ 400-600 K, and P = 500 bar and T = ~400-700 K parageneses of pyrite-pyrrhotite and millerite-heazlewoodite are stable [4]. Therefore, the possibility of Fe_3O_4, FeS, FeS_2, NiS and Ni_3S_2 participation in catalytic reactions of CAF cycle is justified**.** Moreover, in this hydrothermal conditions, both pure greigite (Fe_3S_4) and its nickel form (Fe_5NiS_8) are stable, being the analogue of a CO - dehydrogenase catalytic cluster (Fe_4NiS_5), which effectively binds and reductively activates carbon dioxide.

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Biocatalysis of Theophylline Oxidation by Microbial Theophylline Oxidase in the Presence of Non-Physiological Electron Acceptors

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Microbial theophylline oxidase (ThOx) is a redox enzyme catalyzing 8-hydroxylation of theophylline to form 1,3-dimethyluric acid. In this work, ThOx is characterized as a fragile heme-containing protein complex composed of several non-covalently bound dynamic domains with molecular weights of around 60 and 210 kDa, and capable of formation of 1.5 MDa assemblies as well. The rate of the reaction of theophylline oxidation by ThOx with non-physiological electron acceptor ferricyanide is 0.17 s^{-1}, thus approaching that with cytochrome *c*, 0.33 s^{-1}. The apparent catalytic constant depends on the electron acceptor concentration. At concentrations lower than 0.2 mM the biocatalysis does not fit the Michaelis-Menten scheme, and some non-catalytic processes dominate in the overall reaction. Kinetics of ThOx catalysis is also studied at electrodes modified by self-assembled monolayers (SAM) of hydroxyl- and amine-terminated alkanethiols. Different composition of the SAM provides different orientations of ThOx on these layers. Depending on the orientation of ThOx onto the SAM-modified electrodes, the heterogeneous electron transfer (ET) constant, k_s, characteristic of the ET reaction between the electrodes and the heme of ThOx ($E^{o/}$ of 87 mV (NHE)) is 0.4 s^{-1} and 3.2 s^{-1}. Only the low-ET-rate orientation appears to be productive for the electrocatalytic function of ThOx, thus implying the reaction rates similar to those with ferricyanide and cytochrome *c*. Along with this, the apparent efficiency of ThOx bioelectrocatalysis in the absence of mediators is substantially lower than that mediated by ferricyanide or cytochrome *c*. This lower efficiency is consistent with a correspondingly lower amount of ThOx being in direct ET contact with the electrodes and thus involved in electrocatalysis.

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OP_{10}-IV-3

Metallocene Catalysis in Photopolymerization of Vinyl Monomers

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Much attention has recently been paid to studying metallocene catalysis of the radical polymerization processes. The vast majority of papers therewith deal with substance-initiated polymerization. Photoinitiated processes have been scarcely studied. At the same time, in the absence of a real initiator, specific features of “metal complex” polymerization systems, such as termination-free polymerization, can be directly observed. Availability of metallocenes considerably accelerates photopolymerization of vinyl monomers, which is due to ability of metallocenes, when exposed to UV light, to transform from the singlet to the excited triplet state, and to sensitize photochemical reactions. The polymerization rate increase and the start of the manifestation of the gel effect depend on the nature of the metallocene used. The most significant specific feature of photopolymerization of vinyl monomers in the presence of metallocenes is the long-term postpolymerization effect observed by us. Short-term UV irradiation (5 min) in the presence of metallocenes leads to nearly complete consumption of the monomer to form a glassy polymer mass. Under the same conditions but without metallocene, the reaction is rapidly terminated. The nature of metallocene affects the postpolymerization rate. In addition, the polymer obtained by photoinitiated postpolymerization in the presence of metallocenes is able to initiate polymerization of a new portion of the monomer. All these facts are evidence of the formation of living radical active sites of polymerization in the photoinitiated process. Since the “living” active sites are not consumed during the process, their concentration in the polymerization system increases stepwise in subsequent UV irradiation events. Correspondingly, the polymerization rate in subsequent periods of “dark” postpolymerization also increases. We think that the energy received during photoinitiation is sufficient for excitation of metallocene molecules and formation of complex radical sites between the metallocene and primary radical. As it was previously assumed complex bound sites do not enter into quadratic chain termination reactions due to steric hindrances. Assumptions made are confirmed by quantum-chemical calculations of the interaction reaction heat between the model polystyrene radical $CH_3–CH_2–\bullet CHPh$ and ferrocene resulting in a complex [1]. Thus, this paper originally demonstrates manifestation of long-term effect of vinyl monomer postpolymerization in the presence of metallocenes under short-term UV-irradiation, which is due to appearance of the “living” complex-bound radical sites of chain growth.

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OP_{10}-IV-4

Use of Photocatalyst Against Mold Fungi

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To the beginning of the twenty first century the mankind has realized, what danger represent mold fungi for people health and for buildings and constructions. At the same time now it is impossible to apply hard biocides, which has significant effect on environment. Therefore application of soft biocides, operating by a photocatalysts principle, is a vital topic. A number of so-called 'photosenses', including phthalocyanines, are soft biocides. The interesting additive is detonation nanodiamond (DND). The mechanism of action of DND is not clear till now. The problems of uniform distribution and immobilization of photocatalysts in volume of protected objects arise, when it is necessary to use the catalysts for a long time. Sol-gel technology can be used to these purposes [1]. The hybrid organic-inorganic coatings prepared from sols on the basis of tetraethoxysilane and epoxy resins, containing small additives of lutetium diphthalocyanine sulfonated – SO_3-$LuPc_2$ and DND, successfully protect glass and marble surfaces from a number of the most aggressive mold fungi. Biocide substances in the nanosized state are distributed in all volume of coatings due to epoxy-silicate matrix formation.

Here results of laboratory and field tests of the nanosized epoxy-silicate coatings doped by the above-stated additives are presented. Hypotheses concerning the mechanism of action of DND as photocatalyst substance are put forward.

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Au-Containing TiO_2-SiO_2 Photocatalysts for Water Purification

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Semiconductor photocatalysis is a dynamic field that plays an important role in modern catalytic research. Numerous attempts to improve the photocatalytic performance of titania have included, among other methods, modification by noble metals. Most of such investigation has been focused on Pt/TiO_2 and Pd/TiO_2 systems, but the studies of Au/TiO_2 system are very limited [1].

In our work UV-active TiO_2-SiO_2 photocatalysts were successfully prepared by immobilization of titania nanoparticles on the surface of SiO_2 aerogel. The amount of TiO_2 was varied from 3 to 15% wt. Nano-sized gold particles (1 % wt.) were deposited on TiO_2-SiO_2 photocatalyst surface by the deposition precipitation method to increase photoactivity in destruction of methylene blue.

Catalytic systems were characterized by X-ray diffraction, transition electron microscopy, IR-spectroscopy, ultraviolet-visible method (UV-method). Using XRD it was shown that 99,9% of TiO_2 phase prepared was amorphous, and the average size of TiO_2 and Au nanoparticles are 9-10 nm. The photocatalytic activity of synthesized catalysts was compared with the one of commercial Degussa P25 catalyst under similar conditions. According to experimental results the photocatalytic activity of unmodified TiO_2-SiO_2 was higher. It was shown that the photoactivity of TiO_2-SiO_2 systems modified by Au nanoparticles was more effective in comparison with the catalysts mentioned above under UV and visible light illumination. We have proposed that higher activity is determined by homogeneous distribution of Au nanoparticles on the TiO_2 surface. The modification by gold leads to deacrease in electron-hole recombination as well as efficient charge separation.

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OP_{10}-IV-6

Photocatalytic Degradation of Ethylene over Novel TiO_2 Nanoparticles Photocatalyst: Effect of Calcination and Reaction Temperatures

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Photocatalytic oxidation of volatile organic compounds is an effective and desirable technique for reducing the concentrations of pollutants at low concentrations [1]. In this investigation, photocatlytic oxidation of ethylene (a naturally occurring gas produced by plant tissues, engine exhausts, and plant and fungi metabolism) has been investigated at different temperatures in our new fabricated photocatalytic system with pyrex glass reactor, by using sol-gel method [2] synthesized novel TiO_2 nanoparticles. The results were compared with combustion method synthesized and commercially purchased TiO_2. Photodegradation activity of novel TiO_2 is much higher than of the other samples. Effect of calcination temperatures on the activity is being investigated deeply.

Characterization of the catalysts was obtained by using X-ray diffraction; nitrogen adsorption-desorbtion; scanning electron microscope; and UV-vis diffuse reflectance spectra. Raman spectroscopy and Fourier transform infrared spectroscopy characterization are in process to understand the reaction mechanism and structural changes.

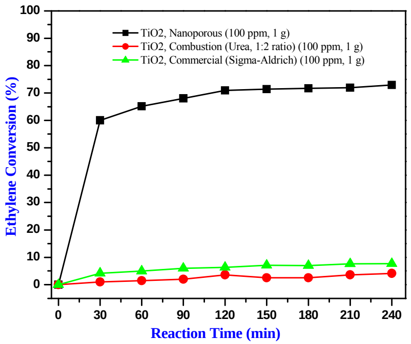

Fig. Comparison of photocatlytic activity of TiO_2 samples

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OP-YS-1

Mechanistic Study of Biomimetic Non-Heme Iron Catalysts for Selective Oxidation: Chemical and EPR Evidence for an Oxoiron(V) Active Species

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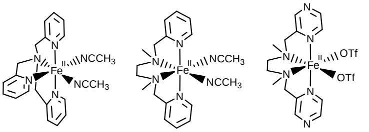
The selective oxidation of organic molecules is fundamentally important to life and immensely useful in industry. Highly effective and selective biologically inspired hydrocarbon oxidation catalysts hold great promise for wide-ranging synthetic applications. Iron complexes with aminopyridine ligands **1** and **2** (Scheme 1) are the best iron-based bio-inspired olefin epoxidation catalysts with H_2O_2 and CH_3CO_3H as oxidants. The epoxidation has been proposed to be conducted by oxoiron(V) intermediate $[(L)Fe^{V}{=}O(S)]^{3+}$, where L = TPA or BPMEN, S = CH_3CN. [1] However, oxoiron(V) intermediates have never been observed in the catalytic systems **1**-**2**/H_2O_2(CH_3CO_3H).

We have succeeded in the EPR detection of new very unstable intermediates in the catalytic systems **1**-**3**/*m*-chloroperoxybenzoic acid(CH_3CO_3H). On the basis of EPR and reactivity studies these intermediates were assigned to oxoiron(V) species $[(TPA)Fe^{V}{=}O(S)]^{3+}$, $[(BPMEN)Fe^{V}{=}O(S)]^{3+}$, and $[(BPZMEN)Fe^{V}{=}O(S)]^{3+}$ [2]. The first two intermediates are highly active towards cyclohexene epoxidation even at −70 °C, whereas the activity of the third one is much lower. In this work we demonstrate that the catalysts based on **1** and **2** give notably higher epoxide yield, than those based on **3**. Interestingly, the catalytic systems based on structurally similar to **1** complexes **4** and **5** convert cyclohexene to cyclohexene oxide only with a few percent yield, and no oxoiron(V) species form in these systems.

