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CATALYST DESIGN – FROM MOLECULAR TO INDUSTRIAL LEVEL

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ABSTRACTS

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4th EFCATS School on Catalysis
CATALYST DESIGN – FROM MOLECULAR TO INDUSTRIAL LEVEL

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Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

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PLENARY LECTURES

MODERN TECHNIQUES FOR TESTING THE CATALYTIC ACTIVITY AND KINETICS OF CATALYTIC REACTIONS

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Activity of heterogeneous catalysts is defined as the specific (in respect to, e.g., the catalyst mass) stationary rate of the catalytic reaction at the given temperature, pressure, and composition of the reaction mixture being in contact with the catalyst. However, at the experimental practice, this correct kinetic approach to the notion of the catalytic activity is used very seldom because the correct catalyst testing is associated with a number of complicated methodological and technical problems. As a result, the experiments on testing the catalytic activity are generally labor consuming and expensive while the obtained kinetic data are not sufficiently reliable from the point of view of the correct kinetics definition.

Usually, the catalyst testing is performed in simple plug-flow reactors and the results of the respective experiments are presented as degree of conversion versus the reaction mixture "residence time" or VHSE. The results of such testing can be considered as integral ones and give only approximate kinetics data. Indeed, it is known that the reaction rate depends on many catalyst properties (technique of its preparation, its chemical composition, texture, shape, particle size, etc.) as well as on the process parameters (temperature, pressure, composition of the reaction mixture, heat-and-mass transfer, etc.) which vary along the reactor. For this reason yet in the quite old IUPAC recommendations [1] it was noted that "contact time" or "residence time" are terms which may be misleading for flow systems in heterogeneous catalysis and thus should be avoided.

The development of reliable experimental methods and devices for correct testing the catalyst activity and kinetics of heterogeneous catalytic reactions is carried out in the Boreskov Institute of Catalysis for more than 20 years [2]. The developed methods allow one to receive one-parameter dependencies of the catalyst activity on the parameters of both the catalyst and the process. The main problem for such experiments appears to be the actual complexity of measuring the reaction rate under the given reaction mixture composition for the processes with the preliminary unknown formal kinetics. Indeed, this is quite usual situation not only for new catalysts but also for many known catalysts. Also, there are many technical problems in maintaining the same temperature of the catalytic bed for different catalysts.

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Many of the mentioned problems are solved at the use of the flow-recycling method (FRM) for catalyst activity testing. The flow-recycling method (or the differential circulation method, as it is somewhere called as well) is one of the so-called "gradientless" methods in which a catalytic microreactor is combined with a mixing device (a recycling pump) placed outside of the reaction volume (Fig. 1). The respective FRM-based catalyst testing set ups are now manufactured in commercial amount by the Boreskov Institute of Catalysis.

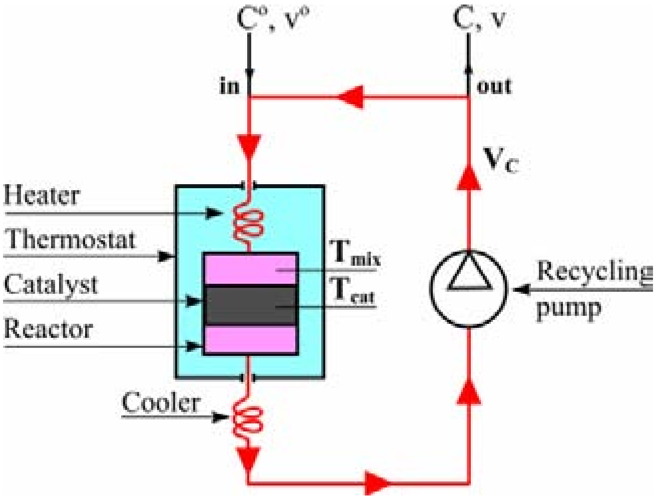

Figure 1. A scheme of the flow-recycling catalytic reactor. C^o and C are the concentrations of the key component in the inlet and outlet reaction mixture, v^o and v are the inlet and outlet reaction mixture flow rates, V_C is the recycling pump capacity, T_{mix} is the temperature of the reaction mixture in front of the catalyst bed, T_{cat} is the temperature of the catalyst bed

The situation when the operation of the system can be really considered as a gradientless one, is attained at a sufficiently large values of ratio V_C/v^o.

In the lecture, several examples will be given which demonstrate how informative can be the kinetics studies with the use of the FRM-based gradientless reactors against studies in common plug-flow reactors. The examples are processes of deep oxidation of several compounds, steam reforming of methane, partial oxidation of methane to formaldehyde, decomposition of methanol, and alkylation of benzene with ethylene. So, for the reaction of steam reforming of methane over nickel- or ruthenium-based catalysts it was found that the reaction proceeds as a homo-heterogeneous one. Studies on the catalytic activity in the partial oxidation of methane to formaldehyde demonstrate also the homo-heterogeneous nature of the process: the best catalysts appeared to be simple SiO_2 rather than VPO, etc. The kinetic studies on the decomposition of methanol exhibit a strong retardation of the process rate by the adsorption of formats formed, etc.

References

1. Burwell, R.L. (1976) Manual of symbols and terminology for physicochemical quantities and units. *Pure & Appl. Chem.* **46**, 71-90.
2. Bobrov, N.N., Parmon, V.N. Rapid catalyst testing in the Boreskov Institute of Catalysis. (2002) *Principles and Methods for Accelerated Catalyst Design and Testing, NATO Science Series, II. Mathematics, Physics and Chemistry – Vol. 69, p.197-215.*

FAST DEVELOPMENT OF INNOVATIVE CATALYSTS APPLYING HIGH-THROUGHPUT KINETIC SCREENING METHODS

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Effective and cost efficient catalysis was and is the key technology to most commercial processes in chemistry. Over the years research has focussed on both, optimising existing materials and finding new or more effective catalysts. Rational methods have dominated catalyst research for the last 100 years. However, the classical development chain can be slow and expensive whereas time-to-market is steadily decreasing and research budgets are shortened more and more. Therefore, researchers are requested to develop new, faster and more efficient tools to speed up research and development of new catalysts.

Some 15 years ago, a new idea of how to deal with this problem came into focus of catalysis research: combinatorial discovery - a technique that revolutionized drug discovery and material science. The combinatorial chemistry method involves (i) the generation of large number of compounds by randomly joining various building blocks together (ii) high-throughput screening methods by which the library can be screened for a specific property and (iii) the identification of active compounds by a specific analysis method.

In the euphoric phase of the adaptation for applications in catalysis research, these combinatorial techniques also seemed to initiate a paradigm change in the catalysis research approach. The words “combinatorial”, “random”, “large libraries”, “statistic approach” pressed into the headlines of scientific catalysis research articles – and still remained.

Today, fast screening methods evolved to standard techniques at least for the large companies in chemical industry. High-Throughput-Development of catalysts has inspired a number of start-up companies which entered business by offering high-throughput development as a service. Large chemical companies also developed this technology platform for their own needs and applications. In academic research, however, high-throughput technologies are still not broadly established, i.e. the total workflow from preparation to evaluation is rarely used.

The present lecture will give an overview on state-of-the-art methods in catalyst development focussing on Degussa’s fast preparation and kinetic screening approach as well as an evaluation of their efficiency in homogeneous and heterogeneous catalysis.

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ISOTOPIC STUDIES OF THE KINETICS AND MECHANISMS OF HETEROGENEOUS CATALYTIC REACTIONS

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In order to improve industrial catalytic processes or design new ones, a precise knowledge of the related mechanisms and micro-kinetics is required to obtain reliable kinetics for engineering studies.

Within the frame of a study confined to the steady-state kinetics, only lumped kinetic parameters can be estimated from a regression of steady-state kinetic data.

By generating transients input signals, such as step functions in the gas concentration, one observes signals out of the steady-state (transient decrease of the product yield, thermodesorption), the relaxation of which may be related to the time scale on which the corresponding global reaction occurs at the steady-state. One unique way to get these time constants pertaining to steady-state conditions is to generate isotopic step functions, which let the overall surface occupancy unperturbed and therefore gives access to true time constants of the reactive intermediates and to their concentration. This technique is referred as steady-state isotopic transient kinetic analysis (SSITKA). It can also be combined with *in situ* physical techniques such as the diffuse reflectance infrared spectroscopy (DRIFT) or the electrical conductivity, leading to a simultaneous observation of the transient changes in surface/bulk and gas composition [1].

Another way to generate transient kinetics consists in pulsing small and known amounts of reactants through a catalyst bed maintained under vacuum and analysing the pulse expansion and relaxation at the reactor exit with a time resolution below the millisecond. This is the temporal analysis of product (TAP) technique [2].

Numerous papers/conferences devoted to these techniques and their advanced mathematical treatment demonstrate the utmost interest to approach as much as possible the reality of the catalytic phenomena (non uniform surface, combination of kinetic, thermal and hydrodynamic parameters) [3-5]. Another direct application of the transient kinetics is to understand and model catalytic processes which are run under non steady-state conditions, such as the circulating beds (FCC) or the reverse flow reactors. Finally, emerging applications related to domestic and on-board catalytic reactors (e.g. for generating hydrogen for fuel cells), require to strictly control the frequent unsteady-state regimes like start-up, shut-down procedures, abrupt changes in reactor productivity.

This course will provide the basic concepts involved in the transient kinetic approach, the tools which are available today and several applications in the field of the gas/solid heterogeneous catalysis will be described. As case studies, two major domains such as syngas generation, hydrogen purification and the selective reduction of NO by methane will be considered in detail.

Syngas generation from natural gas reforming and hydrogen purification

The methane activation occurring on metal surfaces is first considered. The formed C, CH_x and H fragments may recombine on the surface either into higher hydrocarbons in the absence of oxygen (case of the non oxidative homologation), or into carbon monoxide and hydrogen in the presence of oxidising species. For the case of partial oxidation and dry reforming by CO_2, advanced quantitative SSITK and TAP data are presented, which demonstrate the major influence of the metal (noble or non noble), of the support (inert as silica or co-catalyst as ceria, lanthana and/or alumina) and on the operating conditions (contact time, temperature) on the mechanism and the kinetics of the reaction [7]. A mathematical model is proposed to determine the combined hydrodynamic and catalytic kinetic parameters from the TAP data [8]. A sequential non steady-state process for methane activation will also illustrate to way to investigate its mechanism by combining several techniques [9].

The activation on basic oxides involving either an heterolytic splitting into CH_3^- and H^+, or an homolytic splitting leading directly to methyl radicals $CH_3^{\cdot}$ is illustrated by SSITK and TAP experiments designed for investigating the oxidative activation of methane into higher hydrocarbons.

For this case, the role of surface and lattice oxygen species (nature, rate of surface and bulk migration) is emphasised as controlling the overall selectivity.

Finally, SSITK and TAP results obtained for the activation of methane into aromatics [10] which may involve the heterolytic activation over carbide-like active sites are presented.

Selective catalytic reduction of NO with CH_4 over Co-ZSM-5

Despite numerous studies, the kinetic understanding of the selective reduction of NO with CH_4 in the presence of excess oxygen process remains controversial. This course will present *in situ* transient DRIFT (Diffuse Reflectance Infrared Fourier Transform) and SSITKA (Steady State Isotopic Transient Kinetic Analysis) studies carried out over ion-exchanged Co-ZSM-5 catalysts. Emphasis is focused on elucidating the nature of surface intermediate NO_x species (and the associated cobalt species) and their relative activity with methane. Based on a proposed reaction mechanism, a quantitative kinetic model has been derived and it will be demonstrated that various kinetic approaches (SSITKA and steady-state) can converge towards an advanced and consolidated mechanism.

Thus, the surface coverage analysis derived from two formal steady-state kinetic models is compared to values directly obtained from SSITKA/DRIFT for the selective catalytic reduction (SCR) of NO by CH_4 over Co-ZSM-5 catalysts. It is shown that the most abundant reacting intermediates are NOx adspecies, though no clear differentiation between the various adspecies identified by DRIFT spectroscopy was achieved. Less numerous carbon containing adspecies were identified and quantified in the reacting system, essentially as methoxy species. Nitromethane-like intermediates remained undetectable due to a very rapid transformation into N_2 and CO_2. On the basis of these converging kinetic analyses related to each elementary step of the SCR process, a microkinetic model can be derived, which allows describing transient operation, in view of a non steady-state application [11, 12].

Conclusions

The fruitful and complementary approach by kinetic, spectroscopic and possibly theoretical (Monte-Carlo and Quantum Molecular Dynamics) techniques is emphasised. Ideally, the transient kinetics evaluate the concentration and reactivity of the active sites. The spectroscopies (TEM, IR, UV-vis, XPS, ...) reveal the nature of the surface/adsorbates entities. The theory may validate the resulting advanced description of the working catalyst.

References

1 Mirodatos, C., Catalysis Today 9, 83 (1991).

2 Gleaves, J.T., Ebner, J.R. and Kuechler, T.C., Catal. Rev.-Sci. Eng. 30 (1988) 49.

3 "Dynamics of surface and reaction kinetics in heterogeneous catalysis", G.F. Froment at al, Eds., Studies in Surface Science and Catalysis, Elsevier, Amsterdam, 109 (1997).

4 "Transient Kinetics", P. Szedlacsek and L. Guczi, Eds., Appl. Catal., 151 (1997).

5 "Kinetic Methods in Heterogeneous Catalysis", G.B. Marin, R.A. van Santen, Eds., Appl. Catal., 160 (1997).

6 Schuurman, Y., and Mirodatos, C., Appl. Catal. 151 (1) (1997) 305-331.

7 Kroll, V.C.H., Swaan, H.M., and Mirodatos, C., J. Catal. 161 (1996) 409; Kroll, V.C.H., Swaan, H.M., Lacombe, S., and Mirodatos, C., J. Catal. 164 (1996) 387.

9 E. Odier, Y. Schuurman, K. Barral, C. Mirodatos, In "Studies in surface science and catalysis" (ed. X. Bao and Y. Xu), 147 (2004) p.79-84.

10 Décamp, T., Pantazidis, A., Xu, Y., and Mirodatos, C., "Dynamics of Surfaces and Reaction Kinetics in Heterogeneous Catalysis", G.F. Froment, K.C. Waugh, Eds., Studies in Surface Science and Catalysis, Elsevier, Amsterdam, 109 (1997) 351-360.

11 E.M. Sadovskaya, A.P. Suknev, L.G. Pinaeva, V.B. Goncharov, B.S. Bal'zhinimaev, C. Chupin, C. Mirodatos, *J. Catal,* 2001, 201, 159-168.

12 E.M. Sadovskaya, A.P. Suknev, L.G. Pinaeva, V.B. Goncharov, B.S. Bal'zhinimaev, C. Chupin, J. Pérez-Ramírez, C. Mirodatos, *J. Catal*, 2004, 225, 179-189.

L-4

IN SITU AND *OPERANDO* MAS NMR SPECTROSCOPY IN HETEROGENEOUS CATALYSIS: ADVANCES AND PERSPECTIVES

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The growing role of heterogeneous catalysis in chemical technology, biotechnology and ecology has been repeatedly emphasized during the last years. However the progress in this field, in particular, in tuning and mastering of the catalytic properties of the existing catalysts and in the development of new methods of catalyst preparation is limited because of the lack of detailed information on the reaction mechanisms and the nature of active sites. Heterogeneous catalytic reactions are usually studied by analysis of the desorbed reactants and products. This method however does not give information on "working" catalyst directly in course of the catalytic reaction. This information can be best obtained by means of recently developed *in situ* and *Operando* spectroscopic techniques (IR, UV-vis, ESR, NMR, etc.), among which NMR spectroscopy is considered to be one of the most informative.

The aim of this contribution is to review the advances in the *in situ* and *Operando* MAS NMR techniques for the unravel of the mechanisms of heterogeneous catalytic reactions. In the first part of the lecture, the different techniques for NMR experiments in static and flow conditions will be briefly considered. The experimental approaches including temperature-switch and pulse-quench methods, aimed at the investigation of fast reactions and stopped-flow and separated-step techniques, directed at the study of stable reaction intermediates in continuous flow and batch conditions will be discussed.

In the second part, the main application areas and the capabilities of the MAS NMR techniques will be analyzed. It will be demonstrated that *in situ* and *Operando* MAS NMR techniques can be used for the determination of surface active sites and their interaction with adsorbed reactants; the analysis of the state and mobility of adsorbed reactants and products; the identification of surface species formed and the investigation of their reactivity; the direct observation and the indirect identification of reaction intermediates; the studies of reaction kinetics; the observation of real primary products; the probing of reaction mechanisms using ^{13}C tracing techniques and various probe molecules (H_2, O_2, H_2O, CO, C_6H_6 etc.); finally, the direct observation of the shape selectivity, confinement effects in molecular-sieve catalysts and catalysts deactivation.

The advantages of the MAS NMR techniques will be illustrated with examples taken from the literature. The emphasis will be made on the reactions, for which *in situ* and *Operando* MAS NMR was of particular help for the understanding the reaction mechanism. Three types of reactions will be considered in more details: catalytic conversion of olefins and alcohols over acidic zeolites, alkanes activation over bifunctional zeolite catalysts and alkylation of polar aromatics with alcohols over acidic and basic zeolites.

In the case of the reactions of olefins and alcohols the main attention will be focused at the determination of the intermediate species formed over zeolite catalysts using NMR techniques. In particular, the formation of alkoxide or carbenim ion type intermediates will be discussed. Methanol conversion will receive a special attention, due to the unique peculiarities of the mechanism of its transformation on zeolites and zeolite-like materials. In this case, the key question will be the mechanism of C-C bond formation.

While discussing the conversion of alkanes, the main emphasis will be given to the application of in situ ^{13}C tracer techniques and H/D exchange between zeolite protons and deuterated compounds, which were of great help for the elucidation of the mechanism of this class of reactions. A special attention will be focused at the studies of the early stages of light alkanes transformation over Ga- and Zn-containing zeolite catalysts, which show the best performance in aromatization. Different mechanisms proposed for propane activation over Ga- and Zn-containing zeolites will be considered in detail.

Finally, in the case of alkylation reaction, the application of ^{13}C MAS NMR techniques for the determination of the main reaction intermediates and elucidation of the mechanisms of N-, O- and C-alkylation of aromatic compounds over acidic and basic zeolite catalysts will be reviewed.

In the last part of the lecture, the perspectives of the *in situ* and *Operando* MAS NMR techniques will be considered.

Acknowledgments

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STUDIES ON MECHANISMS OF CATALYTIC REACTIONS

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For a long time, studying the mechanisms of catalytic reactions is an attractive task for many researchers. For homogeneous catalytic reactions, there are many excellent examples of elucidation of the mechanisms. Success of these studies has been achieved by application of a number of physical methods. More complex situation is observed for heterogeneous catalytic reactions. The real solid catalysts are morphologically complex multi-component systems, often with microscopic dimensions that limit the application of surface sensitive physical methods to elucidate the nature of the catalyst active sites. To tackle this problem surface science approach to heterogeneous catalysts has been developed. This approach uses simplified model versions of real catalytic systems. Undoubtedly, the profound fundamental investigations, using various spectroscopic and structural surface science techniques have yielded very important detailed information about (i) the elementary steps of surface reactions, as molecular dissociation, adsorption, desorption and interaction between the species present on the surface, (ii) the response of the surface geometric and electronic structure to the presence of atoms and molecules, which are participants in the catalytic reactions, (iii) the surface dynamics, such as propagation of reaction fronts and related to that formation of stationary patterns, which may act as local chemical micro-reactors, etc. This information provides basic knowledge about the elementary steps of the surface reactions used in modeling the chemical reactivity and the mechanism of the catalytic processes.