The obtained EPR and catalytic results reveal oxoiron(V) intermediates to be most likely active species of selective olefin epoxidation in non-heme iron-based catalyic systems.



$[(TPA)Fe^{II}(CH_3CN)_2]^{2+}$ **1** $[(BPMEN)Fe^{II}(CH_3CN)_2]^{2+}$ **2** $[(BPZMEN)Fe^{II}(OTf)_2]$ **3**

Scheme 1. Structures of complexes studied.

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OP-YS-2

Mechanism of Sulfides Oxidation with H_2O_2 Catalyzed by Zinc(II) Compounds

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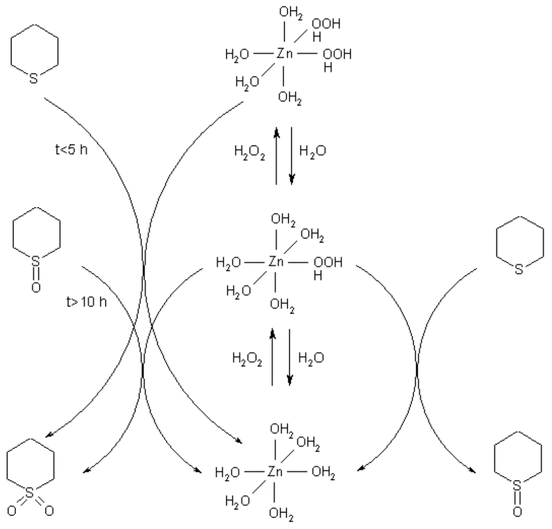
The selective oxidation of sulfides to sulfoxides is an attractive and important transformation in organic chemistry. Various reagents were used as oxygen source for this purpose, although most of these reagents are not satisfactory for medium to large scale synthesis due to the formation of environmentally unfavorable by-products, the low efficiency, and high cost. The use of ‘green oxidants’ like hydrogen peroxide is very attractive, since this oxidant is readily available, inexpensive and environmentally benign with formation of water as the only by-product. Recently, it has been shown that zinc compounds is an effective catalyst for oxidation of alkyl aryl sulfides in the presence of hydrogen peroxide.



In this paper, we report mechanism for the oxidation of sulfide to the corresponding sulfoxide with H_2O_2 in the presence of $Zn(NO_3)_2{\cdot}6H_2O$. The mechanism of sulfoxidation reaction was studied in details using tetrahydrothiopyran (derivatives of this sulfide are contained in crude oil) as the reagent. The observed kinetics can be consistently explained by the proposed catalytic cycle including the activation of H_2O_2 by coordination to Zn(II) ions.

Investigation of the Catalytic Activity and Size Effect in Hydrocarbons and CO Oxidation over PdO/γ-Al_2O_3 Catalysts by Accurate Differential Method

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The catalytic activity is usually evaluated in terms of conversion normalized to quantitative catalyst characteristic such as weight, number of active sites etc. However this is an inaccurate approach because of non-proportionality between these values. The specific reaction rate is only dependent on temperature and component concentrations, so it can be used as the accurate measure of catalytic activity. The reaction rate measurements are most precise when carried out under differential conditions. Moreover the use of accurate differential method for reaction rate measurements and catalytic activity studying allows to found out such interesting effects as structural sensitivity of some catalytic reactions. The turnover frequency (TOF) as a function of particle size of active component is the main criterion of structure sensitivity of reactions. The size sensitivity of some reactions over catalysts is of great interest in heterogeneous catalysis.

The catalytic deep oxidation of hydrocarbons and CO attracts great attention due to the economic and ecological reasons. Many catalysts have been investigated for their activity in these processes and supported palladium catalysts have been reported to show the high activity. The data on size sensitivity of the considered oxidation processes over Pd – containing catalysts are still controversial in literature.

In this work, the dependence of methane, propane and CO oxidation turnover frequencies on PdO average particle size was studied over PdO/γ-Al_2O_3 catalysts. Our goal was to define accurately catalytic activity of catalysts and obtain more information on the size sensitivity of these processes by means of modern flow-recirculation method, providing the gradientless mode in a laboratory reactor [1]. A series of 1 wt % PdO/γ-Al_2O_3 catalysts with a narrow size distribution of PdO particle were tested at large oxygen excess.

The comparative activities of the PdO/Al_2O_3 catalysts with PdO particles different in size showed that all the reactions of methane, propane and CO deep oxidation are strongly size-sensitive. The catalytic activity was found to depend on the PdO particle size. TOF value increased linearly with an increase in the average PdO particle size. The observed linear TOF growth resulted from a minor decrease in the reaction rate normalized to the catalyst weight as the PdO particle increased in size. It should be noted that a similar TOF dependence on PdO particle size was only observed in methane oxidation over PdO supported on ZrO_2 [2].

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OP-YS-4

Selective Oxidation of Glucose on Pd-Au/Support Catalysts

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Using renewable row materials is easily justified by increasing economical and environmental pressures on chemical industry. In particular, carbohydrates like glucose and lactose are indicated as good substratums for future chemo-catalytic processes. New compounds of interesting properties can be obtained as a result of those reactions. One of such products is gluconic acid used in food and pharmaceutical industry and also as a biodegradable chelating agent.

The catalytic reactions of oxidation of glucose are usually carried out in solution using oxygen or air as an oxidation agent in the presence of supported noble metals (Pt, Pd). However, the selectivity of those monometallic catalysts, for example supported Pd, is not higher than 60%. In order to improve the selectivity and reduce the deactivation of palladium catalysts their modification with heavy metals is suggested. We noticed that selectivity of supported palladium catalysts could be improved by an addition of bismuth and thallium [1-3].

In this oral presentation we would like to present an influence of gold addition on the activity and selectivity of palladium catalysts supported on various carriers in the reaction of the oxidation of glucose to gluconic acids. Moreover, the physicochemical properties of bimetallic systems were determined using X-ray diffraction studies, secondary mass ion spectrometry (SIMS – TOF) and temperature-programmed technique (TPO and TPD).

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OP-YS-5

Hydrogenation and Isomerization of α-/β-pinenes on Carbon Supported 8 Group Metals

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The key compounds for manufacture of a broad variety of fragrances and pharmaceuticals are α- and β-pinenes produced from cheap and ecologically safe turpentine oil [1]. Promising way for turpentine oil processing is hydrogenation over 8 group metals [2]. During catalytic α- and β-pinene mixture hydrogenation some different processes take place: double bond migration, the hydrogenation of double bond to *cis*- and *trans*-pinane, and hydrogenolysis of carbon-carbon bond to *p*-menthadienes. An intensity of a side products formation depends on the nature of the catalyst used (Pd, Pt, Ru, Rh, Ir) and the reaction conditions [3].

The aim of the present work is to study the kinetic regularities of competitive α-pinene hydrogenation and isomerization over Pd/C, Ru/C, Rh/C, Pt/C and Ir/C catalysts.

The liquid phase α-/β-pinene hydrogenation were carried out over Pd/C, Rh/C, Ru/C, Pt/C and Ir/C catalysts at $293 \leq T \leq 423$ K and at hydrogen pressure in the range 0.5 - 11 bar using *n*-octane as a solvent. The effects of the catalyst amount, stirring rate, α-/β-pinene concentrations, temperature and hydrogen pressure on reaction rates were investigated. The tentative reaction scheme of α- and β-pinene isomerization and hydrogenation was proposed for the kinetic modeling. The hydrogenation and isomerization rate constants as well as activation energy of α-/β-pinene isomerization and hydrogenation for all applied catalysts were estimated. A good agreement between the calculated kinetic curves and the experimental data was obtained.

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Influence of Acidity and Hydrogenation Activity of Bifunctional Pt/SO_4^{2-}-ZrO_2-Al_2O_3 Catalyst on Benzene and Heptane Hydroisomerization

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Hydroisomerization of benzene containing fractions is one of the ways to reduce benzene level in gasoline. Both metal and acid sites are required for these reactions. Traditional skeletal isomerization catalyst Pt/SO_4^{2-}-ZrO_2 (Pt/SZ) does not suit in this case because of high acidity and depressed hydrogenation activity. Side reactions such as alkanes cracking and naphthenes ring opening readily take place on strong acidic sites. Hydrogenation activity is not enough to eliminate benzene totally. The aim of this work is to modify metal-acid properties of Pt/SZ by alumina and to study how these properties affect the activity, selectivity and reaction pathways during benzene and heptane hydroisomerization.

Alumina content in studied samples was varied from 0 up to 100 wt%. Pt content in all samples was 0.3 wt%. It is shown by H_2 chemisorption, benzene hydrogenation, IR-spectroscopy with pyridine and CO as probe molecules and n-heptane isomerization/cracking that Al_2O_3 strongly affects both acidic properties and hydrogenation activity of Pt/SZ. The number of Bronsted acid sites and strong and medium Lewis acid sites was found to decline as alumina was incorporated into the catalyst. It is explained by dilution effect. At the same time Pt chemisorption capacity, expressed in H/Pt ratio and benzene hydrogenation activity increases with alumina content growth. It is provided by increase of content of Pt, which is located on Al_2O_3 and does not affected by sulfur. It was found, that for benzene-heptane hydroisomerization catalyst with 67.5 wt% Al_2O_3 content has optimal relation between acid and metal functions.

Based on obtained results hydroisomerization reaction pathways are discussed.

OP-YS-7

EPR Study oF Vanadium Species Formed upon Interaction of V(V) and V(IV) Pro-Catalysts with $AlEt_3$ and $AlEt_2Cl$

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Despite the ongoing interest in the synthesis of new vanadium polymerization catalysts, little is known about the reaction mechanism. We present here the results of our EPR spectroscopic studies of the vanadium species formed upon interaction of vanadium pro-catalysts **1-3** (**1** is a bis(phenoxyimine) vanadium(IV) complex with bulky substituents in phenolic and anilinic rings, **2** and **3** are vanadium(V) complexes of N and C-capped trisphenolate tripodal ligands) with $AlEt_3$ and $AlEt_2Cl$ in the presence and in the absence of re-activator ethyltrichloroacetate (ETA) [1]. It was shown that the increase of V(IV) species concentration in the active catalyst systems correlates with their ethylene polymerization activity. Therefore, the active intermediates of olefin polymerization contain vanadium in +4 oxidation state. On the basis of EPR spectroscopic data, we propose the structures of V(IV) and V(II) compounds formed upon the above pro-catalysts activation with organoaluminum co-catalysts. Complexes of the type $LV^{IV}(O)(Et)(AlEt_2Cl)$ (L = phenoxyimine ligand) formed in the catalyst system **1**/$AlEt_2Cl$ can be precursors of the active species of olefin polymerization. Complexes of the type $L_1V^{IV}(Et)(AlEt_2Cl)$ (where L_1 is the initial N or C-capped tris(phenolate) ligand, modified by the reaction with $AlEt_2Cl$) can be precursors of the active species of olefin polymerization of the catalyst systems **2**(**3**)/$AlEt_2Cl$.

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OP-YS-8

Influence of Oxygen Mobility in La-Sr-Mn-O Mixed Oxides on Their Activity in Methane Combustion and High Temperature N_2O Decomposition

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Mixed oxides of general formula $LaBO_3$ (B = Mn, Co, Fe) constitute a broad class of materials including catalysts for many high temperature oxidative processes. Substitutions of foreign M^{2+} (M = Sr, Ca, Ba) cations for La may give rise to either the change of oxidation state of transition metal or the formation of anion defects in the packing of oxygen atoms, thus affecting lattice oxygen mobility. The main object of this study was to get dipper insight into the mechanism of oxygen transfer in the $La_{1-x}Sr_xMnO_3$ ($x = 0 \div 0.5$) lattice and to find possible relationships between oxygen mobility and catalytic activity in the reactions of methane combustion and nitrous oxide decomposition.

The catalysts were prepared by Pechini route, characterized by XRD, XPS and differential dissolution phase analysis, and tested in a plug-flow reactor at 900 °C. Oxygen mobility was analyzed by SSITKA.

The mechanism of oxygen exchange in perovskites at high temperature was elucidated. By numerical analysis of isotope responses it was found that introduction of Sr gave rise to the appearance of the new pathway of faster oxygen exchange in the bulk of the solid caused by creation of oxygen vacancies. The highest values of both the content of fast-exchangeable oxygen and the coefficient of oxygen diffusion were found for multiphase sample, which can be due to the presence on the surface of the particles of the layer-structured K_2NiF_4-type phase - $LaSrMnO_4$ with high concentration of oxygen vacancies. Strong correlation between oxygen mobility and catalytic activity both in the reactions of methane combustion and nitrous oxide decomposition was observed. For the last reaction pathways of oxygen insertion into the reaction products were examined by means of oxygen exchange experiments in the reaction conditions.

OP-YS-9

Mechanisms of Selective Catalytic Oxidation and Hydrogenation Using Polymer-Stabilized Metal Nanoparticles

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Mechanisms of two reactions, which are of fundamental as well as industrial importance, were investigated in this study: Lindlar-type hydrogenation of acetylenic alcohols (dehydrolinalool in particular) and selective direct oxidation of monosaccharides (i.e. D-glucose).

The following types of polymers were chosen as the stabilizers of catalytically active metal nanoparticles: (i) micelles of amphiphilic block-copolymers, (ii) ultra thin polyelectrolyte layers deposited on inert support, (iii) solid hypercrosslinked polymeric matrix.

Kinetic investigations and data of physicochemical analyses allowed us assuming the hypotheses of the reactions mechanisms. In the case of selective hydrogenation over Pd-containing polymeric catalysts the existence of two kinds of active centers (metallic and organometallic) was proposed for all the catalysts with the exception of bimetallic PdAu, which had only one type of active centers and competitive sorption of hydrogen and substrate. Thus for most of the catalysts the mechanism similar to Langmuir-Hinshelwood was proposed.

In the case of catalytic oxidation for all the investigated Pd-, Pt- and Ru-containing catalysts mixed valence structure of catalytically active sites was revealed, which allowed us assuming the mechanism similar to oxidation-reduction mechanism of Mars-van Krevelen, when lattice oxygen is responsible for catalytic activity and selectivity.

NO Reduction by Hydrogen (D_2) over Pd(110)

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The NO, D_2 adsorption and $NO_{ads} + D_{ads}$ reaction was investigated on the Pd(110) surface by means of TDS, TPR and molecular beam technique. It was shown that the reaction has an “explosive” desorption of products (N_2, N_2O and D_2O) as narrow synchronous peaks at $T \sim 480 \div 490$ K. By analysis of TPR spectra for different $NO_{ads} + D_{ads}$ coverages, we suggest an autocatalytic reaction of the “explosive” nature. ND_3 desorption was not observed.

The hysteresis phenomenon in the rate of $NO + D_2$ reaction was established at a constant partial pressure of reactants. Cooling branch of hysteresis at $T \sim 450 \div 500$ K is characterized by the high catalytic activity in D_2O and ND_3 formation unlike N_2O. No hysteresis phenomenon in the rate of N_2 formation was observed. It was shown that N_2 and ND_3 evolving at $450 \div 550$ K is determined by competitive reaction routes depending on the partial pressure ratios D_2/NO (R) in the reaction mixture. N_2 selective formation is preferred for $R < 10$, whereas at $R > 40$ the reaction is characterized by intensive formation of D_2O and ND_3 molecules. In the $NO + D_2$ reaction the availability of a vacant site near the NO_{ads} and N_{ads} may play a central role in the selectivity towards N_2O and N_2. The key role of NO dissociation as the rate-limiting step of $NO + D_2$ reaction has been demonstrated. The mechanism of N_2O and NH_3 formation over Pd(110) in the $NO + D_2$ reaction has been studied by means of molecular beam. According to the proposed model the reaction $D_{ads} + N_{ads}$ (ND_3 take-off $\sim 80^0$ to surface) proceeds on the active centers located between atomic rows of the metal surface, while the reaction $NO_{ads} + N_{ads}$ (N_2O take-off $\sim 30^0$ to surface) proceeds over the side planes of these rows.

Acknowledgements: The study was supported by the RFBR Grants # 08-03-00454 and # 08-03-00825.

OP-YS-11

NO Decomposition at Stepped Faces of Gold Single Crystal and Model Gold Supported Catalysts

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Catalytic activity of gold is studied for about twenty years [1]. Yet, the nature of high specific activity of gold nanoparticles has not been explained up to now. At this moment many reactions of industrial importance catalyzed by gold are reported. The majority researchers consider that gold particles of nanosize are active in catalysis and support acts as stabilizer only [2].

In our work we investigated the state of active component and NO interaction with flat and stepped faces of Au single crystal and gold supported catalysts by X-Ray photoelectron spectroscopy (XPS) in the temperature range 300 K – 500 K and NO pressure up to 100 Pa. Using physical vapor deposition gold particles were deposited at the thin alumina film formed on the surface of NiAl(111) single crystal.

It has been shown that Au(111) face is inactive in NO adsorption. NO adsorption and dissociation occur only at the stepped face of gold single crystal at the temperatures over 320 K and NO pressure of 5 Pa and higher. NO adsorption at the gold particles deposited on alumina film goes readily at $P(NO) = 10^{-4}$ Pa. XPS study reveals two state of nitrogen on the surface of model gold supported catalysts - atomic nitrogen characterized by N1s binding energy of 399.8 eV and N_2O particles characterized by N1s binding energy of 403.5 eV. Size effect on the catalytic activity of the supported gold catalysts within adsorption and decomposition of nitric oxide has been observed. The samples with smaller gold particles are more active in N_2 formation and N_2O decomposition than the samples with larger ones.

The authors appreciate 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)

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OP-YS-12

XPS Investigation of Palladium, Oxygen and Cerium States on Pd/CeO_2 Catalysts Surface during Temperature Programmed Reaction with CO

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Investigation of active sites in Pd-ceria catalysts is of great interest for understanding of synergetic Me-oxide action in catalytic CO oxidation. In this work the combination of temperature programmed reaction with CO (TPR-CO) and X-ray photoelectron spectroscopy (XPS) methods was used to study the active sites states and Red-Ox properties of Pd/CeO_2 catalysts.

It was established that calcined Pd/CeO_2 catalysts are characterized by strong interaction of ionic palladium Pd^{2+} with support with formation of surface interaction phase (SIP) like $Pd_xCeO_{2-\delta}$. The Red-Ox properties of this surface phase were examined during TPR experiments using step-by-step reduction by CO. The initial step of reduction begins at low enough temperature around 300 K determining the reaction ignition. This step is accompanied by partial decomposition of $Pd_xCeO_{2-\delta}$ phase and formation of small metallic palladium clusters. The subsequent step of CO interaction with oxygen of subsurface CeO_2 layers proceeds at low temperatures 300-370 K through the formed palladium clusters. Oxygen composed of $Pd_xCeO_{2-\delta}$ phase possesses a very high mobility. Heating up to 370-450 K results in metallic palladium clusters enlargement with SIP conservation. Then the reduction process of Pd/CeO_2 catalysts at temperatures more than 450 K can be characterized by the reaction of CO with the support oxygen diffused from bulk to the surface of Pd particles.

XPS shows that all steps of the catalysts reduction result in strong change of oxygen and cerium states. The correlation of the states of the residual oxygen (XPS) with amount of oxygen removed from the samples (TPR-CO) is discussed in this work.

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XPS Study of CO Interaction with Nanostructured CuO Film Obtained by RF Activation of Oxygen

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Copper oxides are widely used as an active component of catalysts for oxidation reactions. In the case of CO oxidation copper oxides are usually active at the temperature higher than 450-500 K. Synthesis of catalysts describable of high low-temperature activity (LTA) is very important. LTA can be achieved by the formation of weakly-bound high-reactive oxygen states. It is proposed, that these oxygen states can appear in the samples due to the transition from large copper oxide particles to the nanosized particles with different geometry [1].

In the present work the nanostructured copper oxide CuO film was studied. This film can be obtained on the surface of copper foil by oxidation at the room temperature using RF activation of oxygen in gas phase [2].

The interaction of CuO nanoparticles with carbon monoxide was studied by ***in situ*** XPS. It was established that CuO nanoparticles interact with CO at low temperatures T<400 K. Using step by step titration the full spectral data accumulation was made during the reaction. Analysis of Cu2p and O1s lines was performed using curve fitting procedure by Gauss-Lorenz doublet and individual components, respectively. On the basis of this spectroscopic treatment the kinetic curves of CO interaction with oxygen of CuO and Cu_2O structures were build. From these kinetic curves the reaction probability of oxygen in the nanostructured oxide CuO was calculated. At the initial step of interaction with CO the reaction probability was found to be $\chi{\sim}10^{-4}$, while during the reaction it decreased down to $\chi{\sim}10^{-8}$. It was shown, that high reaction probability of CuO nanoparticles at low temperatures is related to the presence of overstoichiometric oxygen in the CuO lattice.

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OP-YS-14

Low-Temperature CO Oxidation over Co Catalysts

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The elimination of CO at low-temperature is very important in the environment pollution control. Due to high prices and scarce of noble metal, attention has been given to search an alternative catalytic component to reduce using of noble metal. Transition metal oxides are very good substitute catalysts because of their low price. Among them, cobalt oxide catalysts have focused attention because of their high catalytic activity for CO oxidation.