The major drawback of this ‘bottom-up’ approach is so-called ‘pressure gap’. The realistic operation pressures in catalytic reactions are orders of magnitude higher and the chemical potential of the gas, neglected in the UHV experiments, becomes significant contribution to the free energy of the surface layer. This means that the structures monitored under non-realistic UHV conditions does not necessarily involve the equilibrium structures that play role in the catalytic reaction. Along with classical thermodynamic considerations, the significant changes in the morphology of the catalysts can occur, due to dynamic structural rearrangements induced by the reaction participants. The compositional and structural changes of the catalyst surface exert dramatic effect not only on the reaction mechanism.

Physical methods working at high pressures should be applied to tackle this problem. Following this tendency, researchers have developed recently a number of novel physical methods and have modified existing ones for *in situ* measurements at higher pressures.

Among them are X-ray absorption and X-ray photoelectron spectroscopy (XAS and XPS), infra-red absorption spectroscopy (IRAS), polarization-modulated (PM) IRAS, sum frequency generation (SFG) spectroscopy, etc. However, the measurements in millibar pressure range do not mean a-priori *in situ* investigation of the mechanisms of catalytic reactions, since the surface species observed on the catalyst surface under realistic conditions can be not catalytically active or the reaction intermediates. To avoid this disadvantage, *in situ* surface analysis has to be combined with the testing of catalytic properties using mass-spectrometry.

In this presentation I will demonstrate the efficiency of this approach on a number of examples: oxidation of CO over Pt(110) surface; methanol dehydrogenation over Pd(111); partial oxidation of methanol to formaldehyde over copper and ethylene epoxidation over silver. It has been demonstrated that in all cases increase in pressure of reaction mixtures leads to catalytically active species which are not observed under high vacuum conditions. The nature of these species has been identified with surface science methods, and the conclusion about their role in catalytic reactions has been made. On the basis of these data the mechanisms of the above mentioned reactions have been developed or defined more exactly.

For example, ethylene epoxidation over silver polycrystalline foil has been studied using *in situ* XPS and proton transfer reaction mass-spectrometry (PTR-MS). Silver is shown to be practically inactive to synthesis of ethylene oxide at $T \leq 100°C$ due to blocking the surface with carbonate groups CO_3^{2-} and adsorbed carbon-containing species CH_x. When the sample is heated to 150°C, the carbonates are decomposed and CH_x species burnt, ethylene oxide being detected by PTRMS among the reaction products at the reaction mixture (O_2 + C_2H_4) pressure higher than 0.1 mbar. There are two types of adsorbed oxygen species, nucleophilic and electrophilic, on the active silver surface. The further heating leads to an increase in the C_2H_4O yield but the surface is deactivated that is most likely due to the surface blocking with the surface oxygen species. A relationship is established between the ethylene oxide yield and the concentration of electrophilic oxygen. A change in slope of the relevant plot allows the activation energy of the key stage to be determined (~ 50 kJ/mol), this being identical to the literature data for epoxidation of C_2H_4. These data lead to conclude that the electrophilic oxygen is an ethylene epoxidizing species. Based on this result along with the data of isotope experiments obtained before, a new reaction mechanism is suggested which involves three pathways for the formation of the complete oxidation products CO_2 and H_2O: one is the interaction of ethylene with nucleophilic oxygen, another is mediated by acetaldehyde formed through the same intermediate (oxametallocycle) as ethylene oxide and last one is secondary oxidation of ethylene oxide.

This and other examples of model investigations of catalytic systems indicate unambiguously that *in situ* study of the surface of an operating catalyst allows one to elucidate real reaction mechanisms of heterogeneous catalytic reactions.

L-6

STUDY OF CATALYST MICROSTRUCTURE

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The key issue for the rational design of novel high-performance catalyst with low cost and long life time is the knowledge about the activity-structure correlation at the atomic scale. Electron microscopy and the related techniques (Transmission and Scanning electron microscopy TEM and SEM, electron energy-loss spectroscopy EELS, Energy-dispersive X-ray spectroscopy EDXS) are very powerful and versatile research tools to investigate directly the local structure and chemistry of complex heterogeneous catalysts from the macroscopic to the atomic level. The powerful traditional approaches to exploring catalysts based on indirect chemical and spectroscopic methods, results from large areas are averaged. Constructing models of the structure and mechanisms of the changing reactions over complex catalysts needs more precise pictures of the process at nanometer range.

Modern high-resolution analytic electron microscopy provides local structural information at sub-nanometer resolution about the surface and the bulk of the sample, together with chemical, electronic and three-dimensional structural information. In this presentation, case studies using atomic-resolution environmental transmission electron microscopy for directly probing the catalyst´s behaviour during the reaction at the atomic level, field-emission low voltage high-resolution scanning electron microscopy, and Cs-corrected high-resolution transmission electron microscopy (Fig. 1) will be discussed addressing the fundamental issues of the materials and processes in catalysis.

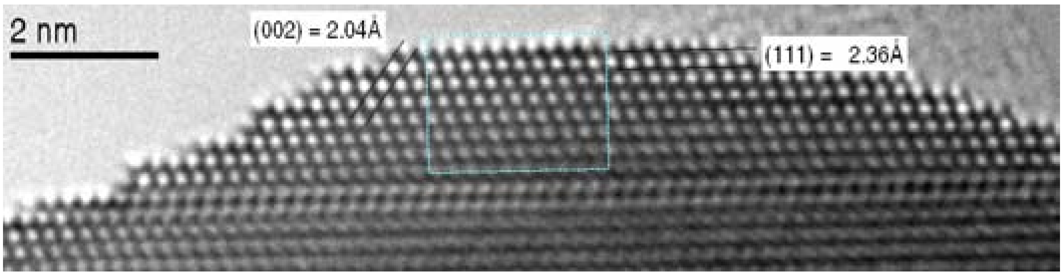

Fig. 1. High-resolution image of the surface profile of a working Ag/SiO_2 catalyst for hydrogenation of acrolein, taken on a Cs-corrected field-emission TEM. The image reveals the steps and kinks that may accommodate the active sites.

Besides the well-known structural information provided by TEM with a spatial resolution adequate to distinguish each phase individually, electron energy-loss spectroscopy (EELS) provides a series of information, for instance, the distribution of light elements, sample thickness, crystallographic structure, bond character and electronic structure. The combination of electron energy-loss spectroscopy with TEM makes spatially resolved studies possible and structure-property relationships can be explored in greater detail with this source of spatially resolved information. This is an excellent advantage of EELS/TEM compared with conventional X-ray spectroscopy.

SEM utilizes a focused electron beam that scans across the surface of a sample. SEM is widely used to characterize the surface topography of bulk powders or pellets. New ultra high-resolution low-voltage SEM with field emission gun, integrated with high-sensitivity EDXS has become nowadays commercialized to explore high-resolution imaging and chemical microanalysis in reflection from bulk samples.

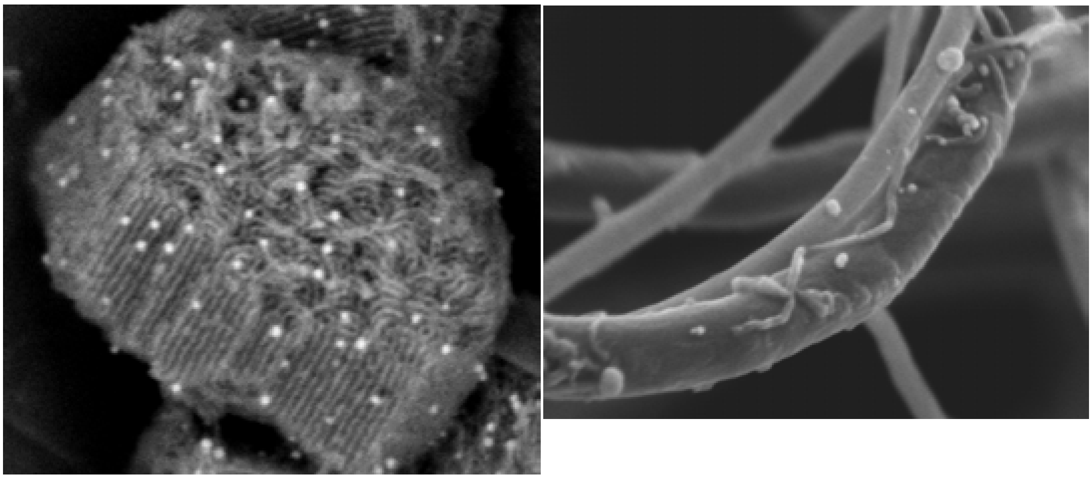

Fig. 2. left, Ag nano-particles supported on SAB-15. The ordered meso-channels of the silicate is cleared imaged. Right: Surface morphology of a multi-walled carbon nanotubes.

Examples of data analysis using TEM, SEM, electron diffraction, EELS and EDXS will be presented in the study of Ag/SiO_2 for hydrogenation of acrolein, nanocarbon for dehydrogenation of ethylbenzene, MoO_x/carbon for selective oxidation of *n*-butane.

L-7

THE ROLE OF THE FERMI SURFACE IN ADSORBATE-METAL INTERACTIONS: AN ENERGY DECOMPOSITION ANALYSIS

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The interpretation of chemical bonding and reactivity has been greatly aided by the development of energy decomposition methods, which afford a quantification of concepts such as Pauli repulsion, electrostatic interaction, (frontier) orbital interaction [1]. Such concepts have been based primarily on orbital models such as the Hartree-Fock model. The Kohn-Sham model of DFT also uses molecular orbitals. It is sometimes stated that the Kohn-Sham MOs do not have physical meaning, in the same sense as the Hartree-Fock orbitals do. We will argue that, on the contrary, Kohn-Sham MOs are physically quite sensible, and indeed have advantages over Hartree-Fock orbitals, and maybe over any orbitals defined to date. The Kohn-Sham orbitals are indeed eminently suitable for energy decomposition analyis of chemical bonding [2]. The Kohn-Sham orbital energies are likewise physically meaningful, being closely related to ionization energies [3].

We will in this lecture start with a brief overview of elementary concepts of chemical bonding in the case of finite systems (molecules). Traditionally, much emphasis has been put on the frontier orbital interactions, and on bonding interactions in general. We will, however, stress the importance of the Pauli repulsion, which is a direct consequence of the Pauli principle. Repulsive interactions are equally important as bonding interactions. They determine for instance the inner repulsive wall of the potential energy curve when one varies a bond length. They also cause steric hindrance. And most important for reactivity: they also cause the existence of transition state barriers for most reactions.

It is possible to highlight the importance of steric repulsion by using energy decomposition methods in which an energy component like the Pauli repulsion is explicitly evaluated. Together with the evaluation of electrostatic interactions between (molecular) fragments and orbital interaction energies (both donor-acceptor type of interactions and electron pair bond formation) they afford a virtually complete analysis of chemical bonding. The actual calculation of energy components was introduced in quantum chemistry by Morokuma a long time ago [4], and is now standard in available codes like ADF [5].

In order to understand the special role of metal surfaces in catalysis, we need to apply similar energy decomposition methods as used for molecules to infinite periodic systems. We will discuss the extension of energy decomposition methods to extended systems, in particular for chemisorption of a molecule on a metal slab. This introduces a new energy component, which we call the relief of the Pauli repulsion due to the existence of the Fermi level in the metal: antibonding levels that rise above the Fermi level will not remain occupied, but they will be depleted by electrons falling down into the Fermi sea. In finite systems, there is a HOMO-LUMO gap, and the destabilization of occupied orbitals due to occupied-occupied antibonding interactions, which embody the steric (Pauli) repulsion, can continue until the highest antibonding level "meets" the lowest empty level. This causes the transition state barrier. When electrons are transferred to the empty level, other bonds are formed, i.e. the reaction proceeds. If there is no gap between occupied and unoccupied states, as in metals, the antibonding states much sooner "meet" empty levels. The antibonding electrons are transferred to states at the Fermi level, preventing that a high barrier is built up.

We will use our implementation of an energy decomposition method for a periodic system to highlight the significance of a Fermi level in metallic systems as the key factor that gives them their singular reactivity properties, which are so much exploited in heterogeneous catalysis.[6] As a typical example we will discuss the difference in transition state barrier for H_2 dissociation over Cu (a barrier of ca. 0.5 eV) and over Pd (no barrier).

[1] F. M. Bickelhaupt, E. J. Baerends, Rev. in Comp. Chem. Vol. 15, pp 1-86 (2000).
[2] O. V. Gritsenko, R. R. T. Schipper, E. J. Baerends, J. Chem. Phys. 107 (1997) 5007.
[3] D. Chong, O. Gritsenko, E. J. Baerends, J. Chem. Phys. 116 (2002) 1760
[4] K. Morokuma, J. Chem. Phys. 55 (1971) 1236; K. Kitaura, K. Morokuma, Int. J. Quantum Chem. 10 (1976) 325.
[5] C. Fonseca-Guerra, J. G. snijders, G. te Velde, E. J. Baerends, Theor. Chem. Acc. 99 (1999) 391; G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca-Guerra, S. j. A.van gisbergen, J. G. Snijders, T. Ziegler, J. Comput. Chem. 22 (2001) 931
[6] P. H. T. Philipsen, E. J. Baerends, J. Phys. Chem. B 110 (2006) 12470

L-8

IN SITU METHODS FOR THE SURFACE CHARACTERIZATION OF CATALYSTS

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Surface microscopy and surface spectroscopy have made significant advances in recent years. Processes on planar model catalysts as well as on high-surface-area technical catalysts can now be studied under realistic catalytic conditions, i.e. at mbar to bar gas pressure. For technical catalysts we may utilize in situ (or high-pressure; HP) spectroscopic and microscopic methods, such as in situ infrared spectroscopy (FTIR), HP-X-ray photoelectron spectroscopy (HP-XPS) and environmental transmission electron microscopy (ETEM). Nevertheless, the complex (porous) structure of technical catalysts makes such studies often very difficult to interpret.

Planar model catalysts, prepared under well-controlled conditions, allow for an easier approach, provided that the models mimic a real catalyst sufficiently well. The recent development of *nanoparticle model catalysts*, consisting of well-defined metal particles supported on thin oxide films, now provides a route to model an increasing number of technical catalysts [1-3]. Thin (~nm) crystalline oxide films are grown on suitable conducting substrates and provide the support for noble metal nanoparticles. Preparation under ultrahigh vacuum (UHV) using ultra pure materials guarantees the absence of undesired elements that are sometimes difficult to avoid (and detect) for conventional catalysts. The mean particle size (~2-10 nm) as well as the particle morphology and defect structure can be accurately controlled (Figure 1). Furthermore, the planarity and electrical and thermal conductivity of the model systems allows applying a wide range of surface sensitive imaging (STM) and spectroscopic (XPS, IRAS, SFG, TPD, etc) techniques. To date, various combinations of Pd, Pt, Rh, Ag, Au, Pd/Co, etc nanoparticles supported by Al_2O_3, SiO_2, Fe_3O_4, Nb_2O_5, etc have been examined.

In parallel, significant advances have been made in carrying out model studies under non-UHV conditions, i.e. at mbar to atmospheric pressure. Photon-based methods such as sum frequency generation (SFG) vibrational spectroscopy [1,3,4] or polarization-modulation infrared reflection absorption spectroscopy (PM-IRAS) [1,5], together with high-pressure X-ray photoelectron spectroscopy (HP-XPS) [6] and high-pressure scanning tunneling microscopy (HP-STM) are among the prime techniques for *in situ* studies of surface processes or catalytic reactions on model systems. Nevertheless, studies on single crystals as well as “classical” UHV experiments are still inevitable to better understand the ambient pressure processes.

Combining nanoparticle model catalysts with *in situ* surface spectroscopy at elevated pressure, utilizing suitable UHV-systems equipped with high-pressure reaction cells connected to on-line gas chromatography [1], now allows monitoring catalytic reactions under conditions approaching technical systems. The model studies can then help in the interpretation of in situ studies on technical catalysts, e.g. by FTIR, HP-XPS and ETEM.

In this lecture, a number of case studies will be presented, dealing both with *model and real catalysts*, including CO adsorption and hydrogenation [7,8,10,11], partial methanol oxidation [5] and olefin and diene hydrogenation [7,8,9], carried out on e.g. Pd-Al_2O_3, Pd-Nb_2O_5 and Pd-Fe_3O_4 model catalysts.

For example, Figure 1 shows PM-IRAS spectra measured during methanol decomposition and oxidation on Pd [5], which eventually revealed that the reaction proceeded via methanol dehydrogenation to CH_2O, which either desorbed or was further dehydrogenated to CO and subsequently oxidized to CO_2. Although the observed vibrational frequencies of adsorbed CO were compatible to metallic Pd, XPS spectra pointed to a partial oxidation of Pd nanoparticles under reaction conditions. XPS also detected significant amounts of CH_x species that were present during the oxidation reaction. Time-dependent PM-IRAS and XPS measurements at low pressure (~10^{-5} mbar) showed a correlation between the formation of CH_x and of CH_2O which suggests a favourable effect of CH_x on the reaction selectivity [5]. The CH_x layers were further analyzed by STM.

Corresponding studies on well-defined technical (impregnated) catalysts will be utilized to illustrate the close relationships between real and model systems [10,11]. Finally, examples for more complex catalysts (SMSI on Pd-Nb_2O_5 [12]) and for more complex reactions (selective butadiene hydrogenation [9]) will be discussed.

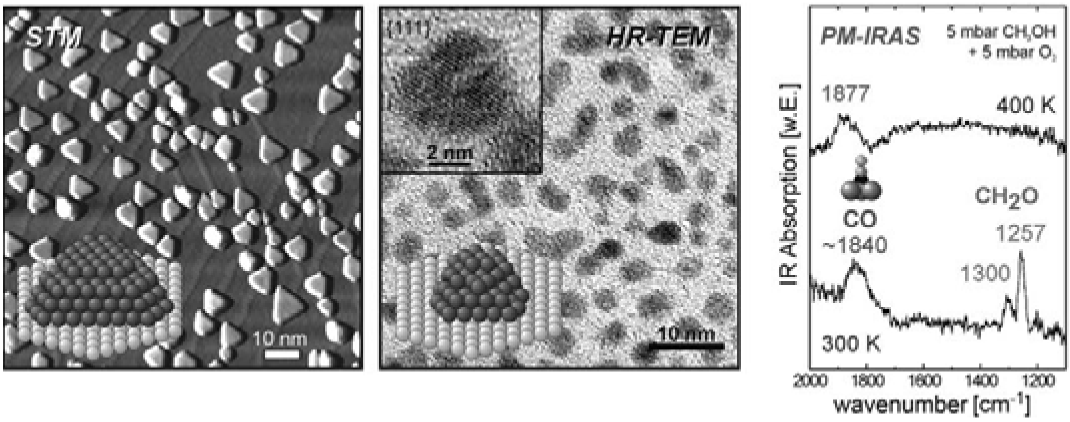

Figure 1: *STM and HR-TEM images of planar Pd-Al_2O_3 model catalysts [1,2]. In situ PM-IRAS spectra of methanol partial oxidation on a Pd model catalyst are shown on the right, displaying only signatures of surface adsorbed species [5].*

[1] G. Rupprechter, Annu. Rep. Prog. Chem. (C) 100 (2004) 237.
[2] H.-J. Freund, M. Bäumer, J. Libuda, T. Risse, G. Rupprechter, S. Shaikhutdinov, J. Catal. 216 (2003) 223.
[3] G. Rupprechter, H.-J. Freund, Topics in Catalysis 14 (2001) 3.
[4] G.A. Somorjai, G. Rupprechter, J. Phys. Chem. B 103 (1999) 1623.
[5] M. Borasio, O. Rodríguez de la Fuente, G. Rupprechter, H.-J. Freund, J. Phys. Chem. B Letters 109 (2005) 17791.
[6] M. Morkel, V.V. Kaichev, G. Rupprechter, H.-J. Freund, I.P. Prosvirin, V.I. Bukhtiyarov, J. Phys. Chem. B 108 (2004) 12955.
[7] G. Rupprechter, M. Morkel, H.-J. Freund, R. Hirschl, Surf. Sci. 554 (2004) 43.
[8] M. Morkel, G. Rupprechter, H.-J. Freund, Surf. Sci. Letters 588 (2005) L209.
[9] J. Silvestre-Albero, G. Rupprechter, H.-J. Freund, Chem. Communications 2006, 80.
[10] T. Lear, R. Marshall, J.A. Lopez-Sanchez, J.M. Winfield, S.D. Jackson, T.M. Klapötke, M. Bäumer, G. Rupprechter, H.-J. Freund, D. Lennon, J. Chem. Phys., 123 (2005) 174706.
[11] S. Bertarione., D. Scarano, A. Zecchina, V. Johanek, J. Hoffmann, S. Schauermann, J. Libuda, G. Rupprechter, H.-J. Freund, J. Phys. Chem. B, 108 (2004) 3603.
[12] F. Höbel, A. Bandara, G. Rupprechter, H.-J. Freund, Surf. Sci. 600 (2006) 963.