In the present work the influence of Ru and ZrO_2 addition to cobalt supported catalysis has been studied. As a conventional supports of cobalt catalysis were used SiO_2, Al_2O_3, TiO_2. Also zirconia modified supports were studied. The supported cobalt catalysts were prepared by wet impregnation method. The samples were examined in CO oxidation test using a fixed bed quartz microreactor under standard conditions. Typically, CO (3% in He) and O_2 (6% in He) were mixed and fed to the reactor at a controlled feed rate (usually 80 cm^3/min) using mass flow controllers, passed through the catalyst bed (0.10 g). Moreover surface species formed in the oxidation of CO on cobalt supported catalysts were studied by DRIFTS method.

Conclusion:

- The activity of 10%Co and 10%Co-0.5%Ru/support (SiO_2, Al_2O_3, TiO_2 and 8.5%ZrO_2 modified bi-oxide supports) catalysts is as follows: $SiO_2 > TiO_2 > Al_2O_3$. The similar results were observed for zirconia modified supported Co catalysts.
- The addition of ruthenium to cobalt supported catalysts improve the catalytic activity of all samples especially for mono- and bi-oxides silica and titania supported catalysts.
- The activity of Co and Co-Ru catalysts was higher for bi-oxides than mono-oxides supports.

XPS Investigation of Metallic and Oxidized Silver Nanoparticles Obtained by Plasma Sputtering

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Silver nanoparticles are extensively studied because of their application in numerous fields such as catalysis, medicine, optics, material science etc. Investigations of the oxidized silver clusters show that new oxygen species can be formed when the particle size decreases. Nature of silver-oxygen bond in these species differs from oxygen in the silver oxides. Therefore development of methods for synthesis of the oxidized silver nanoparticles and study of their physical and chemical properties are of great importance.

The main goal of the presented work was to investigate by photoelectron spectroscopy the metallic and oxidized silver nanoparticles obtained by plasma sputtering of the silver in oxygen and/or argon atmosphere. Application of this method gave us opportunity to study the evolution of silver and oxygen states of the oxidized nanoparticles with increasing their size or plasma sputtering time.

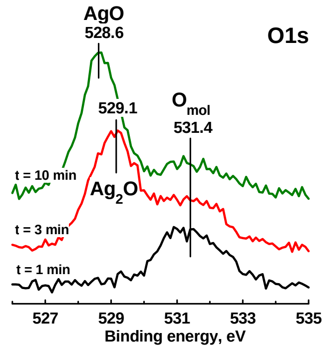

Fig.1. O1s spectra of oxidized silver nanoparticles depending on plasma sputtering time.

It was shown that formation of the particles less then 5 nm leads to stabilization of the oxygen with molecular properties. Increase of the plasma sputtering time results in successive formation of the silver oxides at first Ag_2O and then AgO (fig. 1). Thermal stability and oxygen reactivity of the oxidized silver nanoparticles towards carbon monoxide and ethylene were investigated in this work.

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OP-YS-16

Theoretical Study of Chrome (III) and Manganese (II) Sulfate-Bridged Binuclear Aqua-Complexes

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Salts of variable valence metals are often applied as catalysts in the reactions of liquid-phase oxidation of organic and inorganic compounds by ozone.

Ozonation of chrome (III) salts proceeds with a high rate in acid solution only in the presence of catalysts such as salts of variable valence metals, in particular manganese (II).

We suppose that the ozone oxidation of variable valence metals proceeds with formation of sulfate-bridged binuclear aqua-complexes in water solutions of sulfuric acid. In particular for chrome (III) and manganese (II) aqua-complexes:

$$Cr^{3+}(H_2O)_6 + Mn^{2+}(H_2O)_6 \xrightarrow{H_2SO_4} (H_2O)_5Cr^{3+}-SO_4^{2-}-Mn^{2+}(H_2O)_5 + 2H_2O + 2H^+$$

Substitution of water molecule to ozone in the coordination sphere of manganese helps to oxidation of Mn (II) to Mn (III) in ozone-containing binuclear aqua-complex with further dissociation to molecular oxygen and oxidation intermediate:

$$(H_2O)_5Cr^{3+}-SO_4^{2-}-Mn^{2+}(H_2O)_5 \xrightarrow{O_3,(-H_2O)} (H_2O)_5Cr^{3+}-SO_4^{2-}-Mn^{2+}(H_2O)_4-OOO \rightarrow$$

$$\rightarrow (H_2O)_5Cr^{3+}-SO_4^{2-}-Mn^{3+}(H_2O)_4-O^- + O_2\uparrow$$

All molecular structures and electronic parameters have been calculated by functional density quantum-chemical method DFT/B3LYP using the LANL2DZ basis sets.

Stabilization of sulfate-bridged binuclear aqua-complexes was proposed in sulfuric-acid solutions. The electronic and spin densities of chrome (III) and manganese (II) sulfate-bridged binuclear aqua-complexes were analyzed in comparison with the same set of ozone-containing complexes. So, the possibility of oxidation of manganese (II) in manganese (III) has been shown in the coordination sphere of ozone-containing binuclear aqua-complex.

Stochastic Model of the Equilibrium Shape of the Supported Nanoparticles at Different Temperatures

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As a model of the catalytic metal particle we shall consider the Kossel crystal or, more exactly, the SOS model [1, 2] located on a neutral support. The rigid support surface is represented by a square lattice with periodic boundary conditions. The initial active particle consist of the finite number of elementary cells (metal atoms) situated in the columns of the cubic lattice. The surface morphology of the particle is defined by distribution of heights of the metal atom columns. The particle surface morphology is changed due to the thermal diffusion of the surface atoms (Metropolis algorithm [3] has been used).

At the intermediate range of temperatures (T = 500 K) the surface of the particle is flat enough but the corners and edges are partly rounded. The surface of the metal particle becomes extremely rough at the hemispherical shape (T = 900 K). After the reduction of the temperature the particle shape returns to the initial equilibrium characteristic for the given temperature. The beginning of the dispersal of metal particle over the support surface is located between T = 900÷1100 K. The radius of the dispersal remains unchanged during the process of the equilibration. At high temperatures we can observe two competitive processes – dispersion and the coalescence of closely situated particles at high temperatures (Ostwald ripening) when radii of the dispersal overlap (see in detail [4]). Size distribution of many particles after the increase and the following reduction of the temperature is determined by the procedure of cooling (stepwise or gradual cooling).

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OP-YS-18

Kinetic and Theoretical Study of Asymmetric Hydrogenation of M-Acrylate by Rh (I)/(R, R)-Me-BPE

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The choice of an efficient chiral ligand and a transition metal is determining for the success of catalytic asymmetric hydrogenations processes. However the enantioselectivity is influenced by many other parameters among which the hydrogen pressure, i.e. the actual hydrogen concentration, is a significant example. Recent studies have pointed this effect to be rather general for rhodium based catalysts [1, 2]. In order to identify the origin of enantioselectivity, i.e. the enantiodetermining step(s), and to gain some further understanding on the structure-enantioselectivity relationship, the determination of the kinetic constants is required. We have thus embarked a project aiming at such determination by coupling experimental work and theoretical chemistry.

In a first step, a catalytic system has been identified (***1***), which presents two opposite effects with hydrogen pressure depending on the substrate: a beneficial effect with M-acrylate (MAA) and a detrimental effect with Z-emap (***Fig. 1***).

In order to predict the enantiomeric excess using the rate equations, two studies were undertaken on the asymmetric hydrogenation of both substrates by the Rh (I)/ (R, R)-Me-bpe catalyst. The experimental work, along with a theoretical study on the reaction pathway using GAUSSIAN03 etc…, should lead to the estimation of the constants rates of each elementary stage based on the kinetic model suggested by Halpern [3]. A discussion on the possible enatiodetermining steps with respect to the nature of the substrates will be presented.

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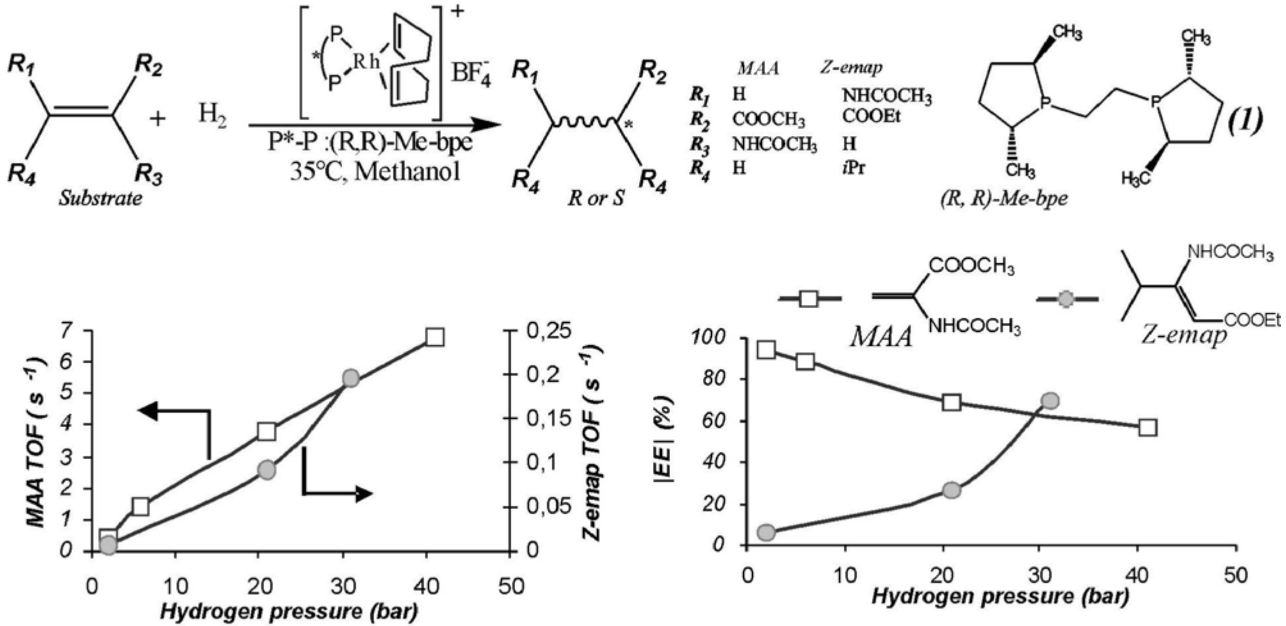

***Figure 1** : Pressure dependency of EE and TOF in the asymmetric hydrogenation of MAA and Z-emap catalysed by the cationic rhodium complex [((R,R)-Me-bpe)Rh(COD)]$^{+}$BF4^{-} .*
Conditions: [MAA]=0.1M, [Z-emap]=0.1 M, [Rh]=10^{-3}-10^{-4}M, L/Rh=1.05, 35°C.

In situ Study of H_2 Addition in Hydrogenation Reaction over Immobilized Wilkinson's Catalyst by Implication of Parahydrogen-Induced Polarization

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Parahydrogen-induced polarization (PHIP) allows one to get information about short-lived intermediates of hydrogenation reaction and possible ways of hydrogen molecule addition due to significant enhancement of signal intensity and its characteristic line forms in ^{1}H-NMR spectra. Since the necessary condition of PHIP observation is pairwise addition of both atoms of one hydrogen molecule to one substrate molecule it has found extensive application only in investigations of homogeneous hydrogenation reactions. Recently, it was shown that for immobilized catalysts, which are combining properties of homogeneous and heterogeneous hydrogenation catalysts PHIP is also observable, and therefore pairwise H_2 addition takes place [1]. The main goal of the present work is a study of stereospecificity of H_2 addition in hydrogenation reaction over immobilized Wilkinson's catalyst by use of PHIP. With this method the H_2 addition stereospecifity can be determined by a presence of polarized ^{1}H NMR signals, which stand for cis- or trans- routes of the addition. It has been found that hydrogenation reaction over synthesized Wilkinson's catalyst immobilized on 2-diphenylphosphinoethyl-functionalized silica gel occur stereospecifically by the route of cis-addition like as it is for homogeneous hydrogenation over Wilkinson's catalyst. Therefore, we can conclude that hydrogenation reaction mechanisms are similar for these catalysts.

We are grateful for a support of the present work by grants from the RFBR (08-03-00661, 08-03-91102, 08-03-00539, 07-03-12147), SB RAS integration grants (67, 88), program of support of leading scientific schools (NSh-3604.2008.3), RAS (5.1.1), CRDF (RUC1-2915-NO07).

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Catalytic Conversion of Hydroxycarboxylic Acid Esters over Silica-Supported Copper: Hydrogenation of Butyl Lactate at Low Hydrogen Pressure

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Ecologically friendly process of propylene glycol production from bio-derived lactic acid is of great interest today. However it is well known that catalytic hydrogenation of carboxylic acid to corresponding alcohols is very difficult and expensive process. For example, the hydrogenation of lactic acid to propylene glycol over Ru-containing catalyst was carried out at 145 bar and 423 K to reach a noticeable lactic acid conversion and selectivity to propylene glycol [1]. According to [2] silica-supported copper is promising catalyst to convert lactic acid carboxylic group to 1,2-propanediol hydroxyl one at low hydrogen pressure, but efficiency of this catalysts is still low.

The hydrogenation of corresponding esters is usually performed in milder conditions. The goal of the present work is to study catalytic behaviour of silica-supported copper catalyst in vapour phase hydrogenation of butyl lactate in order to develop high selective catalytic process of propylene glycol synthesis in mild reaction conditions. On the basis of kinetic data obtained, the tentative scheme of butyl lactate transformation is proposed. The hydrogenolysis of initial substrate leads to formation of n-butanol and 2-hydroxypropanal. The latter is hydrogenated to desired propylene glycol. Formation of the main byproduct, 1-hydroxyacetone, is caused by the equilibrium between the ketone and diol at the associated hydrogen partial pressure.

OP-YS-20

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OP-YS-22

Preparation and Characterization of Ag-Deposited TiO_2 Modified by Ionising Irradiation

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The modifications of TiO_2 by addition of silver provide an interesting way to increase the efficiency of a photocatalytic process [1]. The aim of this work was the modification of TiO_2 with silver in order to enhance photocatalytic degradation of surfactant, sodium dodecylbenzenesulfonate, (SDBS), in aqueous solutions. The catalysts (1%Ag/TiO_2) were prepared by wet impregnation, and irradiated with electron beam from the linear accelerator or γ-rays. The catalysts were characterized by: BET, XRD, TOF-SIMS and TPR methods. The activities of all prepared catalysts were examined by photocatalytic oxidation of SDBS aqueous solutions under medium-pressure Hg-lamp. The reaction run was monitored by TOC (total organic carbon) and COD (chemical oxygen demand) measurements. Reductions of TOC and COD in the range 40–80% were observed depending on catalysts preparation and photo-oxidation processes conditions. The enhancement of photocatalytic oxidation of SDBS on 1%Ag/TiO_2 irradiated with total dose equal to 200 kGy in comparison to SDBS photodegradation with unmodified TiO_2 was observed.

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OP-YS-23

Catalytic Oxidation of Natural Products in Phase-Transfer Conditions

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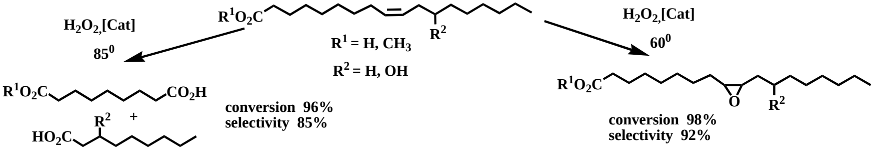
Oxidation in the presence of bifunctional catalytic systems possessing the properties of metal complex and phase-transfer catalysts is the promising method for functionalization of labile natural compounds. By now possibilities of the utilization of products of wood-chemical industry in the producing of valuable chemicals have been far from being exhausted. This method allows producing of various important chemicals in mild conditions with good yields using the wide spectrum of plant raw materials as starting compounds.

Investigations of oxidation of different types of unsaturated natural products have been carried out. Various factors having the influence on the yields of products in the reactions of the oxidation with 30% hydrogen peroxide aqueous solution in the presence of the system based on the tetrakis(oxodiperoxotungsto)phosphate(3-) in combination with quaternary ammonium cations have been studied.



As a result the efficient methods of oxidative functionalization of fatty acids obtained from nonedible natural raw material have been developed. These acids were used for epoxide and mono- and dicarbonic acids synthesis with yields up to 90%. The above mentioned catalytic systems were applied to the mild-conditions oxidation of complex structure natural products having a useful biological activity. The efficient methods of selective oxifunctionalization of betulin, triterpene isolated from birch bark, and peucedanine, a plant coumarine, with the yields up to 95 % have been developed.

OP-YS-24

Photocatalytic Water Splitting with Hydrogen Evolution in the Ce^{3+}/Ce^{4+} Shuttle Charge Transfer System

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Hydrogen as a high-energy fuel has attracted attention all over the world already for several decades. The cleavage of water into hydrogen and oxygen by sunlight was shown to be potentially one of the most promising ways for the photochemical conversion and storage of solar energy [1]. Photocatalytic production of hydrogen from aqueous solutions of organic compounds is a very promising method of hydrogen obtaining. Unfortunately, in the presence of organic electron donors, one can produce only the gas mixture of H_2 and CO_2. The pure hydrogen production is feasible from the aqueous solutions of inorganic donors, for example Ce^{3+} ions.

We have carried out experiments for the hydrogen production in charge transfer system Ce^{3+}/Ce^{4+}. We used aqueous solution of $Ce_2(SO_4)_3$ for photocatalytic hydrogen production, and the $Ce(SO_4)_2$ ones for that of oxygen. Oxygen and hydrogen were obtained in different experiments. Bare and platinized TiO_2 were used as the photocatalysts. Platinum was deposited by either soft chemical reduction (SCR) or photodeposition (PD) techniques. Among non-promoted photocatalysts, the best photocatalytic activity in O_2 production was observed over home-synthesized rutile with specific surface area 63 m^2/g. The photocatalytic activity of the pure rutile specimen grows linearly with the specific surface area of TiO_2.The highest activity among the platinized photocatalysts was shown by 1 % Pt TiO_2 Degussa P25 platinized by PD technique, whereas 1 % Pt TiO_2 Degussa P25 platinized by SCR technique was the most active photocatalyst of the hydrogen production.

The rate of the photocatalytic hydrogen production was lower than the rate of the photocatalytic oxygen production due to the low Ce^{3+} ions adsorption on the titania surface in comparison with that of Ce^{4+} ions. Adsorption isotherm for Ce^{4+} ions on the catalyst surface was obtained.

Kinetic equation for the rate of photocatalytic oxygen production was proposed: it was Langmuir-Hinshelwood equation with taking into account the inner filter effect, caused by Ce^{4+} light absorbance; constants of this equation were calculated. In order to increase the Ce^{3+} adsorption and the rate of hydrogen production, we conducted the treatment of 1% Pt/Degussa P25 SCR by H_2SO_4, H_3PO_4 and NH_4F. The treatment by H_2SO_4 leads to an increase of the catalyst activity in the photocatalytic hydrogen production likely due to a rise of the adsorption of Ce^{3+} ions, whereas the treatment of titania with F^- decreases and H_3PO_4 treatment does not affect the photocatalytic activity.

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Photocatalytic Oxidation of Gaseous Nitrogen Containing Species

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The air purification contaminated with low concentrations of N-containing organic admixtures is an actual problem because such species are widely used in industry, spacecrafts and for military purposes. For example 1,1- dimethylhydrazine (UDMH) is the popular rocket propellant whereas diethyl cyanophosphate (DECP) is the simulant of dangerous chemical warfare agent tabun. Some inorganic species as ammonia, nitric acid and NO_x are also not healthy. Therefore the kinetics of TiO_2 mediated photocatalytic oxidation, final products and intermediates distribution and mass balance of these species were the subject of investigation.

Gas-phase photocatalytic oxidation (PCO) of UDMH vapor in batch reactor using TiO_2 as the photocatalyst was studied with FTIR *in situ* method. FTIR technique is the only method which allows one to detect intermediate species in the gas phase and on the catalyst surface in the course of the experiment (in situ). Carbon dioxide, water, nitric acid and nitrogen were detected as the main products of UDMH PCO. Adsorbed N_2O species was detected as the main surface intermediate. The basic nitrogen-containing product of reaction is molecular nitrogen that is a prominent aspect from the point of view of ecology.

The investigation of dark adsorption of DECP on the TiO_2 surface revealed that almost complete hydrolysis of P-CN fragment proceeds quickly giving the diethyl phosphate and HCN.

$$(C_2H_5O)_2P(O)CN + H_2O \rightarrow (C_2H_5O)_2P(O)OH + HCN$$

The obtaining phosphorous acid ester is practically non-volatile and is quantitatively adsorbed on the TiO_2 surface, whereas cyanhydric acid (HCN) is desorbing into the gas phase giving the 3310 cm^{-1} absorption band.

Only 85% of DECP carbon was converted into the CO_2 form after the 300 min PCO in a static reactor. The rest carbon remained in the form of gaseous HCN, which was supported by mass balance calculation, and IR spectrum of gas phase after the PCO was finished. The best results for PCO HCN were demonstrated by 1% Ag/TiO_2 and 1% Au/TiO_2 obtained by photochemical deposition method. DECP to CO_2 conversion was measured to be 98% for the first 300 min of PCO.