L-9

POLYOXOMETALATES AS CATALYSTS FOR FINE CHEMICAL SYNTHESIS

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The chemistry of polyoxometalates (POM), also known as heteropoly compounds, is a rapidly developing field interconnected with many disciplines. Among numerous applications of POM, catalysis is by far the most important [1-5], followed by electrochemistry (e.g. proton conductive membranes, solid electrolytes and sensors), separation (selective adsorbents), analytical chemistry, etc. [5]. Arguably, catalysis by POM is one of the most successful areas in fundamental and applied catalysis in the last few decades.

POM are composed of heteropoly anions (nanosized metal-oxygen cluster anions) and countercations (e.g. H^+, metal ions, etc.) [1,3]. Many structural types of POM are known to date. The best known and most important for catalysis POM adopt the Keggin structure which involves heteropoly anions of the formula $[XM_{12}O_{40}]^{n-}$ (Fig. 1), where M is the addenda atom (Mo^{6+}, W^{6+}, V^{5+}, etc.) and X is the heteroatom (P^{5+}, Si^{4+}, B^{3+}, etc.). The Keggin anion is composed of a central tetrahedron XO_4 surrounded by 12 edge- and corner-sharing metal-oxygen octahedra MO_6. Typical examples are heteropoly acids $H_3[PW_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$ and $H_3[PMo_{12}O_{40}]$ which are commercially available and widely used for catalysis.

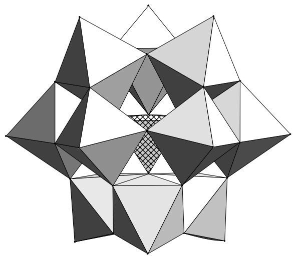

Fig. 1. The structure of Keggin anion.

As catalysts, POM have several advantages, with *multifunctionality* and *structural mobility* the most important [1,3]. On the one hand, they have a very strong Brønsted acidity (heteropoly acids, HPA); on the other, they are efficient oxidants. Their acid-base and redox properties can be varied over a wide range by changing the structure and chemical composition of POM. In the last three decades, POM have found application as acid and oxidation catalysts in several large-scale industrial processes such as hydration of olefins, oxidation of methacrolein to methacrylic acid, oxidation of ethylene to acetic acid and synthesis of ethyl acetate [3].

Due to their enormous versatility POM have the potential to be used effectively as catalysts for clean synthesis of fine and specialty chemicals, offering significant economical and environmental benefits [3,4]. The aim of this lecture is to discuss the scope of application of POM as the catalysts for fine chemical synthesis. The main focus is on the acid and oxidation catalysis by POM in homogeneous, heterogeneous and biphasic reactions in liquid phase. These involve many practically important reactions such as acid-catalyzed Friedel-Crafts alkylation and acylation [6], hydration, esterification, isomerisation and condensation [4]; selective oxidation of organic compounds by oxygen and hydrogen peroxide [7]; and cascade reactions using multifunctional catalysts based on POM [8].

References

1. T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* 41 (1996) 113.
2. M. Misono, *Chem. Commun.* (2001) 1141.
3. I.V. Kozhevnikov, *Catalysts for Fine Chemical Synthesis, Vol. 2: Catalysis by Polyoxometalates*, Wiley & Sons, Chichester, England, 2002, pp. 216.
4. I.V. Kozhevnikov, *Chem. Rev.* 98 (1998) 171.
5. D.E. Katsoulis *Chem. Rev.* 98 (1998) 359.
6. I.V. Kozhevnikov, *Appl. Catal. A* 2003, 256, 3.
7. J.M. Brégeault, *Dalton Trans.* (2003) 3289.
8. R.D. Hetterley, E.F. Kozhevnikova, I.V. Kozhevnikov, *Chem. Commun.* (2006) 782.

L-10

RECENT TRENDS IN CATALYSTS PREPARATION

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The first part of this talk will review some examples of the most up-to-date trends in catalysts preparation, as presented at the *9th International Symposium on the Scientific Bases for the Preparation of Heterogeneous Catalysts* (held in Louvain-la-Neuve on Sept. 10–14, 2006). Nowadays the range of materials used as catalysts is as wide as ever, and the techniques used to prepare them vary as much as their nature. However, some general tendencies can be identified and summarized, by taking as a basis the content of the keynote lectures of the Symposium.

First, microporous and mesoporous oxides remain useful and highly selective catalysts, hence the techniques developed for their synthesis are continuously refined. Research in this area focuses mainly on preparing composite materials with tailored properties, and understanding/directing the effect of the templating agents. Post-synthetic modifications, such as surface grafting and functionalization, play an important role in defining the final physico-chemical characteristics of the porous solids.

Secondly, an important parameter than can now be controlled is particle size, with a general trend towards keeping it in the nanometer range, this being true for the grains of bulk oxides or the metallic/oxide particles of supported catalysts. In particular, the deposition-precipitation technique is very useful to control the size of supported metallic particles. Other aspects of the oxide or support morphology that may be controlled through the preparation method are the porosity, grain shape or crystal phase. Going one step further, investigations aim at preparing nano-structured or hybrid materials, with not only a control on the size but also on the chemical nature of each building block. Support functionalization is sometimes the starting point of such a synthetic strategy, but sol-gel and colloidal chemistry are also widely used. In parallel, the development of macroscopic structures such as monolith, foams, layered materials or films is also important, with crucial questions related to scaling up.

Thirdly, much effort aims today at rational syntheses or preparation methods that are controlled at each step. These developments are usually linked to the application of *in situ* characterization techniques, which allow the monitoring of the catalyst at each stage of its genesis. In this context, the use of model systems, atomically-defined, is another useful tool.

Finally, recent ideas, such as bio-mimetic strategies or the concepts of self-assembly, are also applied to catalysts preparation. The introduction of polymers (or dendrimers) as supports, within a composite, or as sacrificial matrixes, is also an emerging field. Relatively recent techniques, such as the use of microwaves, magnetron sputtering, supercritical fluids, inductive plasma torch, flame spray pyrolysis, CVD, *etc.* are developed as well for solid materials synthesis.

The second part of this talk will be devoted to specific examples developed in our own research groups. The first example concerns the use of zwitterionic polymers as sacrificial matrices for the preparation of well-defined transition metal oxides. The idea here is to use the charges of opposite signs present on the polymer backbone to direct the interaction with metal salts, in order to ensure site-isolation and high dispersion. The hybrid organic-inorganic species is then calcined to produce the desired oxide.

The second example also takes advantage of electrostatic interactions at the precursor stage. It is based on the idea that by knowing the point-of-zero charge of a carbonaceous support and the nature of metallic species present in aqueous solution over the whole pH range, it is possible to optimize the metal species/support interaction during impregnation and hence the final dispersion. This has been applied to the preparation of Pd/C catalysts to be used in liquid-phase selective oxidations. To direct even more the interactions between metallic precursors and support, the concept of grafting has been applied in our groups for various applications. First, palladium complexes have been grafted onto oxygenated functions formerly introduced on a carbon surface. Secondly, organic (alkoxides) or inorganic (chlorides) precursors have been used to modulate the properties of inorganic oxides by grafting. The obtained catalysts are active in methane selective oxidation and combustion.

The last example concerns the use of molecularly defined hetero-metallic precursors to prepare, from a single source, multi-metallic oxides or bimetallic supported catalysts. For instance, hetero-polyacids of the early transition metals or noble metal cluster compounds may be used to produce oxides or bimetallic nanoparticles, respectively.

L-11

DEVELOPMENT OF CATALYTIC REACTORS CONTAINING ZEOLITE FILMS AND COATINGS

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A strong interest has emerged on the development of zeolite coatings on a variety of surfaces of industrial interest. These zeolite films constitute a special type of nanostructured interfaces capable of very specific interactions with individual molecules. Because of this, in many cases it is possible to implement molecular recognition functions, resulting in selective transport across the interface, in addition to exploiting other well known zeolite properties such as their catalytic properties and adsorption capabilities. This lecture reviews examples of zeolite films for reaction and reaction/separation applications.

Zeolites have a remarkable ability to grow, either as individual crystals or as films on a wide variety of supports. This has made them ideal candidates for applications where a large contact area per unit volume is required. Progress on the growth of zeolite films (mostly in the form of membranes) has been the subject of a number of reviews in recent years [e.g., 1-3]. In this work some recent developments, taken mainly from our own laboratory are presented, concerning new applications of zeolite films. These include membrane reactors, where reaction and separation processes are combined, unconventional uses of membranes (e.g. in electrochemical sensors or in drug-delivery capsules) and applications where a zeolite film is grown on a structured support to provide a high surface area per unit volume to be used in adsorption and/or reaction applications.

Zeolite membrane reactors

The uses of zeolites include both conversion-enhancement (e.g., product permeation in equilibrium-limited reactions, removal of inhibitors), and selectivity-enhancement (extraction of valuable intermediate products in consecutive reaction networks, control of the residence time of different species in the reactor) applications. As a consequence, zeolite membranes have been advocated for a variety of esterification reactions, Fischer-Tropsch processes, dehydrogenation of isobutane or ethylbenzene, isobutene oligomerization, etc.

Zeolite-modified sensors

Zeolites have attracted considerable attention in the field of chemical sensors, both reactive and non-reactive with the aim of increasing their sensitivity and selectivity [e.g. 4-6]. We have shown the advantages of zeolite films as selective barriers between the sensing element (Pd-catalyzed SnO_2) and the atmosphere in reactive gas sensors. Other research currently under way involves deposition of zeolite films on piezoelectric and capacitive sensors that use the adsorption properties of different zeolites. It is certainly possible to envision a battery of zeolite-coated mass sensors (QCMs, cantilevers) each responding mainly to a different species thanks to a zeolite coating that has been carefully tailored in terms of pore sizes, hidrophilicity and chemical affinity.

Zeolite films on structured supports and microreactors

The readiness of zeolite films to grow on a variety of surfaces has been used to prepare coatings on different supports, mainly for catalytic applications. Among recent developments in this field are the preparation of zeolite membranes on wire mesh supports [7] and on monoliths [8], where zeolite loadings of up to 50% by weight have been obtained, while preserving the accessibility of individual zeolite crystals.

Another area of rapid development concerns the microreactor field. Among the works in this area, Rebrov et al. [9] coated 500 μm channels on a stainless-steel plate with ZSM-5 crystals and used the resulting microreactor in the selective catalytic reduction of NO with ammonia. Yeung and coworkers [10] have used semiconductor fabrication procedures to prepare microreactors containing zeolite membranes and used them in several reactions. In our laboratory, we have prepared zeolite micromembranes on laser-perforated stainless steel sheets [11], a support that presents very interesting properties in terms of flexibility and heat exchange capability.

References

1. J. Caro, M. Noack, P. Kölsch and R. Schäfer, Micropor. Mesopor. Mater. 38 (2000) 3
2. Coronas, J., Santamaria, J., Topics in Catalysis 29, (2004), 29.
3. Coronas, J., Santamaría, J., Chem. Eng. Sci., 59, (2004), 4789.
4. S. Mintova, S. Mo, T. Bein Chem. Mat., 13 (2001) 901-905.
5. M Vilaseca, J Coronas, A Cirera , A Cornet , JR Morante, J Santamaria, Catal. Today., 82 (1-4): (2003) 179-185.
6. Vilaseca, M., Yagüe, C., Coronas, J., Santamaría, J., Sensors and Actuators B, in press.
7. López, F., Bernal, M.P., Mallada, R., Coronas, J., Santamaría J., Ind. Eng. Chem. Res., 44, 7629-32, (2005).
8. Ulla, M.A., Miro, E., Mallada, R., Coronas, J., Santamaría, J., Chem. Comm. 528, (2004).
9. E.V. Rebrov, G.B.F. Seijger, H.P.A. Calis, M.H.J.M. de Croon, C.M. van den Bleek, J.C. Shouten, App. Catal. A: Gen., 206 (2001) 125.
10. X. Zhang, E.S.M. Lai, R. Martín-Aranda, K.L. Yeung, App. Catal. A: Gen., 261 (2004) 109.
11. E. Mateo, R. Lahoz, G. Fuente, A. Paniagua, J. Coronas, J. Santamaría, Chem. Mat., 16, (2004) 4847.

L-12

ROUTES TO OLEFINS AND DERIVATIVES FROM THE NATURAL GAS WET FRACTION: CATALYSIS AND REACTOR ENGINEERING ASPECTS

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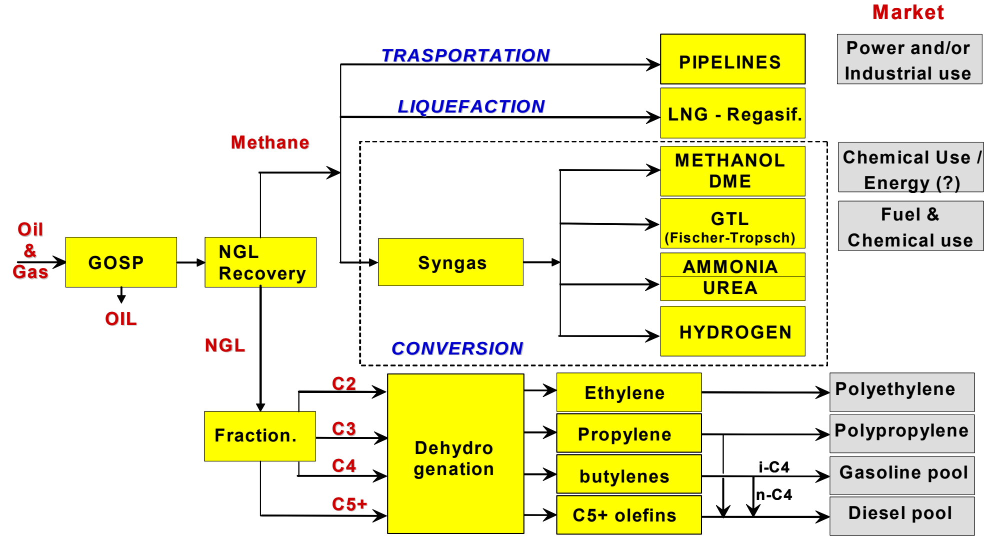
The World of Olefins

The vigorous development of the human society in the second half of the 20th century has been sustained by the use of Oil and Gas as energy sources, and as raw materials. Unfortunately, the geo-biological processes that generated the natural fossil resources have formed mainly saturated or aromatic hydrocarbons. As a consequence, available primary feedstock for chemical industry, contain mainly saturated, paraffinic and naphthenic hydrocarbons and *paraffins* generally show feeblish or unselective reactivity.

The manufacture of some of the most important chemicals, such as polymers, synthetic fibers, elastomers, detergents and fuel components, has been based on the use of molecules offering a definite attack point for further selective reactions, like olefins in particular. Therefore light olefins are favored feedstock fundamental and building blocks for the petrochemical downstream and the refining industry. Ethylene and propylene derivatives form the core of the commodities chemical industry and C_4–C_5 olefins are transformed into valuable components for fuels. Light olefins production requires sophisticated technologies highly demanding in terms of energy and investment, like cracking and deydrogenation.



Dehydrogenation reactions are practiced industrially for the dehydrogenation of light alkanes (propane to propylene for polymers and isobutane to iso-butylene for gasoline and polymers) as well as long linear ones (C_{10}-C_{14} to linear-alkyl-benzenes) and the dehydrogenation of ethylbenzene to styrene. The dehydrogenation of alcohols to ketones and aldehydes is another reaction worth mentioning. The light paraffins dehydrogenation sustains a network of technologies allowing an integrated approach to create value from Natural Gas.

Dehydrogenation Characteristics

Dehydrogenation reaction characteristics give some constraints to its technological implementation.

- Conversion is limited by thermodynamics and equilibrium conversion increases with temperature. Commercially viable conversions require reaction temperature exceeding 500 °C.
- Dehydrogenation is strongly endothermic resulting in a higher heat demand.
- Reactions increase the number of moles: High pressure adversely affects the reactions.
- Coke is a fatal by–product formed on the catalyst. A catalyst periodical regeneration is mandatory.

Dehydrogenation Catalysts

The main types of dehydrogenation catalysts reported in the patent and scientific literature are: a) supported platinum/tin, with promoters (for light and C_{10}-C_{14} paraffins); b) Chromium oxides on alumina or zirconia, with promoters (for light paraffins); c) Fe oxides, with promoters (for EB to SM); d) Cu for alcohols to aldehydes. Recent literature is paying attention to Ga oxide supported or included in zeolites. The principles of conceptual catalyst design are described.

Dehydrogenation in industrial applications

The promoted and optimized catalytic systems Pt-Sn/Al_2O_3 and Cr_2O_3/Al_2O_3 show comparable performances in terms of selectivity to olefins.

A periodical regeneration with air is mandatory for all the catalysts to burn off the coke exposing the catalysts to alternating oxidizing and reducing atmospheres.

Heat must be supplied to the process stream at temperature above 550 °C in such a way that it reduces the reactor ΔT within the range of catalyst activity (< 50-60 °C)

These constraints have stimulated the fantasy of engineers in finding suitable solutions. Available technologies are characterized by different choices as concerns the system catalyst / heat supply mode / catalyst regeneration mode.

Commercial dehydrogenation technologies are Catofin (Houdry Technology), Oleflex, STAR (Steam Activated Reforming), PDH (Propane Dehydrogenation) and FBD (Fluidized Bed Dehydrogenation).

Future of Olefin Technologies

An impressive number of attempts by R&D are devoted to the development of improved or new routes to olefins. Only a few have real chances of being developed into commercial technologies because of the intrinsic technical and economic difficulties connected with the feedstock value/availability.

<u>Pacing technologies for olefins are following several routes:</u>

- Improvements of the dehydrogenation route with new catalytic formulations and/or new reactor concepts.
- The integration of ethylene or propylene production with their downstream use (e.g. production of styrene or cumene).
- Non-conventional cracking processes including catalytic steam cracking.
- Oxidative dehydrogenation of paraffins by burning the produced H_2, with molecular or "structural" O_2.