The ammonia PCO was investigated for a set of photocatalysts modified with noble metals and transition metals oxides. Nitrous oxide N_2O was registered as the gaseous PCO product. The formation of dinitrogen N_2 another gaseous PCO product was estimated from the mass balance. Adsorbed nitrites NO_2^- and nitrates NO_3^- were registered as surface intermediate and final product of NH_3 PCO. The best activity was demonstrated by unmodified high surface area anatase form of TiO_2.

Mechanism and Kinetics of Formic Acid Decomposition on V-Ti Oxide Catalyst. The Effect of Water

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V-Ti-O catalyst is selective towards the oxidation of formaldehyde to formic acid in the temperature range 100-140°C [1]. Introduction of water into the reaction mixture raises selectivity due to decreasing the decomposition and overoxidation rates of the formic acid to carbon oxide.

The aim of current work was study the kinetics and mechanism of the formic acid decomposition over V_2O_5/TiO_2 monolayer catalyst. V/Ti catalyst ($11\%V_2O_5/90\%TiO_2$) was used. The BET surface area was 140 m^2/g.

Kinetic experiments were performed in a differential reactor with external circulation loop providing ideal mixing regime, at ambient pressure and range temperature 100-140°C. The influence of the steam was investigated at a constant conversion of the formic acid. In situ FTIR experiments were performed in a flow IR cell-reactor with a Bomem BM-102 FTIR spectrometer.

The main decomposition products of formic acid were CO and H_2O with a small amount of CO_2. The rate of CO formation is sharply decreased with increasing of the water concentration (from 1 to 15% vol.) in the reaction mixture (2-3% HCOOH in air flow).

FTIR showed that the main reaction intermediates are surface formate species. The rate constants of surface formate decomposition and the activation energy were affected by water coadsorption.

Reaction mechanism determined by IR spectroscopy and experimental kinetic data obtained resulted in the kinetic equations for the reaction rates according to reaction network. The kinetic parameters were calculated by minimizing the function, which represents the difference between the experimental and the calculated rates.

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OP-YS-27

Nanocatalyst Formation by Anodic Oxidation of Nb

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Recently, valve metals have offered promises as cost-effective sources of ordered oxide nanotubes. Their major applications, due to the well-developed and easily controllable specific surface, are in the field of catalysis [1, 2], photocatalytic water splitting and gas sensors. Specifically, the application of niobium oxide is generally as a solid-state acid catalyst in organic synthesis using variety of promoters/activators (Ru, Rh, Pt, Re, Ni, Cr, W, etc.) as well as in presence of other oxides (of V, Cr, Mo, etc.). It features considerable selectivity, which enables the control over the type of products and the degree of oxidation [3]. Another application of niobium oxide in this field is as promoter to a range of catalytic materials (silicate, aluminate, titanate, zeolite, etc.).

The process of electrochemical formation of the nanoporous niobium oxide was recently studied [4-6]. The influence of hydrofluoric acid (HF) concentration and applied potential on the processes of anodic oxidation of Nb in sulphuric acid solution was studied by chronoamperometry, electrochemical impedance spectroscopy and scanning electron microscopy. The rates of the process of porous overlayer formation and subsequent growth of nanopore arrays increase with applied potential as well as with the HF concentration. The films have been characterised *ex-situ* by electrochemical impedance spectroscopy at open circuit potential and capacitance vs. potential measurements to follow the different stages of nanoporous film formation with electrochemical methods.

The impedance spectra and capacitance vs. potential curves have been interpreted using previously proposed models for the amorphous semiconductor/electrolyte interface. An attempt to rationalise the mechanism of nanoporous layer growth is presented by using the conceptual views of the mixed-conduction model and recent ideas for porous film formation on valve metals

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OP-YS-28

Catalysis of Radical Polymerization via Ruthenium Carborane Complexes: Mechanism and Its Peculiarities

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Ruthenium complexes are known to play an important role as efficient catalysts or catalyst precursors in the key radical reactions such as controlled radical polymerization and Kharash addition. Among these, ruthenium derivatives containing carborane ligands appeared to be very attractive, due to the ability of the metal centre in these complexes to exist in the different and, in some cases, non-common oxidation states.

The activities of ruthenium carborane complexes in atom transfer radical polymerization of methyl methacrylate and styrene have been investigated.

It has been found that 18- and 17-electron *closo*-ruthenacarborane systems stabilized by the chelate diphosphine ligands are, in tote, more efficient catalysts for such process as compared to monophosphine species. These allow us to obtain well-defined polymers with low polydispersities and predicted molecular weights. It is important that small structural changes in the architecture of the studied catalysts, such as in length of methylene chain of the diphosphinoalkane bridges, cause a substantial difference in their catalytic activity. It is also shown that the addition of simple amines significantly increases the rate of polymerization leaving it controlled.

The reactivity of the ruthenacarborane catalytic systems including their *exo-nido* to *closo* rearrangement that occurs during polymerization has also been studied. Some intermediates as well as side products were isolated and structurally characterized.

The reaction mechanism of polymerization based on experimental data and theoretical calculations was proposed.

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Au-Cu/Al_3CrO_6 Catalysts for Methanol Synthesis

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Methanol is industrially produced from synthesis gas $CO/CO_2/H_2$ under high temperature and high pressure conditions over a ternary CuO-ZnO-Al_2O_3 catalysts. However, recent studies concentrated on investigation of role of CO_2 in the industrial methanol synthesis and have shown that under industrial conditions methanol is produced by hydrogenation of CO_2. Carbon monoxide only provides a source of CO_2 and acts as a reducing agent. It is known that copper promoted catalysts are careful as the most effective catalysts for methanol synthesis. One can find some studies where copper catalyst promoted by noble metal was investigated. In the present work the hydrogenation of CO_2 to methanol over Cu and Au-Cu/$CrAl_3O_6$ catalysts has been studied. Catalysts were prepared by impregnation and co-precipitation methods and their physicochemical properties were investigated by TPR, XRD, BET, TOF-SIMS and SEM-EDS methods. The reaction of methanol formation under atmospheric and elevated pressure (4MPa) over a series of 60%Cu/$CrAl_3O_6$ and (1-5)%Au - 60%-Cu/$CrAl_3O_6$ catalysts has been investigated.

Conclusion:

1. XRD analysis confirmed the presence of following phases : $CrAl_3O_6$, $CuCr_2O_4$, Au, Au-Cu, α-Cr_2O_3, CuO.
2. The shape of TPR profiles suggested the presence of copper oxide, copper chromite and chromium species reducing during experiment.
3. Investigation of binary system $CrAl_3O_6$ by SEM technique confirmed high homogenic level of sample.
4. The formation of Au-Cu alloy during reaction conditions was confirmed by SEM and TOF –SIMS technique, the highest concentration of gold is observed in rich copper area.
5. The most active catalysts was 5%Au-60%Cu/$CrAl_3O_6$ prepared by co-precipitation method.

OP-YS-30

Low Temperature Decomposition of Hydrogen Sulfide into Hydrogen and Sulfur: A New Catalytic Pathway

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The direct thermal decomposition of hydrogen sulfide into its constituent elements is a strongly endothermic reaction and is thermodynamically unfavorable except at very high temperature.

$$2\,H_2S \Leftrightarrow 2\,H_2 + S_2 \qquad \Delta_rH^o_{298} = +\,40.5\ \text{kcal/mol};\ \Delta_rG^o_{298} = +\,18.9\ \text{kcal/mol} \quad (1)$$

It is well known that catalysts are not able to shift the thermodynamic equilibrium of the reaction (1). However, a particularly chosen catalyst is capable to direct the reaction of the hydrogen sulfide decomposition to another pathway that can reduce sufficiently the temperature of the reaction. Recently disulfane, H_2S_2, was detected as a surface intermediate during temperature programmed desorption from the sulfide HDS catalysts after H_2S adsorption at room temperature [1]. The stoichiometric reaction

$$2\,H_2S \Rightarrow H_2 + H_2S_2 \qquad (2)$$

is thermodynamically prohibited in a gas phase, but occurs spontaneously on the catalyst surface at room temperature. At the same time, decomposition of disulfane is thermodynamically permissible. Hence, the role of solid catalyst is specified as a suitable working substance producing peculiar conditions for conjugated chemisorption of two molecules of hydrogen sulfide on two adjacent metal atoms resulted in formation of sulfur – sulfur bond and release of hydrogen molecule in a gas phase. It is precisely the driving force that provides a new course of reaction (1) at room temperature.

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Catalytic Properties of Transition Metals Oxides and Sulfides in the Reactions of H_2S Oxidation to S or SO_2

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Oxidation of hydrogen sulfide to the elemental sulfur is the attractive way to decrease the H_2S level in Claus tail and others waste gases. But, the yield of sulfur can be decreased by SO_2 production due to a parallel route of deep oxidation of H_2S. For example, the formation of iron disulfide phase in Fe-containing catalysts under the reaction conditions is accompanied by an appearance of SO_2 among the reaction products. The literature data concerning selectivity of H_2S conversion in the presence of oxides and sulfides of other transition metals are conflicting and scarce.

To provide a deeper insight into this question, we prepare a number of silica-supported catalysts using nitrate of Fe, Co, Ni and Mn as precursors and try to follow the active phase transformation and catalytic properties of the samples during the hydrogen sulfide oxidation reaction.

The catalysts were prepared by dry wetness impregnation of SiO_2 with an aqueous solution of Fe(III), Co(II), Ni(II) or Mn(III) nitrate with the subsequent drying and calcinations. The samples after calcinations and catalytic testing were studied using XPS and XRD. The conversion and selectivity of H_2S oxidation were determined in the plug-flow reactor at atmospheric pressure and temperature 220-280°C.

It was shown, that after calcinations at 700°C the samples contain α-Fe_2O_3, Co_3O_4, NiO or Mn_3O_4, accordingly. The study of the samples after the reaction by means of XPS and XRD let us to conclude, that Co, Ni and Mn oxides interact with H_2S during the reaction producing the corresponding sulfide, unlike to the α-Fe_2O_3 that is stable after the reaction conditions and provide for the selective oxidation of H_2S to sulfur. It was stated, that the behavior of the transition metal sulfides in the H_2S oxidation reactions depend on the nature of the metal: while the FeS_2 turn the reaction to the SO_2 formation, in the presence of MnS hydrogen sulfide is oxidized to sulfur with the high selectivity. In the case of CoS_2 and NiS_2 both of the products (SO_2 and S) are formed.

OP-YS-32

Research of Chromium States in Microspheric Cr_2O_3/Al_2O_3 Catalysts for Paraffin's Dehydrogenation

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The catalytic dehydrogenation of isobutane and propane over Cr_2O_3/Al_2O_3 catalysts is an important process which is used worldwide in the chemical industries. These catalysts are composed of chromium oxides dispersed on a porous alumina support, and often contain a dopant such as potassium [1].

The effects of the type of support and of some preparation parameters on the nature of the chromium species have been the object of numerous investigations. However, complete characterization of these catalysts using a combination of several techniques which could give a thorough examination of the relationships between activity and chromium species in catalyst have not yet been reported [2].

In this work microspheric catalyst for dehydrogenation in fluidized bed is produced using product of centrifugal thermal activation (CTA) of gibbsite. Some basic investigations of different states of supported chromium oxide in catalysts, their role in dehydrogenation and changes during their work were made. The presence of grafted and soluble Cr^{6+} species is shown using methods of TPR and chemical analysis, their quantity depends on chromium oxide loading. Promoters adding (K, Zr, Ce) in catalyst leads to increase of Cr^{6+} species overall content, however, their redistribution occurs simultaneously (the amount of grafted species decreases and the amount of soluble species increases). If catalysts calcinations temperature grows the amount of grafted and soluble species Cr^{6+} reduces.

Basic parameters which allow controlling the formation of different supported chromium oxide states were defined using obtained data.

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OP-YS-33

Mechanism of Formation of Synthetic Oligoalkylnaphthenic Oils

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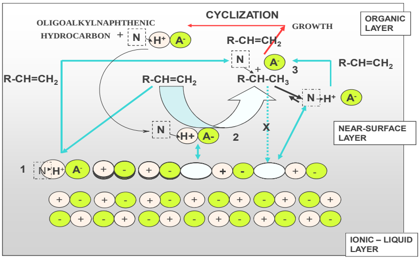
Last years the application of ionic liquid (IL) catalysis in various processes of petrochemical synthesis attracted an increasing interest [1].

1-hexene oligomerization has been performed in the presence of recyclable chloroaluminate type IL catalysts, and their combination with Ti-containing complexes with “grafted IL” type ligands, in the presence of which it is possible the selective obtaining the products with oligoalkylnaphthenic structure and narrow molecular-weight distribution (M_w/M_n =1,03-1,55), characterized by the lack of double bonds.

In the paper the suggested mechanism of selective formation of oligoalkylnaphthenic hydrocarbons by oligocyclization of α–olefins in the presence of IL catalysts is presented. The consecutive reactions of oligomerization and cyclization, mediated by the same catalytic centre take place, which is accepted as the term of oligocyclization. The oils obtained are qualified as the novel class of synthetic oils, namely as the class of synthetic oligoalkylnaphthenic oils.

Evident representation of the mechanism of activation and oligo-cyclization of α–olefin with the involvement of **a**) ion pairs of the IL catalyst, **b**) ion pairs and the "free" ions of the IL catalyst is given.



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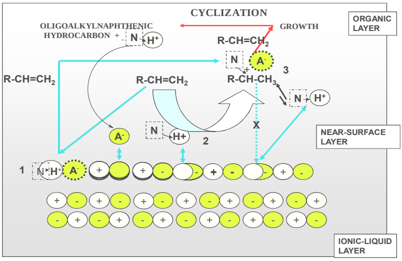

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OP-YS-34

Suzuki Reaction. Distinguishing Nanocatalysis from “Catalysis with Nanoparticle”

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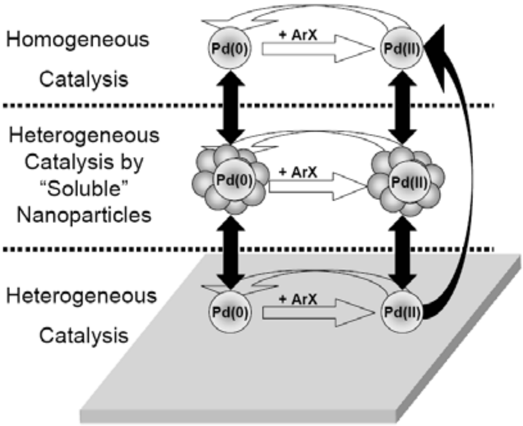
From the previous discussion [1] it can be concluded that distinguishing true homogeneous catalysis from heterogeneous catalysis in the Suzuki reaction is undoubtedly a very complicated task. Unfortunately, the results of the conventional tests on reaction homogeneity-heterogeneity are ambiguous due to the interconversions of different catalyst forms (Scheme). It can be associated with the possible compensative effect of the catalytic system which responses (similar to Le Chatelier's principle) to the removal of one of the catalyst forms used in the tests.



Scheme. *Contributions of homogeneous and heterogeneous catalysis in the Suzuki reaction.*

The combination of our experimental results - comparative kinetic studies of the Suzuki and Heck reactions; the modified tests on homogeneity-heterogeneity, studies of the selectivity, an implementation of solid-phase variant of the Suzuki reaction – indicates the significant contribution of heterogeneous mechanism to the Suzuki reaction catalysis. So both concepts that are discussed in the literature to be exclusive homogeneous or exclusive heterogeneous catalysis of the Suzuki reaction are not consistent with the data obtained in this work. The possibility of the "soluble" Pd nanoparticle formation after Pd leaching from the surface of supported catalysts suggests that previous analysis of several experiments including results of three-phase tests and activity-Pd leaching relationships may need to be reinterpreted.

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OP-YS-35

Liquid Phase Selective Acetylene to Ethylene Hydrogenation in the CO Presence on Pd/Sibynit Catalyst

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Acetylene obtaining by oxidative pyrolysis of associated petroleum and natural gases is a very perspective industrial process [1]. The following step is the selective hydrogenation of C_2H_2 into C_2H_4 in CO presence. It is then allowed to use the obtaining reaction mixture in several significant processes. The example of C_2H_2 selective hydrogenation in liquid phase is shown in [2].

The aim of our work was the investigation of the regularities of selective C_2H_2 hydrogenation in liquid phase. N-methylpyrrolydone was used as a solvent. The 0.5% Pd/Sibunit catalyst was prepared by impregnation of support (graphite-like carbon material “Sibunit” with S_{BET} 320 m^2/g) by $Pd(NO_3)_2$ solution, drying and following reduction in H_2 flow at 300ºC. The catalytic characteristics (conversion X, activity R and selectivity S) were measured at 30 – 90 ºC and gas composition 2 - 12% of C_2H_2, 2 - 8% CO, 6% He and balanced H_2.

The interpretation of obtaining results is based on the fact of competitive adsorption of CO, C_2H_2, and oligomers on Pd active sites under reaction conditions. The scheme of reaction is suggested.

It was found that at optimal conditions (2% C_2H_2, 90% H_2, 2% CO, 6% He, 90^0C) the selectivity S = 89.6±1.5% at X = 95.8 ± 1.3%.

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Effect of Ionic Liquid BMImBr on Palladium Catalyzed Oxidation of Ethylene with $LiNO_3$

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Ionic liquids are used as perfect solvents for organic compounds, inorganic salts and gases. In the present study, 1-butyl-3-methylimidazolium bromide (BMImBr) operates as not only a solvent, but also reagent, resulting in changing mechanism of the palladium catalyzed oxidation.

Conversion of ethylene in the presence of the $Pd(OAc)_2$- $LiNO_3$ catalytic system was revealed to proceed as oxidative bromination in the two-component BMImBr-HOAc solvent, instead of hydroxyacetoxylation in HOAc. As a result, ethylene formed 1,2-dibromoethane and 2-bromoethyl acetate in the presence of BMImBr, instead of ethylene glycol monoacetate without BMImBr. Small additives of water slowed down oxidative bromination, but elevated selectivity to 1,2-dibromoethane.

UV-Vis spectroscopy showed that the solution of $Pd(OAc)_2$-$LiNO_3$ in the two-component solvent contained Pd(II) bromide complexes before the contact with ethylene. Interaction with ethylene was observed to lead to formation of NO_2 and, probably, NO_2^-, and to consumption of bromide anions to production of Br-containing compounds which appeared from oxidation of Br^- with nitrite to Br^0 and BrO^-, and their following oxidative addition to ethylene.

In solution containing 40 wt.% of BMImBr, 1,2-dibromoethane was produced with selectivity up to 95 mol.%, that offered a promising way of effective oxidative bromination of alkene compounds under mild conditions.

OP-YS-37

Catalytic Hydrodechlorination of 2,4-Dichlorophenol on Pd-M/SiO_2 Catalysts (M = Au, Bi, Fe, Tl)

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Chlorophenols (CPs) are commercially important organic compounds used in the manufacture of herbicides, dyes, wood protectors and plant regulators. Chlorophenols are highly toxic and poorly biodegradable compounds. Because of this, there is a need for efficient methods of dechlorination of these dangerous substances. At present, catalytic hydrodechlorination (HDC) is widely used. The metal which is applied most frequently in these processes is palladium. In our oral presentation, the results of the study of activity and selectivity of Pd-M/SiO_2 (M = Au, Bi, Fe, Tl) catalysts will be shown.

The catalysts containing 5%-wt. of palladium and 1÷5%-wt. of second metals (Au, Bi, Fe, Tl) were prepared trough aqueous coimpregnation. Before the catalytic tests, the catalyst samples were calcinated at 773 K for 4 h in air atmosphere and reduced in hydrogen atmosphere at 573 K for 2 h. Hydrodehalogenation of 2,4-dichlorophenol was performed for constant initial concentrations of substratum (C_0 = 0.12 mmol/dm^3) in the temperature 293 K ad pH = 7. In addition, the bimetallic Pd-M/SiO_2 catalysts were characterized by X-ray diffraction (XRD), Time-of-Flight Secondary Ions Mass Spectrometry (TOF-SIMS), sorption of carbon monoxide and temperature-programmed techniques (TPO, TPR).

The effect of metal particle size and of existence of intermetallic compounds on the catalytic hydrodechlorination (HDC) over Pd-M/SiO_2 will be discussed in this presentation.

The Mechanism for Low-temperature Methanol Oxidation over V_2O_5/TiO_2 Monolayer Catalyst

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Vanadia supported on titania is known as an effective catalyst in the selective oxidation of hydrocarbons, aldehydes, and alcohols, and in other industrially important reactions. In this work, the methanol oxidation over V_2O_5/TiO_2 monolayer catalyst was examined at low temperature. In catalytic testing, dimethoxymethane (DMM), methyl formate (MF), formaldehyde, formic acid, carbon oxides and water were detected as products. We found that the product distribution strongly depends on temperature and methanol conversion. Between 70-100ºC, DMM is the main reaction product. Increasing reaction temperature leads to a sharp decrease in DMM selectivity and to a shift towards formation of MF. At 140-150ºC, MF becomes the main reaction product. Similar selectivity changes were observed at increasing conversion at constant temperature. An increase in temperature also results in generation of minor quantities of formaldehyde and formic acid.