References

All relevant references are reported in: D. Sanfilippo, I. Miracca, Cat. Today 111, Jan. 2006, 133-139

L-13

CATALYTIC HYDROCARBON PRODUCTION

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Electronic structure methods based on density functional theory have reached a level of sophistication where they can be used to describe complete catalytic reactions on transition metal surfaces. This gives an unprecedented insight into these processes, and it allows us to pinpoint the origin of the catalytic activity of a metal in terms of its electronic structure. We use the approach to understand in detail the catalytic production of hydrocarbons, focussing in particular on the methanation reaction ($CO + 3H_2 \rightarrow CH_4 + H_2O$) [1]. It is discussed how the activation of CO depends on the metal and surface geometry and the d band model is introduced to understand these variations [2-4]. The full reaction is described theoretically, and it is shown that a volcano curve is found, when the activity is plotted against the dissociative CO chemisorption energy [5,6]. Finally, it is shown how this insight can be used to search for new catalysts [1].

1. M. Andersson, T. Bligaard, A. Kustov, J. Greeley, T. Johannessen, A. Larsen, C. H. Christensen, J. K. Nørskov, J. Catal. (2006) doi:10.1016
2. B. Hammer and J. K. Nørskov, Nature 376, 238 (1995).
3. M. Mavrikakis, B. Hammer, and J.K. Nørskov, Phys.Rev.Lett. 81, 2819 (1998).
4. A. Nilsson, L. G. M. Pettersson, B. Hammer, T. Bligaard, C. H. Christensen, J. K. Nørskov, Catal. Lett. 100, 111 (2005).
5. J.K. Nørskov, T. Bligaard, A. Logadottir, S. Bahn, L.B. Hansen, M. Bollinger, H. Bengaard, B. Hammer, Z. Sljivancanin, M. Mavrikakis, Y. Xu, S. Dahl, and C.J.H. Jacobsen, J. Catal. 209, 275 (2002)
6. T. Bligaard, J.K. Nørskov, S. Dahl, J. Matthiesen, C.H. Christensen, and J.S. Sehested, J.Catal. 224, 206 (2004)

L-14

MICROCHANNEL REACTORS IN CHEMISTRY AND CATALYSIS

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Fine chemistry applications

Significant revenue shares for fine-chemical plants refer to raw-material supply, waste disposal, operator salaries, and finally the investment of the plant itself. Microstructured reactors may improve selectivity and in this way reduce the two first portions, leading to higher marginal income. In some preferred cases this can be achieved by simply transferring a batch protocol into a continuous-flow microreactor operation with increased mass and heat transfer and kinetically-derived (shorter) residence times. Often overlooked so far, however, is the potential of microstructured reactors for process intensification in the truest sense, i.e. an order-of-magnitude change in productivity or respectively decrease in plant size per given production rate, targeting the latter two cost portions. This is achieved by not only exploiting the engineering potential of microstructured reactors, but by using the latter to utilize essentially novel organic chemistry – e.g. at high temperatures combined with high pressures and very short residence times, say {>200°C; >50 bar; <1 s} – alike gas-phase chemistry, termed 'high-p,T processing'. Other means are the solvent-free processing, reduction of steps in multi-step synthesis, simplification of protocols, and exploration of so far 'hidden' explosive regimes. At the example of the aqueous Kolbe-Schmitt synthesis to di- and tri-hydroxy benzoic acids, the 'high-p,T' concept will be demonstrated. Increases in productivity by three orders of magnitude were achieved. Mechanistic and calorimetric studies help to optimize further the reaction studies, e.g. by (high-pressure) DSC, TGA and EGA studies.

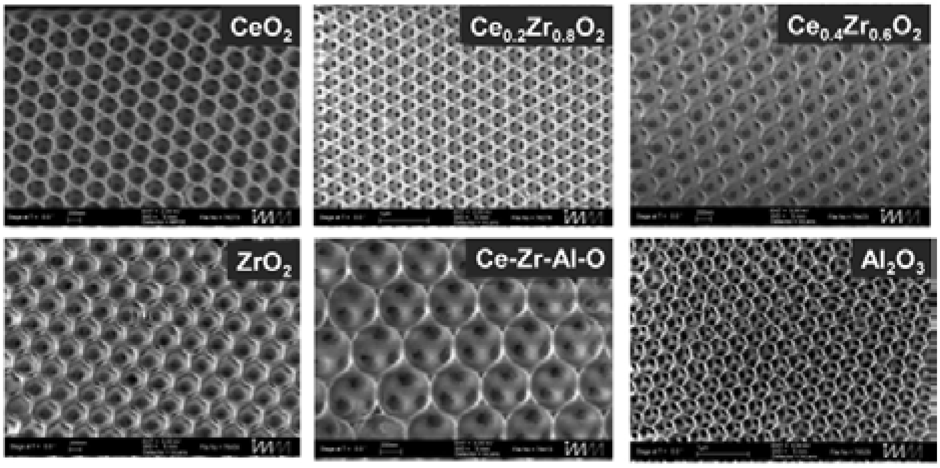
The commercial transfer demands for tailored reactor solutions meeting production demands and robust scale-out concepts in conjunction with competitive plant & process design to maximise annual earnings and RoI. Scale-out concepts to reach production (for 100 to a few 1000 t/a; or more) included use of simple pilot-sized micromixer-tube reactors in selected cases, internal and external numbering-up, multi-scaled architectures, plate architectures with no real dimensional limitation for width and length, substitution of structural by process approaches ('micro effects'), and plant upgrading by retrofit. The pharmaceutical nitroglycerine manufacture and the customized imidazole-based ionic-liquid synthesis will be presented. Cost analyses will be given for micro-chemical production plants, at the two extremes of operator-cost (above mentioned Kolbe-Schmitt synthesis) and high-value raw material (4-cyano phenyl boronic acid synthesis) dominance. The latter is a commercial chemical product of the custom manufacturer AzurChem, an IMM spin-off, using micro process technology.

Catalysis applications in fuel processing

Microstructured reactors provide both an entirely new reactor and processing concept with highly intensified mass and heat transfer, whereas their construction and operation may result in higher technical expenditure as compared to traditional reactors such as fixed-bed reactors. Thus, in order to fully exploit their beneficial properties at the expense of the drawbacks and the risk of facing the "unknown", the development of tailored catalysts and the reactor system design are and remain the major issues. Following today's dominant application, which is fuel processing for fuel cells, the main issues are described - catalyst and catalytic reactor development as well as system-level analysis.

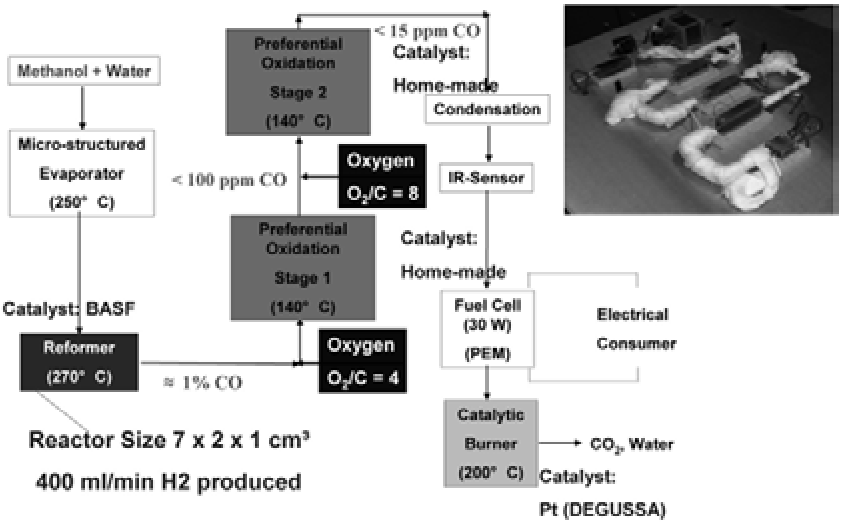
The finding of *highly active catalytic systems* is the major issue for alcohol fuels such as methanol and ethanol, since the operating temperature of the reformer itself is significantly lower compared to hydrocarbon reforming. On the contrary, catalyst activity typically is given for high-temperature micro-fuel processor operation, but then to have *catalyst stability* is most relevant. This holds for propane, butane and mixtures such as LPG. The higher operating temperature, normally exceeding 700°C, promotes catalyst deactivation, e.g. by sintering procedures. WHSV values of up to 2400 $Ndm^3/(h\ g_{cat})$ were achieved for the partial oxidation of propane. For gasoline, deactivation by coking gets more an issue compared to light hydrocarbons. The addition of air to the reformer feed is one viable option to cope with coking problems. Advanced *catalyst coating- and reactor material technology* is crucial for steam reforming of higher hydrocarbon fuels such as diesel due to the very high reaction temperature exceeding 800°C. A microstructured heat-exchanger / reactor was developed and operated for more than 40 hours already, which completely converts diesel fuel.

While much attention has so far been paid to the above mentioned reactor and process engineering as well as experimental catalyst studies, a *bottom-up engineering of the catalyst itself* for micro-channel layers is missing, with the goal to achieve a counterpart in regularity and functionality on the nano-scale to the microengineered reactor: 'structured reactors – structured catalysts'. As one first step, *highly homogeneous sub-micronscale catalyst structures* were prepared. These inverse-opal silica and alumina coatings owe uniform pore size, interconnected pore network with ordered structure and regular pore wall, and tailored surface properties and are being tested for preferential carbon monoxide oxidation and propane catalytic combustion.



Inverse opals as novel nanostructured catalyst carriers made out of different materials.

System integration is the final challenging task and will be exemplified by integrated plate heat-exchanger reactors for the combined propane steam reforming / propane combustion, diesel steam reforming / combustion and for the steam generation fed by hydrocarbon combustion. These devices are operated at temperatures >750°C and up to a size range of 5 kW_{el} of the fuel cells supplied. Cooling capabilities have been introduced into reactors designed for the partial oxidation of propane, the water-gas shift and the preferential oxidation of carbon monoxide. Balance-of-plant components such as cross-flow heat-exchangers working up to 900°C, evaporators, condensers and pre-heaters for fuel cells and fuel processors complete this list. At IMM, a complete fuel processor capable of feeding a 5 kW_{el} fuel cell and working with autothermal reforming of iso-octane as a model for gasoline has been assembled and successfully put into operation. At TU/e, issues of *heat management* were largely resolved for the preferential oxidation, which resulted in a tailored integrated design with three micro-structured heat exchangers and one reactor. *Flow distribution* issues were addressed for the same purpose. Recently, such complex reactor system modelling was extended to a process system engineering with an exergy analysis and a performance benchmarking to fixed-bed reactors.



Complete breadboard-type methanol fuel processor with fuel cell.

[1] Review: Kolb G., Hessel V., „Micro-structured reactors for gas phase reactions” *Chem. Eng. J.* **98** (2004) 1.

[2] Review: Hessel V., Löwe H., Müller, A., Kolb G., 2005, ’Chemical Micro Process Engineering - Processing, Applications and Plants’, Wiley, Weinheim, ISBN-13 978-3-527-30998-6, p.281 ff.

[3] Kolb G., Zapf R., Hessel V., Löwe H., *Appl. Catal. A: General* **277** (2004) 155.

[4] E.R. Delsman, B.J.P.F. Laarhoven, M.H.J.M. de Croon, G.J. Kramer, J.C. Schouten, J.C. *Chem. Eng. Res. Des.* **83**, A9 (2005) 1063.

[5] G. Kolb, H. Pennemann, R. Zapf *Catal. Today* **110** (2005) 121.

[6] V. Cominos, V. Hessel, C. Hofmann, G. Kolb, R. Zapf, A. Ziogas, E.R. Delsman, J.C. Schouten *Catal. Today* **110** (2005) 140.

[7] E.R. Delsman, M.H.J.M. de Croon, A. Pierik, G.J. Kramer, P.D. Cobden, C. Hofmann, V. Cominos, J.C. Schouten *Chem. Eng. Sci* **59** (2004) 4795.

CATALYTIC COMBUSTION FOR ADVANCED ENERGY GENERATION TECHNOLOGIES AND ENVIRONMENTAL PROTECTION

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For the past 20 years extensive R&D work on catalytic fuel combustion for energy production and the application of catalysis for environmental protection has been carried worldwide.

Catalytic combustion is proved to be effective technique for clean combustion of fuels. It is fundamentally different from traditional flame combustion because fuels are oxidized flamelessly on the surface of catalysts at relatively low temperatures: 400-1000 °C.

In many laboratories the fundamental research was conducted in following main directions:

- study of kinetics and mechanism of catalytic combustion of organic compounds of various nature (hydrocarbons, alcohols, amines, etc);
- synthesis and characterization of novel efficient combustion catalysts containing both transition metal oxides and noble metals. Methods of catalyst preparation in shape of granulated, honeycomb, fibrous, foam material supported, etc. have been developed.
- modeling of catalytic combustion
- development of technologies for practical application

A very attractive feature of catalytic combustion is the possibility to reduce drastically NO_x emissions. Rather low temperature of catalytic combustion allows nearly complete elimination of thermal NO_x. The problem of fuel NO_x control was reliably solved by studying kinetics of oxidation of a series of N-containing compounds, choosing selective catalysts and providing conditions of prevailing conversion of fixed N to N_2.

The future prospects of application of catalytic combustion for gas turbine catalytic chambers and organic fuel reformers for all types fuel cells will be discussed in detail.

A review of main types of processes and apparatuses for catalytic fuel combustion developed at BIC will be presented:

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Catalytic heat generators (CHG) based on the use of fluidized bed of granulated spherical catalyst particles with a capacity of 10-1000 kW. The CHGs provide high heat efficiency due to the use of fluidized bed and catalysts with high performance. Pilot and industrial CHGs were tested with various fuels: natural gas, diesel fuel, residual oil, etc. They were shown to be efficient for heat production, drying and thermal treatment of powder materials, treatment of dust loaded off-gases, treatment of waste water containing organic admixtures and hazardous organic wastes.

Catalytic air heaters working on natural gas with a capacity 70-1000 kW. Air heater performance is based on two-stage combustion. At the first stage flame combustion proceeds under fuel rich conditions at α=0.95-0.98. Then the combustion products with additionally injected air pass into the second chamber equipped with an assembly of honeycomb monolithic catalyst. The catalyst provides total oxidation of CO and HC and reduction of NO_x. The purified flue gas is further diluted with air behind the catalyst and ejected from the apparatus to heat premises.

Catalytic gas burning domestic space heaters with a capacity of 2-3 kW. Two types of heaters were developed: for combustion of city gas from cylinders and natural gas. The active component comprising combination of transition metal oxides and Pt is supported on silica-alumina fiber mat (Termocat-1), or on multichannel ceramic plates (Termocat-2, 3). The original construction and use of high performance catalytic materials provides complete burning of fuel and concentrations of NO_x and CO in flue gases below sanitary standards.

Catalytic water-heating boiler based on foam catalysts with a capacity of 20 kW. The boiler works with natural gas. It operates with original catalysts supported on highly porous foam materials and catalytic heat exchangers. The heat efficiency of the boiler is 88-94%. The concentrations of CO and NO_x in the flue gas are below 5 mg/m^3.

Recent advances in application of catalytic combustion to problems of waste destruction and off-gas treatment in the nuclear and space industries are presented: destruction of mixed organic wastes in a fluidized catalyst bed , mixed waste oxidation in catalytically active molten salts and catalytic treatment of liquid rocket fuel – unsymmetrical dimethylhydrazine.

CHEMICALS FROM RENEWABLES AND BIOMASS: ROLE OF CATALYSIS

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Derivatives of wood and other biomass serve as raw materials for a large number of other chemical and reprocessing industries. End uses are as diverse as liquid fuels, explosives, pharmaceuticals, food products and paints. Chemical wood pulping processes also extract many other chemicals from wood - depending on the chemistry of the wood being pulped and the chemical process used. The liquors produced during kraft pulping cooking contain significant quantities of resin acids, tall oil, complex sugars and other organic compounds.

Since wood extractives cannot be used *per se* chemicals transformations of them are required. Catalytic processes in particular bring advantages being environmentally benign and industrially attractive. While the use catalysis for production of e.g. sugar alcohols as well as in terpene transformations is well known, catalytic processes for utilization of fatty acids, phytosterols and lignans as raw materials are very scarcely reported.

The lecture will summarize the recent research activities in the laboratory of the author as well as literature data on kinetics, deactivation, stereo- and chemoselectivity of several reactions of biomass derived chemicals, which represent different typical cases of multiphase organic catalytic transformations.

Key-Note lecture

IS IT POSSIBLE TO GENERALIZE THE PROBLEMS OF CATALYSTS SUPRAMOLECULAR AND ATOMIC STRUCTURE (TEXTURE AND STRUCTURE) FORMATION AND CONTROLLING?

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Formation of the majority of modern catalysts, adsorbents and other materials is considered from uniform fundamental position based on allocation of two different but general levels of the materials science: molecular (atomic) and supramolecular (textural). We consider interconnections between molecular and supramolecular levels, the laws of colloid, surface and supramolecular chemistry and physics, stereochemistry and crystallography, modern molecular physics and statistical thermodynamics, topology and morphology from geometry, etc. These fundamental relationships and laws are discussed in application to several typical examples of formation of catalysts and adsorbents texture and structure. Such approach open way for conversion from multitude “scientific basis of catalysis preparation” to a general fundamental theory.

ORAL PRESENTATIONS

NMR IMAGING AS A METHOD TO STUDY CATALYSTS AND CATALYTIC PROCESSES

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The necessity to elaborate new efficient catalysts and catalytic processes requires the development of the instrumental methods of investigation, especially *in situ* methods, which allow one to study the peculiarities of the occurrence of various processes in the real reaction conditions. From this point of view one of the most promising methods for the *in situ* investigations of catalysts and catalytic processes seems to be NMR imaging (MRI) that allows one to get nondestructively the spatially resolved information about the distribution of a liquid phase, diffusion coefficients, flow velocities, temperatures, etc., in the object under study.

MRI has been used in this work to study the transport of a precursor of an active component and different additives inside the support pellet in the course of the supported catalyst preparation, as well as the distribution of an active component and additives inside the catalyst pellet after the drying stage. The objects under study were Co-Mo-containing catalysts widely used in industry for the hydrotreating processes. The influence of the conditions of the impregnation process (concentrations, additives, pH) on the distribution of an active component in the catalyst pellet in a liquid phase during impregnation and in a solid phase after drying has been studied.

In situ MRI has been also employed to characterize the operation of a trickle bed reactor, in which a heterogeneous catalytic reaction of hydrogenation of octene has been performed. MRI has allowed us to directly visualize the existence of dry and partially wetted pellets inside the catalyst bed, permanently supplied with a liquid reagent and hydrogen. Their existence is concerned with the heat generation in the course of an exothermic reaction.

Acknowledgements

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ELECTROCHEMICAL CATALYST POTENTIAL AS A PARAMETER FOR *"IN-SITU"* MONITORING OF SURFACE PROCESSES

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The value of catalyst potential is related to processes taking place on the metal surface of a catalyst [1]. Therefore, catalyst potential is sensitive to all parameters affecting the rate of a chemical reaction, such as pH, temperature and feed rate of the reactants [2]. In the present study catalytic experiments were performed in a semi-batch mode. A tailor made shaker reactor was applied for *"in situ"* catalyst potential measurements. High shaking frequency was applied resulting in the elimination of stagnant zones in reaction mixture, and improved gas-to-liquid mass transfer. Catalyst potential behaviour was studied over different supported metal catalysts in three phase reaction of lactose oxidation. Several reaction parameters were varied to investigate the possibility to predict catalyst activity as well as deactivation from the measured values of catalyst potential. In the latter case the behaviour of catalyst potential was related to the surface processes such as oxygen poisoning, coke formation, or oxygen feed limited regime which can be the reasons for poor reaction performance. The example, represented in the Fig. 1, demonstrates a possibility to indicate unfavorable temperature regime almost immediately after reaction start up.

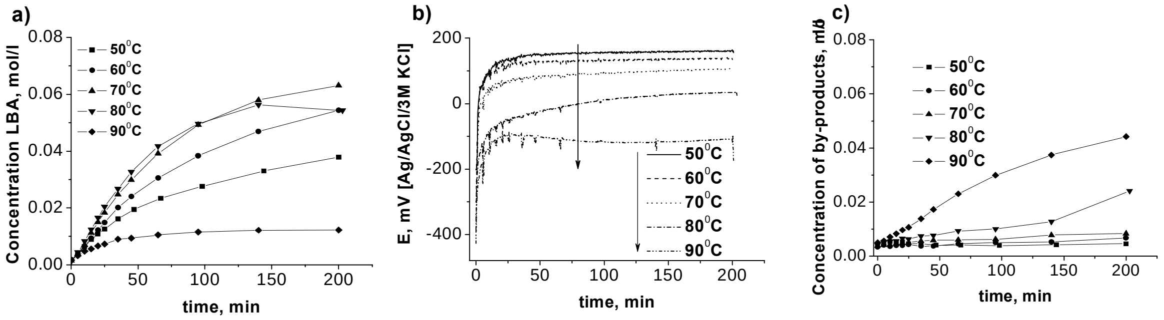

Figure 1. The influence of temperature on lactose oxidation over Pd (5 wt. %) /Al_2O_3, m = 0.5 g, at pH = 8, oxygen feed rate 2.5 ml/min: a) product concentration (lactobionic acid), b) catalyst potential (the trend indicated by arrows), c) by-products concentrations.

References

[1] T.Mallat, A.Baiker, Topics in Catal. 8 (1999) 115

[2] A.V. Tokarev, E.V. Murzina, J. Kuusisto, J.-P. Mikkola, K. Eränen, D.Yu. Murzin, J. Mol. Cat. A (in press).

IR SPECTROSCOPIC STUDIES OF TECHNICAL Pd CATALYSTS AND MODEL SYSTEMS

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Supported Pd catalysts are used for a variety of technologically important processes, especially for hydrogenation reactions. Vibrational spectroscopy of CO adsorbed on metal catalysts is a very useful tool for investigating the properties of the metal and can provide much information. However, it is often difficult to interpret the obtained information and to deduce structural information on the catalysts. Thus, model systems with well-defined surface structure have been used for comparison with technical catalysts [1,2]. For instance, single crystal surfaces and well-defined (evaporated) Pd nanoparticles can be utilized for assigning CO bands. The findings obtained from the model systems can then be applied to interpret CO spectra of technical catalysts for determination of the available adsorption sites, which also provides information on the morphology of the technical Pd catalysts [3,4].

Pd supported on various oxidic carrier materials was prepared by incipient wetness impregnation at different metal loadings. Characterization of the catalysts was done by IR spectroscopy after CO adsorption, TPD, XRD and XPS. FTIR measurements on the technical systems were carried out in transmission mode in a heating vacuum cell, which allowed in situ pre-treatment of the samples. Adsorption of CO on the model systems was studied by vibrational sum frequency generation spectroscopy and polarization-modulation infrared reflection absorption spectroscopy.

As test reactions selective hydrogenation of dienes and hydrodehalogenation of chlorinated compounds were chosen.

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References:

[1] H. Unterhalt, G. Rupprechter, H.J. Freund, J. Phys. Chem. B 106 (2002) 356.
[2] H.J. Freund, M. Bäumer, J. Libuda, T. Risse, G. Rupprechter, S. Shaikhutdinov, J. Catal. 216 (2003) 223.
[3] T. Lear, R. Marshall, J.A. Lopez-Sanchez, S.D. Jackson, T. Klapötke, M. Bäumer, G. Rupprechter, H.J. Freund, D. Lennon, J. Chem. Phys. 123 (2005) 174706.
[4] J. Sa, H. Vinek, Appl. Cat. B: Environmental 57 (2005) 247.

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UNSTEADY STATE PHENOMENA IN CO OXIDATION ON Pd(110)

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The unsteady state phenomena (hysteresis and oscillations) in $CO+O_2$ reaction on Pd, Pt and Ir were observed for the first time in 80-s by Sales, Turner and Maple [1], who proposed the reversible formation of oxide layer PdO_x in reaction conditions (~ 1 mbar). Afterwards Ladas, Imbihl and Ertl [2] found the unsteady state phenomena on Pd(110) single crystal surface at lower pressures ($< 10^{-2}$ mbar) and deduced that the formation of “subsurface oxygen” species (O_{subs}) was a driving force for reaction rate oscillations. Till now there is still no common agreement in the nature of such unusual phenomena in CO oxidation on Pd(110) [3].

Using the X-ray photoelectronic spectroscopy (XPS) we found, that on a polycrystalline palladium surface in conditions $P(O_2)=10^{-2}$ mbar, $P(CO)\sim10^{-6}$ mbar ($P(O_2)/P(CO)\sim10^{4}$), T=525 K, close to conditions of self-oscillation regime on Pd(110), oxide formation did not occur but there was a penetration of oxygen atoms into the top layer of metal and formation of subsurface oxygen layer. Transient kinetic experiments on Pd(110) showed that CO_{ads} molecules did not react chemically with subsurface oxygen below 300 K. O_{ads} atoms are highly active compared to O_{subs} species due to the rapid reaction with CO_{ads} beginning at temperature ~ 150 K. Based on experimental data, the detailed mechanism of CO oxidation on Pd(110) was proposed. During the imitating experiments, carried out by Monte Carlo calculations, the set of parameters has been found where the model showed a self-oscillatory regime. The hysteresis in oscillatory behaviour was observed under step-by-step variation of oxygen partial pressure. Two different oscillatory regimes exist at one and the same parameters of the reaction. The parameters of oscillations (amplitude, period and the shape of the waves on the surface) depend on the kinetic prehistory of the system. The possibility for the appearance of the cellular and turbulent patterns, spiral, ring and stripe oxygen waves on the surface has been shown.

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[1] Sales B. S., Turner J. E., Maple M. B., Surf. Sci. 112 (1981) 272
[2] S. Ladas, R. Imbihl, G. Ertl, Kinetic oscillations during the catalytic CO oxidation on Pd(110): the role of subsurface oxygen, Surf. Sci. 219 (1989) 88
[3] V. A. Bondzie, P. Kleban and D. J. Dwyer, XPS identification of the chemical state of subsurface oxygen in the O/Pd(110) system, Surf. Sci. 347 (1996) 319

PHOTOCATALYTIC DEGRADATION OF DICARBOXYLIC ACIDS ON TiO_2 STUDIED BY IN SITU ATTENUATED TOTAL REFLECTION INFRARED SPECTROSCOPY

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In situ Attenuated Total Reflection Infrared (ATR-IR) spectroscopy has been used to study band gap irradiation of TiO_2 (P25) particle thin film in contact with organic and inorganic species. [1] The method is well suited to study the solid-liquid interfaces of powders yielding molecular level insight into the processes that occur at the solid-liquid interface. In this lecture we will consider photocatalytic mineralization of dicarboxylic acids over TiO_2 thin film, studied by in situ ATR-IR spectroscopy (Figure 1). [2] Upon illumination the coverage of adsorbed malonic acid is decreasing and oxalic acid is observed on the TiO_2 surface. During band-gap illumination a large fraction of the surface is not covered by acid. Oxalate is a major intermediate in the mineralization of malonic acid. However, the observed transient kinetics of adsorbed malonic and oxalic acid indicates additional pathways not involving oxalate. The rate constant of oxalic acid is slightly larger than the one for malonic acid. The modulation of the light flux and a phase sensitive detection yields even more details about the processes occurring at the catalytic solid-liquid interface.

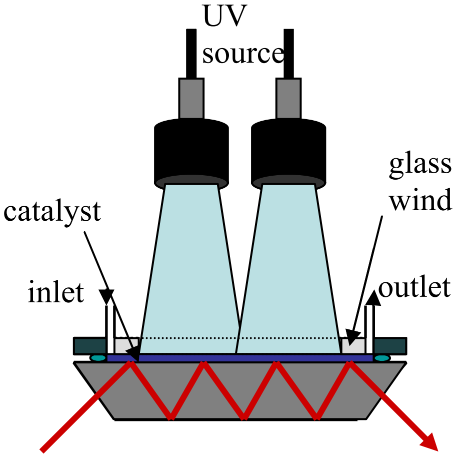

Figure 1: Schematic set-up for in situ ATR-IR spectroscopy of photocatalytic reaction in a small volume flow-through cell.

References:

1. Paula Z. Araujo, Cecilia B. Mendive, Luis A.Garcia Rodenas, Pedro J. Morando, Alberto E. Regazzoni, Miguel A. Blesa, Detlef Bahnemann, Colloids and Surfaces A: Physicochem. Eng. Aspects 265 (2005) 73-80
2. I. Dolamic, T. Bürgi, submitted for publication

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SSITKA STUDY OF deNO$_X$ REACTION MECHANISM

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This work is devoted to *in situ* study of deNO$_X$ reaction mechanisms (selective NO reduction with methane over Co-ZSM-5 and fiberglass catalysts) with Steady-State Isotope Transient Kinetic Analysis (SSITKA) technique [1]. The dynamics of ^{15}N, ^{18}O and ^{13}C label transfer from reagents to the reaction products was investigated allowing us to determine the scheme of the reaction mechanism as well as to estimate both the concentrations of intermediate surface species and the rates of separate reaction steps. In particular, it was found that:

- deNO$_X$ reaction over Co-ZSM-5 catalyst proceeded via two parallel route with participation of both nitrite-nitrate complexes and $NO_2^{\delta+}$ species. These reactions were proved to take place over cobalt cations and Co…OH paired sites, respectively. As a result, an influence of acid sites on the reaction kinetics was quantitatively estimated. The rate-determine reaction steps were revealed, which was adsorbed complexes formation for nitrite-nitrates and interaction with methane for $NO_2^{\delta+}$. It was shown that turnover number (TON) of the reaction was about 20 times hither for Co…OH paired sites [2,3].
- Original results were obtained on the kinetics of NO interaction with Pt-containing fiberglass catalysts. The rate constants of NO interaction with both Pt sites and OH groups of the fiberglass were estimated. The mass-transfer processes in the fiberglass materials were also studied, and diffusion coefficients of NO and H_2O into the fiberglass bulk were determined, which were found to be abnormally high [4].

References

1. Sadovskaya E.M., Bulushev D.A., Bal'zhinimaev B.S. // Kinetics and Catalysis. 1999. V. 40. No.1. P. 54.
2. Sadovskaya E.M., Suknev A.P., Pinaeva L.G. ., Goncharov V.B., Bal'zhinimaev B.S., Chupin C. , Pérez-Ramírez J. , Mirodatos C. // J. Catal. 2001. V. 201. P. 159.
3. Sadovskaya E.M., Suknev A.P., Pinaeva L.G., Goncharov V.B., Bal'zhinimaev B.S., Chupin C. , J. Pérez-Ramírez J. , C. Mirodatos C. // J. Catal. 2004. V. 225. P. 179.
4. Sadovskaya E.M., Suknev A.P., Toktarev A.V., Simonova L.G., Paukshtis E.A., and Bal'zhinimaev B.S. // Kinetics and Catalysis. 2006. V. 47. No.1. P. 131.

KINETICS OF THE OXIDATIVE DEHYDROGENATION (ODH) OF METHANOL TO FORMALDEHYDE BY SUPPORTED VANADIUM-BASED NANOCATALYSTS

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Introduction - In recent years, the interest in formaldehyde production by the oxidative dehydrogenation of methanol has strongly increased, provided that high activities and selectivities can be achieved under mild conditions of temperature (140-250 °C) and pressure (1 atm). Supported vanadium oxide based nanoparticles have been found to be active and selective. A large number of factors may determine their catalytic performances such as: (i) the nature, dispersion and structure of the active sites; (ii) preparation method; (iii) acid-base properties of the support and (iv) vanadium loading.

Objectives - The aim of the present contribution was to develop a detailed kinetic analysis of methanol ODH reaction to formaldehyde on a nano-structured vanadium oxide supported catalyst selected in a preliminary screening phase.

Experimental - The selected vanadium catalyst, supported on TiO_2/SiO_2, has been prepared by grafting vanadyl alkoxide, dissolved in dioxane, and characterized by BET, XRD, Raman, XPS and SEM. An exhaustive set of experimental runs has been conducted in an isothermal packed bed tubular reactor by investigating several operative conditions such as: temperature, contact time, methanol/oxygen feed molar ratio and water feed concentration.

Results and Discussion - Depending on the operative conditions adopted, the main products observed were formaldehyde and dimethoxymethane while lower amounts of methyl formate and CO_2 were also found. At low contact time the main reaction product was dimethoxymethane which was then converted into formaldehyde through the reverse equilibrium reaction with water. As a confirmation of this observation, a peculiar behaviour was detected consisting in an increase of selectivity to formaldehyde by increasing methanol conversion. The obtained experimental data of methanol conversion and products selectivity were modelled by means of an integral reactor model and the related kinetic parameters were determined by non-linear regression. The adopted reaction rate expression was of the Mars van Krevelen – Langmuir Hinshelwood type and a good agreement was found between the theoretical prediction and the experimental data.

Conclusions - A new reaction mechanism (*rake-type*) and a detailed kinetic scheme were proposed for methanol ODH on a nano-structured catalyst that was able to interpret correctly the collected experimental observations.

O-8

TESTING SUPPORTED GOLD CATALYSTS BY HIGH-THROUGHPUT EXPERIMENTAL TECHNIQUES

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Last years high-throughput experimentation techniques (HTET) are widely used in various areas of materials research. In the area of heterogeneous catalysis HTET is often combined with combinatorial approaches. In this presentation we shall describe the application of HTET both in catalyst screening using Temperature Programmed Reaction (TPR) technique and in reaction kinetic studies. The oxidation of carbon monoxide was chosen as a model reaction using MS method for product analysis. The high-throughput reactor had 16 channels and was connected via a flow selector valve to a quadruple mass spectrometer. The whole system is fully computer controlled. 12-14 channels were used to test the catalysts, while 2-4 channels were applied to get the background MS signals. The amount of catalysts was in the range of 10-30 mg, while the flow rate varied between 10-60 ml/min.

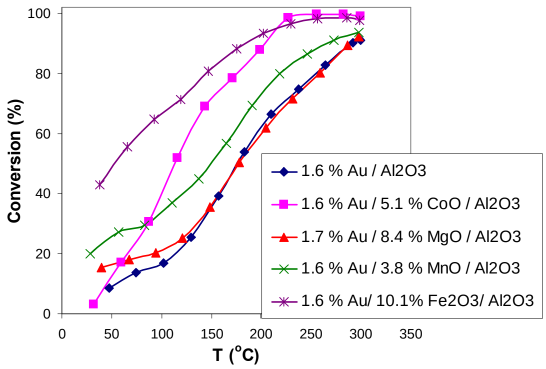

Figure 1

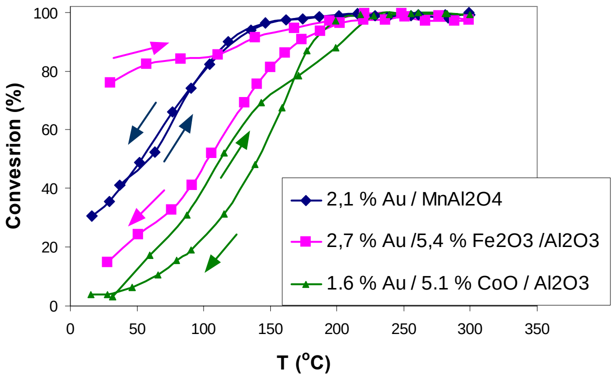

Figure 2

Supported gold catalysts, such as Au/Al_2O_3, Au/Mg/Al_2O_3, Au/CoO/Al_2O_3, Au/MnO/Al_2O_3, Au/Fe_2O_3/Al_2O_3 and Au/$MnAl_2O_4$ were tested. $HAuCl_4$ was used as the gold precursor. The kinetic experiments were performed between 40 and 70 °C, while TPR runs were carried out between 25 and 300 °C investigating both the increase and the decrease parts. Typical TPR curves are shown in Figure 1 and 2. The results show that the modifier enhances the activity of the parent Au/Al_2O_3 catalyst. Further TPR and kinetic results will be shown and discussed in this presentation. Results obtained in this study provided unambiguous proof that HTET can be used in catalysis research. This new approach provides reliable and reproducible data and improves the efficiency of research more than one order.

CO OXIDATION BY O_2 OVER $Au/Ce_{1-x}Zr_xO_2$ CATALYSTS

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The *CO* oxidation is one of the key reactions in exhaust gas emission control, both in the cleanup of vehicle emissions, especially during the cold start of engines, and the purification of breathing air in enclosed spaces. Consequently, there is a strong interest to developing of catalysts with better oxidation activity at low temperatures. Since the pioneering work of Haruta (1), several research groups confirmed that low-temperature *CO* oxidation is successfully catalysed by *Au* nanoparticles highly dispersed on appropriate supports (2). The clue to produce active *Au* catalyst lies in obtaining well-dispersed particles in the range of the nanometer size. The unique redox properties, high lability of lattice oxygen, high thermal stability and the ability of promoting dispersion of noble metals lead us to choose CeO_2-ZrO_2 as a support for *Au*. So far, CeO_2-ZrO_2 systems, widely studied in other applications (3), have not been examined as *Au* supports in the *CO* oxidation.

The aim of this work was the dispersion of *Au* nanoparticles on different $Ce_{1-x}Zr_xO_2$ mixed oxides (*Ce/Zr* molar ratio=3, 1, 0.33), CeO_2 and ZrO_2 and the attempt of understanding the relationship between the nature of the support, catalytic activity and *Au* dispersion.

The $Ce_{1-x}Zr_xO_2$ solid solutions, CeO_2 and ZrO_2 were prepared by sol-gel method. The 2 and 5 wt. % *Au* catalysts were prepared by *DAE* (Direct Anionic Exchange) method (4). The obtained systems were characterized by *XRD*, *BET*, H_2-*TPR*, *CO-TPR*, *AAS*, *TEM* and tested in the *CO* oxidation reaction, using different gas mixtures (rich, stoichiometric and lean in O_2). The effect of the particular stages of the preparation on the properties of the obtained catalysts was also investigated. The poisoning effect of chloride was confirmed. The average *Au* particle size was higher for the catalysts prepared without washing of chloride. In order to remove residual Cl^- from the catalysts, different washing procedures were used. According to the washing procedure, changes in activity and particle size were observed. In general, the highest activity was obtained over $Au/Ce_{0,75}Zr_{0,25}O_2$ washed in ammonia. It was observed that catalytic performance of *Au* catalysts in *CO* oxidation highly depends on the properties of the supports, particularly on their reducibility.