Combining the catalytic testing with *in situ* FTIR, *in situ* XPS and TPR measurements provided additional insight into the mechanism for selective methanol oxidation. FTIR showed that the main reaction intermediates are surface methoxy, dioximethylene and formate species. Their concentrations depend on temperature. XPS showed that the reaction involves the reversible reduction of V^{5+} cations. It indicates that the lattice oxygen of vanadia takes part in the methanol oxidation via the classical Mars-van Krevelen mechanism, which consists in reduction of vanadia by methanol and its subsequent reoxidation by gaseous oxygen. The detail mechanism for selective methanol oxidation over V_2O_5/TiO_2 monolayer catalyst is discussed.

OP-YS-39

Characterization of the Hydrothermal Aging Effects on Precious Metals

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Three-way catalysts (TWC) are materials composed of precious metals and metal oxides that are able to simultaneously abate important pollutants such as CO, NO_x and hydrocarbons. TWCs are formidable in resisting dramatic changes in temperature and in reaction conditions. However, they are subject to aging which typically causes loss of activity on mileage manifesting in increased level of emissions. A facet of TWC aging is hydrothermal aging which occurs because of high temperature and the presence of water in the car exhaust. Metal nanoparticles are typically greatly affected by the harsh conditions encountered in the automotive catalytic converter.

As prepared and hydrothermally aged (700°C and 1000°C, 16h, 10% H_2O, 10% O_2) 2 wt.% M/Al_2O_3 (where M is Rh, Pt, Pd) have been chosen to systematically study the effect of aging on the precious metal component of TWC. The catalysts have been characterized using BET, XRD, TEM, DRIFT, CO chemisorption and XAS. Whereas ex situ characterization of materials is only partially able to give information on structural changes induced by aging, in situ DRIFT and XAS (catalytic reduction of NO by CO) studies with simultaneous MS analysis are the most promising to observe the structural and reactivity differences of the precious metals. The results indicate that the response of the three noble metals to hydrothermal aging is different. In the case of Rh/Al_2O_3, aging affects mostly the oxidation state of Rh and therefore the selectivity in the reduction of NO by CO. The Pt-containing samples display considerable particle sintering with increasing aging temperature. The response of Pd component towards aging is similar to Pt but it additionally shows the formation of the oxidic phase (PdO). Besides, Al_2O_3 is also observed to change phase according to the aging temperature.

The Effect of Binary Support ($MgAl_2O_4$ and $CrAl_3O_6$) Performance on the Kind of Carbon Deposition Formed in Partial Oxidation of CH_4

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The improvement of catalytic performance of nickel catalysts can be achieved by the modification of support, which does not only act as the catalyst carrier but also take part in catalytic process.

The aim of this work was to find correlation between kind and performances of supports (Al_2O_3, $CrAl_3O_6$ and $MgAl_2O_4$) and their resistance to carbon deactivation.

The physicochemical properties of catalysts were investigated by TPR, XRD, TOF-SIMS, SEM techniques. The activity test in partial oxidation of methane (POM) at 25-900°C and the stability test during 24 hours at 900°C were carried out. The carbon deposition was studied by TOC and TPO measurements.

The 5%Ni/$CrAl_3O_6$ and $MgAl_2O_4$ demonstrated several times higher activity in comparison to 5% Ni/Al_2O_3 in POM reaction, showing nearly 100% of CH_4 conversion and CO selectivity at 900°C. Their activity after 24 hours was high without any significant change. These systems were much more resistant for carbon deposition while 5% Ni/Al_2O_3 catalyst showed 23% wt. of carbon. The decrease of carbon content to 5% wt. for 5%Ni/$CrAl_3O_6$ was caused by the participation of chromium in oxidation process. The other mechanism was responsible for the fall of carbon content to 2% for 5%Ni/$MgAl_2O_4$. It was caused by increase of basicity of surface and the removal of carbon from catalyst. The kind of support influence also on type of formed carbon. The carbon deposition forming on 5% Ni/Al_2O_3 consists mainly of filamentous and graphitic carbon responsible for deactivation, which was oxidised in high temperature 500-800°C. The significantly smaller amount of these species was observed for $CrAl_3O_6$ and any for $MgAl_2O_4$.

OP-YS-41

Influence of Phase Transfer Agent and Second Metal in Pd-Containing Catalysts on the Selectivity of p-Chloroacetophenone Reaction with Hydrogen

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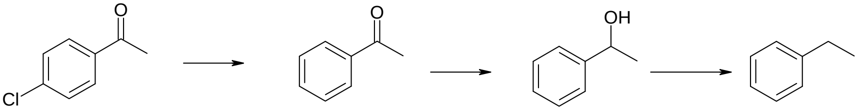
In this work reductive treatment by hydrogen of *p*-chloroacetophenone was studied. As a model substrate, *p*-chloroacetophenone can undergo different types of reductions: hydrodechlorination (HDC), reduction of carbonyl or hydroxyl groups and aromatic rings.

Pd supported on modified zirconia and ultradispersed diamond (UDD) were used in this work. Reaction was performed under multiphase conditions [1]. The general reaction scheme is following:



In the presence of Pd/UDD HDC proceeds very fast, after ten minutes there are no signs of chlorinated substrate in the mixture. Then the slow hydrogenation proceeds consequently to form acetophenone, then correspondent alcohol and finally ethylbenzene. The hydrogenation of aromatic ring does not proceed. The addition of 5%Ni to 5%Pd/UDD stops the reaction on the stage alcohol formation, with no significant amount of ethylbenzene formed. Modification of 2%Pd/UDD by 5% Co or 5% Cu changes selectivity towards achetophenone.

Influence of phase transfer agent addition was studied for the reaction on Pd supported on zirconia modified by small amounts of Ga_2O_3 or Y_2O_3. The addition of Aliquat 336 changes the selectivity of the reaction. In the absence of Aliquat 336, the hydrogen treatment of *p*-chloroacetophenone leads to the formation of acetophenone as the only product after 1 hour of the reaction. When the Aliquat 336 is added the reaction proceeds toward methylphenilcarbinol formation and then stops. It takes about 2 hours for total conversion of *p*-chloroacetophenone to methylphenilcarbinol with no signs of further hydrogenation.

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Oligomerization with Chromium Complexes

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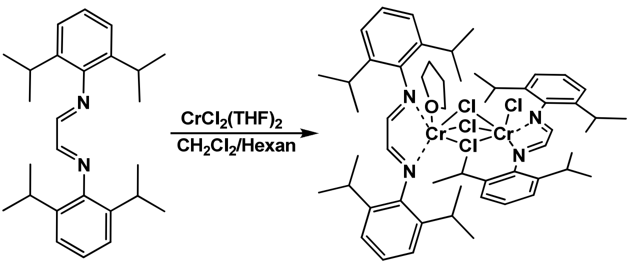
The oligomerization of ethylene is a widely used process for the production of Linear alpha-Olefins (LAOs). Regarding the mechanisms for selective and unselective oligomerization it is commonly accepted that the unselective oligomerization of ethylene proceeds via a chain growth mechanism leading to a Schulz-Flory-distribution of LAOs. In contrast to that the intermediates in selective oligomerization consist of metallacycles formed by oxidative addition of two molecules ethylene. It follows ring expansion and liberation of one major product e.g. 1-hexene or 1-octene [1].

In an attempt to find new homogeneous catalysts for the oligomerization of ethylene different chromium complexes were synthesized, characterized and tested in catalysis. Additionally the influence of different co-catalysts, e.g. MAO or $AlEt_3$, was tested.

In this contribution two different ligands, a diazabutadiene and a bidentate bis-N-heterocyclic carbene, will be discussed and the results of their chromium complexes in the catalytic oligomerization of ethylene will be interpreted [2].



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Nature of the Ti-Ba Interactions on the $BaO/TiO_2/Al_2O_3$ NO_x Storage System

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In the last decade, NO_x storage/reduction (NSR) technology originally developed by Toyota Motor Corporation[1,2] has attracted considerable attention as a promising after treatment technology for the catalytic NO_x removal from mobile sources. Numerous efforts[3] have been directed towards designing highly active NSR catalysts with long term durability and improved sulfur tolerance. As a support material of the NSR catalysts, TiO_2 was found to have a noticeable ability to suppress sulfur deposition.[4] This was associated with the surface acidity of TiO_2, inhibiting the adsorption of acidic sulfur species and making the sulfates less stable on the TiO_2 compared to other oxide supports. In order to elucidate some of these crucial aspects, in the current study[5], we synthesized and characterized a ternary oxide based NO_x storage material in the form of $BaO/TiO_2/\gamma\text{-}Al_2O_3$. Thermally induced structural changes occurring on the surfaces of the support $TiO_2/\gamma\text{-}Al_2O_3$ material and the NO_x storage $BaO/TiO_2/\gamma\text{-}Al_2O_3$ systems were studied in a comparative manner within 300 K – 1273 K via X-ray diffraction (XRD), Raman spectroscopy, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX) spectroscopy and BET surface area analysis. The surface acidity of the studied oxide systems was also investigated via pyridine adsorption monitored by in-situ Fourier transform infrared (FTIR) spectroscopy. $BaO/TiO_2/\gamma\text{-}Al_2O_3$ ternary oxide was synthesized by incorporating different loadings of (8 - 20 wt. %) BaO onto the $TiO_2/\gamma\text{-}Al_2O_3$ support material which was originally prepared using the sol-gel method. In the $TiO_2/\gamma\text{-}Al_2O_3$ binary-oxide support material, anatase phase exhibited a relatively high thermal stability at $T \leq 1073$ K. The presence of TiO_2 domains on the surface of the alumina particles was found to alter the surface acidity of alumina by providing new medium-strength Lewis acid sites. SEM/EDX results indicate that in the $BaO/TiO_2/\gamma\text{-}Al_2O_3$ system, TiO_2 domains exhibit a significant affinity towards BaO and/or $Ba(NO_3)_2$ resulting in a strong Ti-Ba interaction and the formation of overlapping domains on the surface. Presence of TiO_2 also leads to a decrease in the decomposition temperature of the $Ba(NO_3)_2$ phase with respect to the Ti-free $Ba(NO_3)_2/\gamma\text{-}Al_2O_3$ system. Such a destabilization is likely to occur due to a weaker interaction between $Ba(NO_3)_2$ and $\gamma\text{-}Al_2O_3$ domains in the ternary oxide as well as due to the change in the surface acidity in the presence of TiO_2. At relatively high temperatures (e.g. 873 K – 1273 K) formation of complex structures in the form of $BaTiO_3$, $Ba_{1.23}Al_{2.46}Ti_{5.54}O_{16}$, $BaTiO_5$ and/or $Ba_xAl_yTi_zO_n$ were also observed.

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Section of the young scientists: "Physical methods for the study of nano- and biosystems in catalysis"

VIII International Conference
“Mechanisms of Catalytic Reactions”,
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ABSTRACTS
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