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References:

1. Haruta M., Yamada N., Kobayashi T., Iijima S., J. Catal., 1989, **115**, 301
2. Bond, G.C., Thompson, D.T., Cat. Rev. – Sci. Eng., 1999, **41(3&4)**, 319
3. Trovarelli A. (ed.) Catalysis of Ceria and Related Materials. ICP, **2002**
4. Ivanova S., Petit C., Pitchon V., Appl. Catal. A: General 2004, **267**, 191

O-10

BIMETALLIC Au-Ni/Al_2CrO_6 and Au-Ni/Al_2MgO_4 CATALYSTS FOR SYNGAS PRODUCTION

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The aim of this work is determination of the role of gold addition to nickel catalysts supported on Al_2CrO_6 and Al_2MgO_4 for partial methane oxidation to syngas production. The surface area, phase composition, the reduction behavior and the catalytic activity of nickel-gold supported on different supports (Al_2O_3, Cr_2O_3, MgO, Al_3CrO_6 and $MgAl_2O_4$) were examined. Supported mono and bimetallic nickel-gold catalysts containing 5% Ni and 2% Au respectively were prepared by conventional wetness impregnation. As precursors of active phase $Ni(NO_3)_2{\cdot}6H_2O$ and $HAuCl_4$ were used. The supports were prepared from: $Cr(NO_3)_3{\cdot}9H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and $Mg(NO_3)_2{\cdot}6H_2O$ compounds. Mono-oxide (MgO, Al_2O_3, Cr_2O_3) and two-oxide supports (Al_3O_6Cr contained Cr and Al with molar ratio 1:3 and Al_2MgO_4 with molar ratio Mg/Al = 1:2) were prepared by ammonia precipitation or co-precipitation method; next samples were dried and calcined in air at 400°C for 4h. Active phase was introduced on appropriate supports by impregnation method and then supported catalysts were dried at 105°C and finally calcined in air at 400°C for 4h. Results of specific surface area measurements show that the addition of alumina leads to increase the surface area of Cr_2O_3 as well as MgO support. The surface area depends on the kind of the support and it is in the range from 6 m^2/g (for Cr_2O_3) up to 360 m^2/g (for Al_2O_3). The promoting effect of gold addition, especially for magnesium containing catalysts, was confirmed by TPR method. It changes the shape of TPR profile and moves it into lower temperature region. Phase composition was determined by XRD method. Only the traces of Cr_2O_3 phase were found in the case of Al_3CrO_6 support. The expected spinel as well as Al_2O_3 phase were not experimentally detected. The XRD measurements for $MgAl_2O_4$ support show only $MgAl_2O_4$ spinel phase. In the case of supported nickel-gold catalysts the additional phases of gold and nickel were found. High temperature reduction leads to nickel-gold alloy formation. Those catalysts revealed high activity in POM reaction. Syngas formation is observed above 650° C. The 100% selectivity to syngas can be reached in temperature range 700-850°C. Gold addition to nickel supported on alumina or $MgAl_2O_4$ catalysts resulted in high activity system, but in the case of catalysts supported on Al_3CrO_6 the slightly decreasing of activity was observed.

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CATALYTIC OXIDATION OF HYDROGEN OVER Au/TiO_2 CATALYSTS

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The catalytic dehydrogenation of light alkanes is an important reaction, much due to the growing demand for light alkenes as propene and ethene as feedstock in chemical industry. The catalytic dehydrogenation, e.g. of propane, is strongly endothermic (ΔH^0_{298} = 124 kJ/mol) and is favoured by low pressures due to the stoichiometry. The produced hydrogen can be combusted catalytically to provide *in situ* heating, and can be coupled with the dehydrogenation reaction in an autothermal process [1, 2]. At 500 ºC the heat of combustion of hydrogen is approximately twice the heat required for propane dehydrogenation, thus, to get a heat-balanced process it is necessary to combust approximately half of the hydrogen produced in the dehydrogenation. The key issue in this process is to avoid the nonselective combustion of the hydrocarbons.

The catalysts reported here are 1.5, 3 and 5 wt% Au, prepared by a sol technique and supported on TiO_2. All catalysts were tested in a fixed-bed quartz reactor, placed inside an electrical furnace. The total flow of feed gas was 100 ml/min, the H_2-flow was 2 ml/min, and in some experiments C_3H_8 was added (10 ml/min). The O_2 flow was varied to achieve different H_2/O_2 ratios, the balance being He. The experiments were done at temperatures between 20 and 550 °C and 1 atm, with a loading of 0.15 g catalyst.

The Au based catalysts are active for the hydrogen oxidation reaction, both in an inert gas and in the presence of propane. Around 100 ºC the catalyst are active for hydrogen oxidation, achieving full conversion at approximately 140 ºC. But at 500 and 550 ºC temperatures dehydrogenation occurs, the selectivity is dependent of the H_2/O_2 ratio. As longs as the $H_2 : O_2$ ratio exceeds 2 (stoichiometry), the oxygen reacts preferably with H_2 than H_2O. The CO and CO_2 selectivity increases when the ratio is reduced.

Acknowledgements. We thank the Norwegian Research Council for financial support.

References

[1] L. Låte, J.-I. Rundereim., E.A. Blekkan: Appl. Catal. A ,262 (2004) 53
[2] J.G. Tsikoyiannis, D.L. Stern., R.K. Graselli: J. Catal. ,184 (1999) 77

O-12

Ni AND Rh SUPPORTED ON CeO_2 – ZrO_2 MATERIALS AS EFFECTIVE CATALYSTS FOR HYDROGEN PRODUCTION VIA ACETIC ACID STEAM REFORMING

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Hydrogen production from renewable sources such as biomass, is gaining attention as a CO_2 neutral energy supply. Steam reforming of pyrolysis oil (bio-oil) is one of the promising routes for hydrogen production. The water-rich phase of the bio-oil containing mostly carbohydrate-derived compounds consists of 20% organics and 80% water. We report here experimental results for steam reforming of acetic acid, representative compound of bio-oil, over Ni and Rh catalysts.

A number of different catalysts containing Ni and Rh were synthesized using the wet impregnation technique. The supports used were calcium aluminates with Ca/Al ratios 1/2 and 12/7 and ceria-zirconia with Ce/Zr ratio 1/5. The activity of the catalysts in the steam reforming of acetic acid was tested in an experimental setup employing a fixed bed reactor at steam/carbon ratio 3 and high space velocity $G_{c1}HSV=33500\ h^{-1}$.

Both the nature of the support and the active metal affect the conversion of acetic acid and the hydrogen yield. The catalysts supported on calcium aluminates showed interesting results with most promising one the 5% Ni supported on $CaO\cdot 2Al_2O_3$ catalyst. Full conversion of acetic acid was obtained at 750°C with hydrogen yield approaching 90%.

Ni and especially Rh catalysts supported on Ce/ZrO_2 exhibit unique performance in acetic acid reforming. Their activity is extremely high with almost full conversion of acetic acid at temperatures as low as 550°C. The yield to hydrogen is high approaching that of thermodynamic equilibrium. Their advantage over the calcium aluminate supported catalysts lies in the much lower tendency for carbon formation. The amount of coke deposited after 3h time on stream with the 5%Ni/Ce-ZrO_2 catalyst is 3 times lower than that of the catalyst supported on calcium aluminate. The performance of 0.5%Rh/Ce-ZrO_2 catalyst is very promising. The affinity of the catalyst for carbon formation in acetic acid steam reforming is even less. Combined with the high hydrogen yield, this catalyst formulation deserves further testing and characterization.

CuO-CeO$_2$ CATALYSTS FOR METHANOL FUEL PROCESSORS

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Solid Polymer Fuel Cells operate on H_2, which can be obtained on-board from a methanol processor via catalytic steam reforming (SRM) and preferential CO oxidation (PROX) reactions. Using O_2 with steam (combined steam reforming of methanol, CSRM) offers advantages such as high reaction rates and thermo-balanced conditions. On the other hand, purification of H_2 can be achieved via the PROX process. In this work, the results of a detailed study of the effects of copper content and preparation method (i.e. combustion method) on the catalytic properties of CuO-CeO$_2$ catalysts are reported and related with their performance in SRM, CSRM and PROX processes. Catalytic tests were performed in a typical flow system, with varied contact times (0.03-0.257 g s cm^{-3}).

Samples prepared with excess urea were more active and selective than those prepared with stoichiometric quantity, in agreement with BET and XRD measurements. XPS studies revealed surface segregation with both Cu^{2+} and Cu^{1+} species. H_2-TPR profiles consisted of three overlapping peaks in the temperature range of 150-250 °C compared to a single peak at 290 °C for unsupported CuO. TPD experiments showed that adsorbed CO desorbs mainly as CO_2 (peak maxima at ~100-120 °C) and as CO at ~70 °C. O_2-TPSR experiments showed that adsorbed CO reacts fully with gaseous O_2 and desorbs as CO_2. The catalytic activity was maximized for both processes for the catalyst prepared with 75% excess of urea and Cu/(Cu+Ce) = 0.15. Under autothermal conditions (CSRM process) the catalytic behavior was improved and 99.8% MeOH conversion was obtained at 280 °C (>97% H_2 selectivity) with $Cu_{0.15}Ce_{0.85}$ catalyst. The same trend was observed in more concentrated feeds (20% MeOH, autothermal conditions), where 99.7% MeOH conversion was achieved at 320 °C (95% H_2 selectivity). CuO-CeO$_2$ catalysts showed ideal selectivity up to 120-170 °C for PROX reaction. These catalysts were considerably more active than unsupported CuO. In tests with simulated reformate gas (co-addition of H_2O and CO_2), inhibition of the oxidation reaction was more severe for pure CuO. Compared to catalysts used in powder form, the foam catalysts prepared via the in-situ combustion method exhibited similar catalytic performance. Based on the adsorbed quantity of CO, the TOF of CO oxidation was calculated. The promoting effect of CeO$_2$ can be attributed on the creation of additional active sites, probably at the interface between the two oxides.

O-14

Ni-Au/Al_2MgO_4 CATALYSTS FOR OXIDATIVE CONVERSION OF METHANE TO SYNTHESIS GAS

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Reforming of methane to synthesis gas is one of the main processes in industrial chemistry. Partial oxidation of methane (POM) is an alternative method of CO and H_2 mixture production. This paper is focused on the relationship between the activity of Ni-Au/Al_2MgO_4 catalyst in POM reaction and its physico-chemical properties: specific surface area, reduction behavior and phase composition.

Catalysts containing 5 % Ni and 2 % Au were obtained by wet co-impregnation of $Ni(NO_3)\cdot 6H_2O$ and $HAuCl_4$ on support Al_2MgO_4 surface. The catalyst support was prepared from precursors: $Al(NO_3)\cdot 9H_2O$ and $MgNO_3\cdot 6H_2O$ by ammonia co-precipitation. Finally they were dried and calcined in 400°C during 4 hours. The results of specific surface area of catalysts after previous calcination at 400°C, selectivity to CO and conversion of CH_4 at 900°C in POM reaction are presented in Table 1.

Table 1. Catalysts characterization

Metal/support catalyst	Specific surface area (m^2/g)	Selectivity to CO (%)	Conversion of CH_4 (%)
5%Ni/Al_2MgO_4	66	90	90
5%Ni-2%Au/Al_2MgO_4	63	10	61
5%Ni/Al_2O_3	168	84	97
5%Ni/MgO	59	77	38

A simple correlation between catalyst specific surface area and its activity was not observed. The catalyst 5%Ni/Al_2MgO_4 had the highest selectivity to CO in POM reaction. The conversion degree of CH_4 for 5%Ni/Al_2MgO_4 and 5%Ni/Al_2O_3 catalysts was similar and above 90%. The NiO reduction effect was observed on TPR profiles. In the case of 5%Ni/Al_2MgO_4 catalyst wide peak was found in temperature range 250-500°C. Sharp and symmetrical peak representing NiO reduction for 5%Ni-2%Au/Al_2MgO_4 catalyst was observed. The addition of gold to nickel catalyst resulted in uniform NiO crystallite phase. The formation of $MgAl_2O_4$ spinel was confirmed by XRD method. The increase of crystallinity was observed with temperature of calcination. The Au metallic phase was observed in nickel-gold/support catalysts, however NiO phase was not observed, probably because of the high metal dispersion on catalyst surface.

NANOCRYSTALLINE CATALYSTS BASED ON CeO_2-ZrO_2 SOLID SOLUTION DOPED BY Gd AND Pr: PROPERTIES AND EFFECT OF THE LATTICE OXYGEN MOBILITY

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Ceria-zirconia-based systems are promising as components of three-way catalysts, catalysts of selective oxidation/autothermal reforming of hydrocarbons into syngas at short contact times, oxide ion conductors for oxygen sensors application and cathodes/anodes in solid oxide fuel cells (SOFC). Doping this system with low-valence cations allows stabilizing this solid solution in hydrothermal conditions and tuning the lattice oxygen mobility due to formation of oxygen vacancies or more complex defects.

In this work, nanocrystalline samples of Pr- or Gd- doped ceria-zirconia $Pr/Gd_x(CeZr)_{(1-x)/2}O_{2-\delta}$ (x (Pr, Gd)=0,05-0.3) prepared by polymerized precursor (Pechini) route and calcined at 500 °C were studied. Pt (1.4 wt.%) was supported by incipient wetness impregnation with H_2PtCl_6 solution. The samples were characterized by using XRD, XPS, EXAFS, FTIRS of adsorbed CO test molecules, and oxygen mobility was estimated by using oxygen isotope exchange. Catalytic properties of Pt-loaded samples were studied in the reactions of syngas generation by methane selective oxidation and acetone autothermal reforming at short contact times.

For studied systems, supported Pt mainly present as cationic Pt^{2+} species, which is explained by ability of fluorite-like oxide supports to stabilize these cations at surface defects, probably, in vicinity of domain boundaries. At high (880 °C) temperatures, the rate of syngas generation in both reactions correlates with the lattice oxygen mobility as well as concentration of Pt^{2+} species – precursors of small reactive Pt^{o} clusters. This suggests bi-functional mechanism of these reactions occurring at Pt-support interface. At lower (680-780 °C) temperatures, the rate of syngas generation from acetone correlates with concentration of unsaturated isolated Me^{4+} cations (Ce^{4+}, Zr^{4+}) probably due to a partial blocking of Pt by coke.

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O-16

OXYGEN FORMS IN SUBSTITUTED PEROVSKITES $La_{1-x}Ca_xMnO_{3+y}$ (x=0-1) AND THEIR REACTIVITY IN OXIDATION REACTIONS

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Oxygen species and their reactivity in $La_{1-x}Ca_xMnO_{3+y}$ perovskites prepared by mechanochemical and ceramic routes were studied by temperature-programmed reduction (TPR) by hydrogen. The experimental data were compared with data on the catalytic activities in oxidation reactions along with real structure and surface compositions of the samples, investigated in details earlier in [1].

Increasing of the calcium content in the $La_{1-x}Ca_xMnO_{3+y}$ system increases reduction degree of these samples and results in the shifts of the maximums sets (T_{max}) of the peaks of TPR-H_2 curves to the region of lower temperatures. Thus, an increase of calcium content promotes the diversity and reactivity of oxygen forms in $La_{1-x}Ca_xMnO_{3+y}$ system. It was concluded that subsurface process of reduction $Mn^{4+}\rightarrow Mn^{2+}$ occurs in region of low and moderate temperature of TPR experiments. In the region of high temperatures, the process of bulk reduction $Mn^{3+}\rightarrow Mn^{2+}$ takes place. The influence of preparation conditions (synthesis route) on oxygen species and their reactivity was studied also. Increase of the temperature and time of calcination leads to the decrease of relative oxygen amounts removed in the course of TPR according to corresponding peaks and results in the shifts of temperature maximums sets of the peaks to the region of higher temperatures. Observed differences for synthesis routes are supposed to be concerned with different structures and compositions of surface/subsurface layers. So, samples of mechanochemical series are characterized by the calcium segregation in subsurface layer, whereas samples of ceramic series are microheterogeneous composites, according to [1].

Specific catalytic activity of the $La_{1-x}Ca_xMnO_{3+y}$ samples in the reaction of CO catalytic oxidation, was found to correlate with the amount of reactive oxygen forms easily removed by H_2-TPR at temperatures ~ 250-300 °C. There is no correlation between lattice oxygen amounts removed at high temperatures of H_2-TPR processes and catalytic activity values.

1. *L.A. Isupova, S.V. Tsybulya et al.* // Solid St. Ionics. 2001. V.141-142. P. 417.

O-17

CATALYST DEVELOPMENT FOR HYDROLYSIS REACTION OF SODIUM BOROHYDRATE

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Hydrolysis of sodium borohydrate is seen to be a safe and portable hydrogen production route, because it is stable under ordinary conditions and liberates pure H_2 in a safe and controllable way. $NaBH_4$ contains 10.8%wt of hydrogen. In the presence of a selected catalyst, hydrolysis reaction of $NaBH_4$ solution gives 4 moles of H_2 and half of the produced hydrogen comes from water. The aim of the study is to develop an active $Pt/LiCoO_2$ catalyst using $LiCoO_2$ support obtained by different methods.

The first method studied for preparation of $LiCoO_2$ was solid state reaction. Li_2O, $Co(NO_3)_2 \cdot 6H_2O$ and heat generating material were used as precursors and by investigation of preparation parameters an ideal preparation route has been developed. $LiCoO_2$ was also prepared by the precipitation method. Effect of preparation parameters, such as compositions of $LiNO_3$, $Co(NO_3)_2 \cdot 6H_2O$ and citric acid, pH, temperature and solvent type, on catalyst activity were investigated. All prepared $LiCoO_2$ supports were impregnated with 1.5 wt% Pt and these catalysts were tested in reaction of H_2 production. XRD analyses of the prepared supports were performed to determine the catalyst structure. The activity of catalysts in hydrolysis of $NaBH_4$ was measured in a semi-batch jacketed reactor at atmospheric pressure and room temperature. Reaction parameters of H_2 production from $NaBH_4$ were also investigated.

Our results showed that preparation of $LiCoO_2$ by solid state reaction gave higher hydrogen production rates than precipitation. In preparation of $LiCoO_2$ by solid state reaction method, equal amounts of heat generating material to the reactants was determined as optimum amount. NH_4NO_3 was chosen as an ideal heat generating material. Samples calcined between 500-700 °C showed approximate H_2 production rates, but samples calcined at higher temperatures showed less activity. Investigated hydrolysis reaction parameters were $NaBH_4$ and NaOH concentrations, reaction temperature and catalyst amount. Decreasing of $NaBH_4$ and NaOH concentrations leads to the increasing of H_2 production. Increase of the reaction temperature and catalyst amount also increases productivity to H_2.

O-18

PREPARATION OF MESOPOROUS CATALYTIC FILMS ON BOROSILICATE GLASS FOR APPLICATION IN MICROSTRUCTURED REACTORS

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Thin mesoporous silica films with an ultrahigh specific surface area and a tunable pore size distribution have a large potential as a catalyst support in microstructured reactors. These materials allow processing of larger organic molecules, which are usually intermediates in the production of fine chemicals. In this work, thin (300-1000 nm) mesoporous silica films with hexagonal and cubic ($Im\bar{3}m$) mesostructures have been prepared on Pyrex® 7740 borosilicate glass substrates by the evaporation induced self assembly assisted sol-gel route. Prior to the films synthesis, a 50 nm TiO_2 layer has been deposited on the glass substrate by atomic layer deposition from titanium tetrachloride and water to reach better adhesion of the films to the walls of the substrate. The mesoporous films were produced by templating a silica precursor (TEOS) with an $EO_xPO_yEO_x$ amphiphilic triblock copolymer (EO = ethylene oxide, PO = propylene oxide, x = 106, y = 70) at a pH of 2. A surfactant/silica ratio of 0.0076 was found to be optimal at a spinning rate of 1500 rpm to obtain films with a surface area above 500 m^2/g and a monomodal pore size distribution with a mean pore size of 6.9 nm.

Well-ordered hexagonal and cubic mesostructured thin films with a mean pore size from 3 to 8 nm were prepared by using ionic and non-ionic surfactants as the structure-directing agent in the spin coating process. The dried films were then calcined in flowing air with slow heating rate. The surfactant removal procedures were optimized based on the results of Thermogravimetric Analysis (TGA) and Fourier Transform Infrared Spectroscopy (FTIR). The obtained films were characterized by 1D and 2D X-Ray diffraction and high resolution transmission electron microscopy (HR TEM). The morphology of the films was studied by scanning electron microscopy. Ellipsometric porosimetry (EP) was used to determine the mean pore size and pore size distribution.

A mixed-metal cluster precursor $[Ph_4P]_2[Ru_5PtC(CO)_{15}]$ was deposited on the mesoporous silica films. Then, the mesoporo-encapsulated clusters were activated by gentle heating in vacuo at 200 ºC to obtain bimetallic catalysts. The supported bimetallic catalysts were characterized by HR TEM. The average diameter of the resulting, well-dispersed, isolated and anchored bimetallic nanoparticles is 1.4 nm. By this approach, the functionality of the relatively fragile metallic clusters is mediated through the rigid inorganic framework providing protection and the 3D distribution of the catalytic function. The resulting films will be used in a number of fine chemicals synthesis reactions in microstructured reactors (e.g., selective oxidation, hydrogenation).

HIGH SURFACE AREA GRAPHITE AS SUPPORT IN MICRO-FABRICATED REACTORS: A NEW POSSIBILITY FOR OPTIMIZING SMALL SCALE CATALYSTS

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Ammonia has gained significant interest as hydrogen carrier for fuel cells. Stored safely, the ammonia can become a favorable energy source [1, 2], but for use in low temperature fuel cells it must be catalytically decomposed to the elements before it can be utilized in the fuel cell.

One perceived area where fuel cells could make great impact is for miniaturized systems known as “lab on a chip”. Often, power supplies or batteries for such systems are very bulky compared to the system it supports. Thin fuel cells would be optimal for solving this problem, if the fuel could be delivered from an equally compact system.

Promoted Ru catalyst on porous graphitized carbon is generally recognized as the most active for decomposition of ammonia [3, 4]. So far, it has not been possible to integrate significant amounts of porous graphitized carbon support in micro-fabricated reactors, and the best miniaturized systems have thus used less optimal supports [5, 6].

Here, a method for such incorporation is presented, and high activities for ammonia decomposition are demonstrated. Furthermore, micro-fabricated reactors are well suited for catalyst studies, as the reactors can be kept absolutely isothermal under reaction conditions and the gas flow stays laminar over a large range of space velocities. This has been used to investigate promotion of the Ru/C system with Cs and Ba.

References

1. R. Metkemeijer and P. Achard. Int. J. Hydrogen Energy, 19 (1994) 535 – 542
2. C. H. Christensen, R. Z. Sørensen, T. Johannessen, U. Quaade, K. Honkala, T. D. Elmøe, R. Køhler and J. K. Nørskov. J. Mater. Chem. 15 (2005) 4106–4108
3. W. Rarog-Pilecka , D. Szmigiel , A. Komornicki , J. Zielinski , Z. Kowalczyk. *Carbon* 41 (2003) 579– 625
4. S.F. Yin, B.Q. Xu, X.P. Zhou, C.T. Au. Applied Catalysis A: General 277 (2004) 1–9
5. J.C. Ganley, E.G. Seebauer, R.I. Masel. Journal of Power Sources 137 (2004) 53–61
6. R. Z. Sørensen, L. J. E. Nielsen, S. Jensen, O. Hansen, T. Johannessen, U. Quaade, C. H. Christensen. Catalysis Communications 6 (2005) 229–232

O-20

CATALYTIC CVD-SYNTHESIS OF CARBON NANOTUBES WITH ETHYLENE AS CARBON SOURCE

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Carbon nanotubes have great scientific interest, both from a fundamental point of view and for future applications. The main question in their synthesis consist in creation of scalable industrial process for reproducible obtaining of nanotubes with given structure (chirality) and enough purity. The most promising way for solving indicated problems consists in application of catalytic chemical vapor deposition (CVD) from carbon-containing compounds on the surface of nanostructured catalyst.

In this work we synthesized carbon nanotubes in a CVD catalytic process in atmosphere of ethylene in presence of water vapors. Water selectively removes amorphous carbon but not damages the nanotubes at the growth temperature, because coating of the catalyst particles by amorphous carbon during chemical vapor deposition (CVD) reduces their activity and lifetime [1]. We changed in experiments concentration of ethylene and water in gas mixture with argon and hydrogen. Chemical structure of SWNTs and their physicochemical properties were examined by transmission electron microscopy and Raman spectroscopy. Varying of ethylene concentration in gas mixture causes changing of intensity of characteristic lines in Raman spectra which correspond to nanotubes with various diameter. This fact allowed us to make some conclusions about possible chemical mechanism of carbon nanotubes growth and influence of changing of concentration of ethylene and water for obtaining nanotubes with necessary chirality.

Reference

1. *Hata K., Futaba D.N., Mizuno K., Namai T., Yumura M., Iijima S.* Water-Assisted Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes // Science.- 2004.- V.306.- P.1362-1364..

DESIGN OF NEW METAL CATALYSTS FOR THE SYNTHESIS OF THE SILICON CARBIDE WHISKERS

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SiC whiskers have many superior properties, such as high hardness and strength, Young's module, and chemical inertness. This material can be used as good reinforcing component for different ceramic and polymer composites. Another possible way of the usage of SiC whiskers is linked with their good semi-conducting properties, such as wide bandgap (2.4-4 eV depending on the polytype of SiC). Silicon carbide whiskers can be used in various electronic devices, such as sensors, emitters etc.

Nowadays the most perspective way of synthesis of the SiC whiskers is usage of metal catalysts, such as transition metals (Fe, Ni, Co). Usual temperature of catalytic synthesis of SiC whiskers is 1200-1300 °C, which is less acceptable for high-tech applications because of the low control of the crystal parameters, such as type of crystal lattice and potential risk of thermal damaging of the substrate.

In this work we used analysis of the phase diagrams of various multi-component systems, based on transition metals combined with thermodynamic analysis of the nucleation step for the metal-SiC system for development of new low-temperature catalysts for synthesis a SiC whiskers. It was shown that this approach may be successfully used for design of new catalysts, working at low temperatures. Different methods were used for preparation of mono- and bimetallic catalysts. Catalysts prepared were tested in synthesis of silicon carbide whiskers under various experimental conditions, such as temperature and pressure (1000-1200 °C, 0.01-1 bar). Decomposition of methyltrichlorosilane and dimethyldichlorosilane in hydrogen atmosphere was used for production of C- and Si-containing gaseous precursors.

Synthesized crystals were investigated using different physical-chemical methods, such as TEM, SEM, XRD. Relationship between reaction conditions (temperature, pressure, catalyst and precursor composition etc.) and morphology and properties of SiC whiskers was also investigated.

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O-22

SELECTIVE HYDROGENATION OF CROTONALDEHYDE ON Ru/SUPPORT (α-Ga_2O_3, β-Ga_2O_3, α-GeO_2) CATALYSTS IN A GAS PHASE

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The catalytic hydrogenation of organic functional group is probably the most common application of heterogeneous catalysis in the synthesis of organic compounds. Catalytic hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols is an important step in preparation of various fine chemical products. Desirable is to find catalyst which preferably hydrogenate C=O bond and keep olefinic double bond inact. Ga_2O_3 and GeO_2 may be considered as a reducible oxide of potential usefulness as a catalyst support.

In this work hydrogenation of crotonaldehyde in the gas phase at atmospheric pressure over Ru/support (5, 2 and 1 wt. % Ru) catalysts was investigated.

The catalysts were prepared by wet impregnation method using $Ru(NO)(NO_3)_3$ and $RuCl_3 \cdot 3H_2O$, and three supports: α-Ga_2O_3 (home-made from metallic gallium), β-Ga_2O_3 (Aldrich, 99,99%) and α-GeO_2 (Teck Cominco Metals Ltd.). The catalysts were calcined at 400 °C. BET, TPR, XRD, IR methods were applied to characterized the catalytic systems. Catalytic tests were carried out at the temperature 80 °C. Before the reaction the catalysts were reduced in hydrogen at the temperature range from 80 to 300 °C.

XRD and TPR results show that for all catalysts reduction starts at the temperature about 75 °C and is completed at about 160 °C (Ru crystallites on the surface).

Catalytic tests in the reaction of hydrogenation of crotonaldehyde in a gas phase were carried at 80 °C. For catalysts supported on both α-Ga_2O_3 and β-Ga_2O_3 the optimum reduction temperature was 250 °C and for the germania supported catalyst – 200 °C. The row of the catalytic performance of the catalysts is as follows: Ru/α-$Ga_2O_3 > Ru/\beta$-$Ga_2O_3 > Ru/\alpha$-GeO_2. The best catalyst was 5 wt. % Ru/α-Ga_2O_3 which shows high selectivity (above 85%) at the activity ca. 300 μmole $s^{-1}g_{Ru}^{-1}$.

To sum up we can say that ruthenium catalyst, especially those supported on gallium oxide, show high activity and selectivity in the reaction of selective hydrogenation of crotonaldehyde in a gas phase. Optimum reaction parameters are: calcination temperature 400 °C, reduction temperature 250 °C (catalysts supported on α and β-Ga_2O_3) and 200 °C (catalyst supported on α-GeO_2) and reaction temperature 80 °C.

ETHYLENE POLYMERIZATION USING PHENOXY-IMINE CATALYSTS WITH DIFFERENT STRUCTURE

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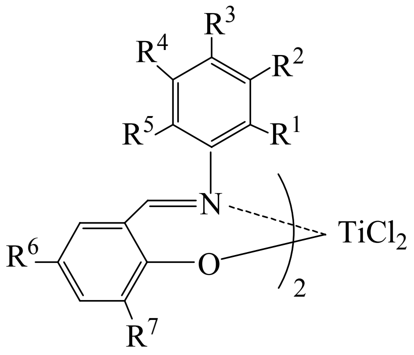
Ethylene polymerization kinetics is studied using five catalyst systems based on titanium complexes with phenoxy-imine ligands differing mainly by the substituents at imine nitrogen



I: R$^{1-5}$ = H, R^6 = Me, R^7 = ^{t}Bu
II: R$^{1-5}$ = H, R$^{6-7}$ = ^{t}Bu
III: R^1 = cyclopentyl, R$^{2-5}$ = H, R$^{6-7}$ = ^{t}Bu
IV: R^1 = cyclohexyl, R$^{2-5}$ = H, R$^{6-7}$ = ^{t}Bu
V: R^1 = cyclohexyl, R$^{2-4}$ = H, R^5 = Me, R$^{6-7}$ = ^{t}Bu

The polymerizations were performed using methylalumoxane (MAO) as a cocatalyst at temperatures 10-70 °C, ethylene pressure 0.3 MPa and different MAO:Ti ratios.

The polymerization rate is found to significantly depend on the bulk of substituents in the aryl ring at imine nitrogen according to the following trend:

II > I >> IV > III > V

The complexes **I** and **II** provide living ethylene polymerization with polyethylene molecular weight linearly growing with the process time within 5-20 min followed by the further slight increase. The living polymerization mechanism is confirmed by obtaining ethylene – 1-hexene block-copolymers.

The prepared polymers are featured with high melting temperatures (Tm = 140-145 °C), linear structure and high molecular weights.

O-24

FAVORED FORMATION OF ERYTHRULOSE AND 3-PENTULOSE IN FORMOSE REACTION

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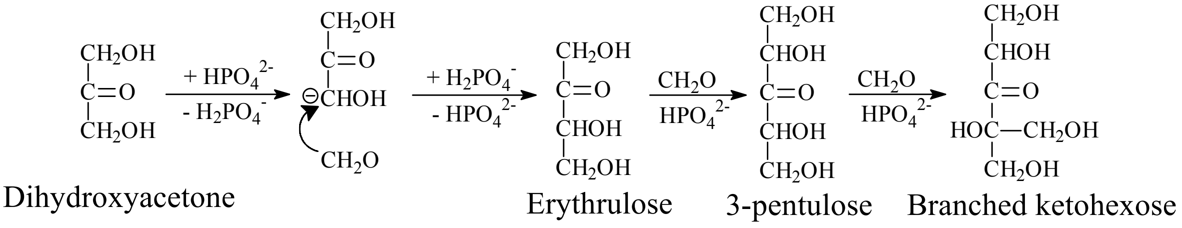
The autocatalytic oligomerisation of formaldehyde in aqueous alkaline media yielding “formose” - a complex mixture of monosaccharides, polyols and organic acids, is known as Formose reaction. The control of the selectivity of this reaction is very promising for the purpose of rare monosaccharides synthesis. In this work we describe the significant increase of the process selectivity in the presence of phosphate catalysts in neutral aqueous medium.

Natural mineral apatite $Ca_5(PO_4)_3(OH, Cl, F)$, synthetic hydroxylapatite $Ca_5(PO_4)_3(OH)$, calcium phosphate and carbonate were used as heterogeneous catalysts. The initial solutions contained formaldehyde and one of the lower carbohydrates (dihydroxyacetone, glycolaldehyde and glyceraldehyde) at pH = 7.3. The products of the reaction were analyzed using HPLC, GLC, GLC MS, ^{1}H- and ^{13}C-NMR spectroscopy.

It turned out that in such conditions the interaction between formaldehyde and dihydroxyacetone leads to the preferential formation of erythrulose (45%) and 3-pentulose (40%). Branched ketohexulose and ketopentulose were also detected in the reaction mixture.

To establish the role of the heterogeneous catalyst the reaction was carried out in presence of natural apatite and after 35% conversion of dihydroxyacetone the catalyst was removed from the reaction mixture. The removal of the apatite led to more than 10-fold decrease of the reaction rate. Nevertheless, the process did not stop. Several experiments were carried out in the homogeneous solution of the phosphate buffer (Na_2HPO_4+KH_2PO_4). Homogeneous catalyst was found to be even more active than heterogeneous. The reaction rate is proportional to the phosphate buffer concentration. Therefore one can suppose that both heterogeneous and homogeneous phosphates perform a specific catalytic action on the reaction under discussion. The overall scheme of the investigated process is proposed below.



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O-25

CATALYTIC PROPERTIES OF COPPER SUBSTITUTED SILICALITE-1 IN NO$_X$ NEUTRALIZATION

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Zeolites ZSM-5 are applied as very active and selective catalysts. The MFI structure can be obtained also as metallosilicate with various framework metal atoms. The isomorphous substitution of Al for other elements affects substantially the catalytic properties of the products. Zeolite ZSM-5 modified with Cu^{2+} cations have been found a very active but not stable catalysts for decomposition of nitrogen oxides. The main aim of the study is to check whether copper introduced into the framework positions of metallosilicalite-1 can be also used as active catalyst for NO_x abatement.

The coppersilicalites were prepared by means of conventional crystallization of the initial gel formed from the mixture of water glass, $CuSO_4$ (Si/Cu = 12.5-100) and template. The products were modified with H^+, Cu^{2+}. The products showed a high crystallinity (XRD) particularly at low metal loading. IR spectra showed weak band at ca. 960 cm^{-1} that could result from Cu-O vibration. The band vanished after heating which could reflect a migration of some Cu atoms from the framework. ^{29}Si MAS NMR spectra of the as made samples show two signals: at –104 ppm assigned to Q_3 (3Si, 1Cu) and at –115 ppm due to Q_4 (4Si, 0Cu). The first signal decreased on heating, which confirms the conclusion suggested by IR spectra. The in situ DRIFT spectra of H- and Cu-forms of the samples, showed the bands of bridging OH groups (3600 cm^{-1}) and of silanol groups (3730 cm^{-1}). The IR spectra of NO adsorbed on H forms indicated two significant bands at 1880 and 1635 cm^{-1}, due to Cu^{2+}NO bonds and Cu^{2+} combined with NO_2^- or NO_3^- , respectively. Contrary to Cu-ZSM-5 the band at 1810 cm^{-1} assigned to Cu^+ complex with NO has never been recorded in our samples. It reflects the different nature of copper moieties. The catalytic activity of the series for propan-2-ol decomposition increased with growing metal content up to Si/Cu=16 and then it declined with further metal loading. The dehydration prevailed over the low metal loaded samples, whereas the metal rich samples led the reaction to acetone. The H forms of the studied metallosilicalites showed a considerable activity in the NO reduction with propene. The starting activity was comparable to that of Cu-ZSM-5, but contrary to the latter, it increased with time. The activity always declines with growing Cu content. An introduction of Cu^{2+} cations into the copper-silicalite samples always resulted in drastic decrease in activity.

O-26

MIXED HETEROPOLY CATALYSTS FOR ENVIRONMENTAL PROTECTION

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An economical and effective way for destructive removal of chlorinated volatile organic compounds (VOCs) is the catalytic oxidation of the compounds to carbon dioxide, HCl and water. The subject of the present work is to investigate the potentialities of developing new active and thermally stable catalysts on the basis of mixed heteropoly compounds with Keggin structure for total oxidation of Cl-benzene. It was studied the effect of the temperature treatment, the number of V atoms and the kind of peripheral atoms (Mo or W) on the surface and catalytic properties of the mixed heteropoly catalysts.

The catalysts were obtained by wetness impregnation of synthesized mixed heteropoly compounds $H_{3+X}[PMo_{12-X}V_XO_{40}]$ and $H_{3+X}[PW_{12-X}V_XO_{40}]$, X = 1 or 3, on TiO_2 support. The structure and availability of crystal phases were measured by X-ray diffraction (XRD), infrared spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS).

The IR spectra of mixed MoV and WV heteropoly catalysts show that tungstophosphate heteropolyanions are more thermally stable than molybdophosphate heteropolyanions. On the other hand, increasing the number of V atoms introduced into heteropolyanions leads to improving its thermal stability. Increasing the temperature of treatment and the number of introduced V atoms leads to increase of the dispersion of molybdenum, tungsten and vanadium-oxide species, which is observed by XRD and is suggested by calculated values of the XPS Mo/Ti and W/Ti atomic ratios. Vanadium centers are quite stable in the Keggin anion and may act as a structural promoter in the catalyst precursor facilitating the formation of the active (Mo,V or W,V) oxide species. In this way, the presence of these vanadium centers appears to be responsible for the activity enhancement in total oxidation of Cl-benzene. Molybdenum-vanadium catalysts show higher catalytic activity in the reaction of total oxidation of Cl-benzene compared to tungsten-vanadium catalysts.

NITROUS OXIDE AS A SELECTIVE OXIDANT FOR HYDROCARBONS OXIDATION

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Selective oxidation of hydrocarbons towards oxygenates is one of the most difficult fields in catalytic chemistry. Recently, one of the most promising reagents for oxidative functionalisation of hydrocarbons has appeared to be nitrous oxide (N_2O). The use of iron modified zeolite ZSM-5 in the presence of N_2O as an oxidant has opened a new perspective in selective oxidation of both aromatic and aliphatic hydrocarbons [1-3].

The presented study was focused on the catalytic oxidation processes performed on iron modified zeolites ZSM-5, in the presence of N_2O as an oxidant. The interaction of hydrocarbons and N_2O with active centers of catalytic surface has been defined by means of spectroscopic techniques (FT-IR and EPR). Iron modified samples were also characterised by means of XRD measurements and UV-Vis spectroscopy. Catalysts were prepared on the base of commercial zeolites of MFI structure. Zeolites were modified with iron (III) ions by means of ionic exchange from aqueous solution, followed by calcinations at 600 or 900^{o}C. Acidity of the samples calcined at different temperatures (600 or 900^{o}C) was estimated on the grounds of FT-IR spectra of adsorbed pyridine and by TPD of ammonia. The samples were tested in the reaction of benzene to phenol hydroxylation and also in light paraffins oxidation. The catalytic tests were performed in continuous flow reactor, in the range of temperature 350-450^{o}C.

Catalytic performance of Fe-ZSM-5 was significantly affected by the nature of the oxidized molecule. In catalytic oxidation of benzene the oxygen insertion with OH group formation was predominant reaction, whereas light paraffins oxidation resulted in oxidative dehydrogenation with the formation of carbon - carbon double bond and production of corresponding olefins. Both activity and selectivity of oxidation processes over iron modified zeolites was influenced by the samples acidity, iron concentration, temperature of calcination and Si/Al ratio of zeolite matrix.

References

1. V. N. Parmon, G. I. Panov, A. Uriarte, A. S. Noskov, Catal. Today 100 (2005) 115.
2. B. Wichterlová, Z. Sobalik, J. Dědeček, Appl. Catal. B: Environmental, 41 (2003) 97.
3. A. Held, J. Kowalska, K. Nowińska, Appl. Catal. B: Environmental 64 (2006) 201.

O-28

THE PRODUCTION OF ETHENE VIA OXIDATIVE DEHYDROGENATION OF ETHANE OVER Pt-Sn MONOLITHS

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Ethene is an important feedstock for many chemical processes. Traditionally ethene is produced by steam cracking. However, steam cracking suffers from several limitations. One promising alternative to this process is oxidative dehydrogenation of ethane which offers advantages such as short contact time, adiabatic operation and reduced reactor volumes. It has been shown that high yields of ethene can be obtained by oxidative dehydrogenation of ethane at short contact times using Pt-Sn monoliths and co-feeding hydrogen [1-4].

Cylindrical pieces of cordierite (Corning) were used as support. The monoliths were washcoated with γ-alumina before impregnation with Pt and Sn. The monoliths were reduced *in situ* prior to the experiment in a flow of hydrogen. Experiments were carried out at atmospheric pressure and in the temperature range of 600 – 900 °C in a conventional flow apparatus consisting of a quartz reactor with an inner diameter of 15 mm. The coated monolith was placed between two inert monoliths acting as radiation shields. The furnace temperature was measured at the outlet of the active monolith. Two condensers at the reactor outlet removed any water from the product gas. The dry samples were analyzed by two on-line gas chromatographs.

Results from experiments with catalyst were compared to results using only a washcoated monolith at different temperatures and C_2H_6/O_2-ratios. These experiments showed that the catalyst increased the conversion and selectivity significantly at the lower furnace temperatures, but when the temperature was increased to 800 °C and more, the gas phase reactions start to dominate.

Experiments were also run with different loadings of catalysts. Practically no effect was observed on the conversion or product distribution when reducing the Pt loading from 1 wt% to 0.1 wt%. The Pt/Sn-ratio was 0.5 in all experiments.

References

1. B. Silberova, J. Holm, A. Holmen, Stud. Surf. Sci. Catal.: 147 (2004) 685.
2. D.A. Henning, L.D. Schmidt, Chem. Eng. Sci., 57 (2002) 2615.
3. A. Bodke, D. Henning, L.D. Schmidt, Catal. Today, 61 (2000) 65.
4. C. Yokoyama, S.S. Bharadwaj, L.D. Schmidt, Catal. Lett., 38 (1996) 181.

INVESTIGATION OF ACTIVE SITES ON Pt CONTAINING SULFATED ZIRCONIA

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Introduction: The skeletal isomerization of n-alkanes to iso-alkanes over solid acid catalysts is one of the important technologies for improvement of the octane number in oil refining. The importance increases as environmental regulations on gasoline composition continue to grow. Pt promoted sulfated zirconia (Pt/SZ) attracted a lot of interest due to its high activity for the isomerization at low temperatures. Until now a discussion exists about the nature of the active sites on SZ. The aim of this work is to investigate the influence of the sulfate and platinum content of Pt/SZ on the catalytic activity for n-hexane and n-heptane conversion and further to point out what criteria must be met in order to obtain an active catalyst.

Experimental: Self-prepared and commercial SZ catalysts obtained from MEL chemicals were used in this study. Sulfation and platination of the zirconium hydroxide was done via impregnation with sulfuric acid and $PtCl_4$-solution respectively. Afterwards, the samples were calcined at 873 K. The catalysts were characterized by BET, XRD, TG/DSC, TPD and IR methods after pyridine and CO adsorption and kinetic measurements were carried out in a fixed-bed plug-flow reactor at 423-523 K in hydrogen atmosphere.

Results and Discussion: It can be concluded that the catalytic activity for n-alkane conversion increases with the sulfate and platinum content. With increasing sulfate content the ratio of Brønsted (BS) to Lewis-acid sites (LS) increases. A catalyst without BS is found to be inactive. Furthermore there are at least two different sulfate species present on the surface of sulfated zirconia. The sulfate species, which are more weakly bonded to the surface after a reductive step and are thus evolved at lower temperatures (below 873 K) in inert gas, are essential for catalytic activity, whereas the sulfate groups, which are removed at temperatures above 873 K under the same conditions, are inactive for n-alkane conversion. A strong interaction between metal and acid sites was observed, which had a significant impact on the properties of both types of sites and thus on the catalytic activity and isomerization selectivity of the catalysts.

O-30

INFLUENCE OF THE INITIAL FORM OF THE SUPPORT ON THE PROPERTIES OF WO_X-TITANIA CATALYSTS

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Since the pioneering work of Hino and Arata, [1] tungstated zirconias have been considered active for n-alkane isomerization only when obtained by impregnation of amorphous support. Catalysts synthesized from a crystallized zirconia were essentially inactive. We have recently shown that the structure, the acidity and the catalytic activity of these catalysts were not significantly affected by the initial state of the support, Zr oxyhydroxide (amorphous) or crystallized (mainly tetragonal) zirconia. The results suggest that the reported influence of the crystalline nature of the support is due to its presence in monoclinic form. The objective of the present work was to extend the study to the corresponding titania-based system. Specifically, it seeks to determine the eventual influence of the initial form of the support (amorphous Ti-oxyhydroxide or crystalline titania in anatase form) on the surface structure, acidity and activity of WO_x/TiO_2 catalysts.

Two series of WO_x/TiO_2 catalysts (0-4.4 at.W/nm^2) prepared either from titania (anatase form) or from Ti oxyhydroxide were characterized by XRD, Raman and IR spectroscopy. The catalytic activity was tested for isopropanol dehydration and n-hexane isomerization.

For a given W surface density, XRD and Raman results showed that the crystalline composition of the support and the nature of the W species of solids of both series were similar. W, in all catalysts, was present as a surface phase. IR results indicated an increase in the degree of polymerisation of W species with increasing W surface density. For both series, lutidine adsorption results, followed by IR spectroscopy, showed that Brønsted acid sites were only present above a threshold of 1.3 at.W/ nm^2. The abundance of these sites was correlated with the formation of polymeric W species and with isopropanol dehydration activity. For both catalytic tests, the activity, for a given W surface density, was little affected by the initial form of the support. A minimum of W surface density (1.3 at.W/nm^2 for isopropanol dehydration and 3.6 at.W/nm^2 for n-hexane isomerization) appears to be required for the development of activity. The shift in the W threshold was attributed to the more demanding character of the latter reaction. The overall results clearly show that the surface structure, acidity and catalytic properties of WO_x/ TiO_2 catalyst are not determined by the initial form of the support (amorphous Ti-oxyhydroxide or crystalline titania in anatase form).

1. Arata, K.; Hino, M. in *Proc. 9th I.C.C.*; Philips, M. J., Ternan, M., Eds., 1988; pp 1727

A DFT STUDY OF ETHANE DEHYDROGENATION OVER Ga/ZSM-5 ZEOLITE

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Hydrogen forms of ZSM-5 zeolite modified with gallium are known to be active catalysts for light alkane aromatization [1]. A generalized mechanism consists of activation of paraffinic molecules by dehydrogenation over the modifying cation and subsequent oligomerization of the resulting olefin over Brønsted acid site. Recent experimental study [2] on the propane dehydrogenation over well-defined Ga/ZSM-5 zeolites prepared via chemical vapor deposition of $Ga(CH_3)_3$ to the hydrogen form of ZSM-5 has shown that the activity of the samples strongly depends on the pretreatment procedure of the catalyst and, hence, on the nature of the active sites. It was suggested that the catalyst predominantly containing $[Ga=O]^+$ exchanged species exhibit the highest initial activity, whereas $[GaH_2]^+$ sites are almost inactive initially. However, both these active sites decomposed during the catalytic reaction and the activity of the sample became equal to that one obtained for the zeolite predominantly containing Ga^+ sites.

In the present work different pathways of ethane dehydrogenation, as a model reaction, over different Ga-containing active sites in ZSM-5 were studied using a density functional theory. The results obtained very well agree with the experimental data. The mechanism of the decomposition of $[Ga=O]^+$ and $[GaH_2]^+$ species is described. The very high initial activity of the exchanged oxo-gallyl ion is explained with secondary reactions of molecular ethane with very stable intermediates formed during the primary C_2H_6 dehydrogenation path over $[Ga=O]^+$ sites. The initial activation of C_2H_6 over Ga^+ cation exchanged in ZSM-5 zeolite is shown to be resulted from indirect “oxidative addition” reaction, which proceeds via two-step mechanism: the first step is heterolytic dissociation of C-H bond of the adsorbed ethane resulting in formation of $Ga-C_2H_5$ species and Brønsted acid site, which easily interact on the next step with each other resulting in formation of the product of oxidative addition of C_2H_6 to Ga^+ ion: $[H-Ga-C_2H_5]^+$. To our knowledge such mechanism has never been reported before for this type of reactions.

[1] A. Hagen and F. Roessner, Catal. Rev. 42 (2000) 403.
[2] N. Rane, A.R. Overweg, V.B. Kazansky, R.A. van Santen and E.J.M. Hensen, accepted in J. Catal. doi:10.1016/j.jcat.2006.03.004

POSTER PRESENTATIONS

ROLE OF Pd-Ag INTERLAYER IN IMPROVING STABILITY OF CATALYTIC MEMBRANES BASED ON A THIN Pd FILM ON A CERAMIC SUPPORT

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Recently, there is an increasing interest to the catalytic membranes applications for continuous on-line separation of H_2 from steam reforming gases or direct synthesis of hydrogen peroxide from hydrogen and oxygen. While the latter process is only starting to be investigated, the use of Pd-based membranes for the separation of H_2 is a more extensively studied field. However, dense Pd-based membranes are essentially used. In order to have enough H_2 flux and thus productivity, thin membranes are necessary, but this creates problems of wrinkling and stability. There is thus an increasing interest towards the development of thin Pd-based films on ceramic membranes in order to combine the selectivity characteristics of the Pd thin film to the robustness characteristics of the ceramic membrane. But this poses new questions regarding the ceramic-metallic adherence and interface, the central aspect investigated in this communication.

For our experiments we used as supported ceramic membranes consisting of an α-alumina macroporous support (3 μm pore size) with a α-alumina mesoporous layer (pore size 50 – 100 nm) on which Pd was deposited as a thin layer (1-10 μm) by electroless plating deposition. In this technique palladium metallic particles are produced by reduction from the plating bath consisting of amine-complexes of palladium in the presence of a reducing agent. Metallic particles grow on palladium nuclei which have been pre-seeded on the substrate surface through a successive activation and sensitisation procedure and which also act as a catalyst for the reduction of the palladium complexes.

For practical applications, catalytic membranes based on pure palladium metallic films cannot be used for the direct oxidation of hydrogen to H_2O_2 or for hydrogen separation due to their structural instability. In fact, when a pure palladium membrane operates below 300 °C, a β-palladium hydride phase is formed, which is accompanied by a discontinuous lattice expansion. This phase transformation leads to the formation of pinholes and ultimately to the rupture of the Pd-membrane, and consequently the permeselectivity of the Pd-membrane for hydrogen is lost.

We will demonstrate in this contribution that the β-hydride phase formation is avoided or suppressed by formation of an intermediate layer of palladium alloy with group IB metals. In this communication we report the results on membranes where between the α-alumina support and the external metallic Pd film an interlayer of a Pd-Ag alloy was created. This layer was obtained also by electroless plating deposition through reactions involving both the Pd-amine and Ag-amine complexes and hydrazine as the reducing agent. For alloy formation, the membranes were heated after deposition and drying at 773 K in a nitrogen atmosphere for 5 hours.

Both types of membranes were characterized by optical and electronic microscopy, as well as XRD, which demonstrated clearly the formation of the intermediate alloy and permitted to follow the different morphological characteristics of the Pd film grown or directly on the α-alumina membrane or on the Pd-Ag alloy. Moreover it was possible to follow the stability of the external Pd film in both cases during several hours of time on stream of hydrogen during hydrogen peroxide synthesis. Data evidenced that in the absence of the intermediate layer of the Pd-Ag alloy just after 10 hours of time on stream a clear detachment of the Pd film was detected (Figure 1). Whereas in the case of the presence of the Pd-Ag alloy a good stability in reaction condition was observed.

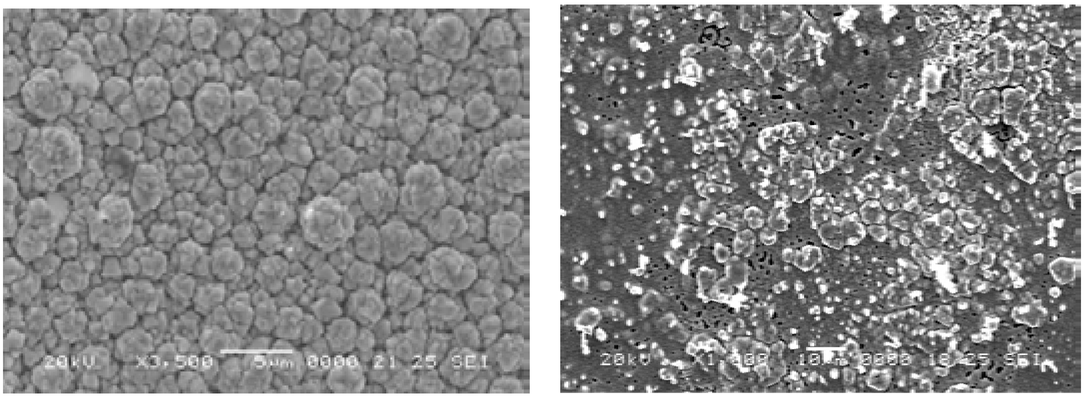

Figure 1 – SEM of palladium film before and after 10 h in flow of H_2

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References

G. Centi, R. Dittmeyer, S. Perathoner, M. Reif, *Catal. Today*, 79-80C (2003) 139-149.

V.R. Choudhary, S.D. Sansare A.G. Gaikwad, US Patent No 6,448,199 (2002)

P-2

ABOUT THE MECHANISM OF FORMATION OF POROUS STRUCTURE OF ALUMINUM HYDROXIDE IN NON-STATIONARY CONDITIONS OF SYNTHESIS

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Researches of last years have shown importance of creation of carriers and catalysts with the set of structural and textural characteristics since they are determining factors of effective work of catalytic systems. Widespread carrier and the catalyst in many large-tonnage industrial processes is alumina which is produced mainly by thermal processing of its predecessor – aluminum hydroxides. It is known, that each separate stage of multiphase manufacture of aluminum hydroxides brings the contribution to formation of a structure of the resulting product. Therefore purposeful industrial synthesis of alumina with required structural and textural characteristics demands studying of the character of transformation of porous structure aluminum hydroxides.

The purpose of work consists in revealing the mechanism of formation of porous structure of aluminum hydroxides in conditions of industrial synthesis.

Experimental part

The objects of research are the samples of aluminum hydroxides, taken on different stages of industrial synthesis: 1 - sedimentation; 2 - stabilization during τ =90 min; 3 - stabilization during 240 min; 4 - hashing; 5 - on filter-press; 6 - repulping. Sedimentation was carried out on sulfo-aluminate from solutions of aluminate of sodium and sulfate of aluminium at constant pH.

Researches were carried out with the help of the following physical and chemical methods: XRD, DTA, IR spectroscopy, SEM and low temperature adsorptions of nitrogen. Mathematical processing of X-ray diffraction spectra was carried out with the help of the software package «Material Analysis Using Diffraction » (MAUD).

Discussion of results

XRD and DTA methods were used to investigate phase structure and morphology of samples of aluminum hydroxides at separate stages of synthesis. Calculation of experimental X-ray diffraction spectra has allowed to establish formation in industrial aluminum hydroxides of two morphological phases of pseudoboehmite (designated as Pb1 and Pb2) which differ by structural characteristics: phase Pb1 is characterized by the significant content (1.48-1.78 мol H_2O/мol Al_2O_3) of structural water, the size of microcrystallites 11-165 Å and the content of planar defects in a direction [020]; phase Pb2 is characterized by the content of 1.17-0.89 мol H_2O/мol Al_2O_3 in crystal lattices and large primary particles with the size up to 650-900 Å.

According to differential curves of distribution of pore volume, a well defined maximum is shown for pores with diameters: ~ 22, ~ 34, ~ 46, ~ 55, ~ 64, ~ 76, ~ 82 and ~ 90 Å caused by the directed coordination of relatively similar microcrystalline Pb1. Pores of the given diameter bring the basic contribution to the porous volume V (up to 93 %) and specific surface S (up to 79 %).

It is proved, that the directed mutual coordination of microcrystalline Pb1 occurs on crystalline planes (020) therefore formation of two types of primary porous fragments is revealed: fragment I is formed by coordination of two microcrystallites on a plane (020) with corresponding diameter 34 Å; the fragment II - microcrystallites on a plane (020) – with corresponding diameter 46 Å. The maximum at 22 Å on all curves of pore distribution s is caused by porous wedges structures.

Proceeding from this model of a structure of a porous skeleton, the mechanism of formation of porous structure is developed. In a case of lability of contacts between microcrystallites Pb1 on planes (020), formation of wide cavities will occur by mutual introduction of porous fragments I and II in places wedges backlashes along a direction [020] (fig.).

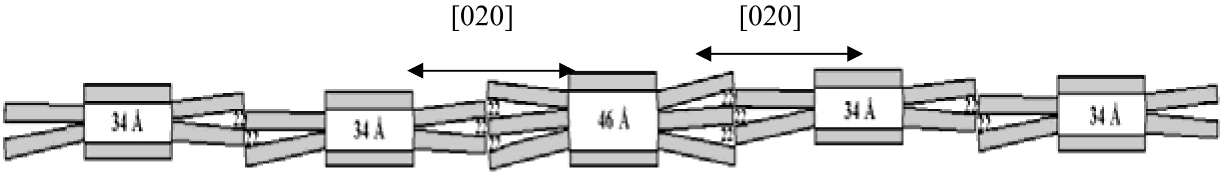

Figure. The circuit of transformation of primary porous fragments.

Transformations of thin pores with the size ~ 34 and ~ 46 Å in a cavity diameters ~ 72, ~ 82 and ~ 90 Å can be achieved as a result of direct mutual transition of one size to another or consecutive transition through intermediate state (~ 54 and ~ 64 Å) by discrete translation of fragments I and II.

XPS STUDY OF CeO_2-ZrO_2 THIN FILMS ELECTROCHEMICALLY DEPOSITED ON STAINLESS STEEL

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Cerium-zirconium mixed oxide has been the subject of extensive study in recent years mainly because of its high oxygen storage efficiency in the latest generation of the three-way catalysts (TWCs) used for purifying automobile exhaust gases, and other applications such as its use as ionic conductor (e.g., in fuel cells) or as active support in catalysts for reforming or water gas shift reactions.

In the present work, CeO_2-ZrO_2 thin films were deposited on stainless steel by cathodic deposition. The electrodeposition offers the advantages of low processing temperature, normal handling pressure, high purity of deposition and controlled thickness of the film. XRD, SEM and XPS methods were used to investigate the structure, surface morphology, composition and chemical state of $Ce_{1-x}Zr_xO_2$ thin films ($0.1<x<0.9$), after deposition and after thermal treatment at 450 °C. It was found that the composition and structure, which are strongly related to oxygen storage capacity, depended on the parameters of deposition. X-ray diffraction analysis indicated that the electrochemical deposition induces the formation of solid solution with a contraction of the cell parameter for cubic ceria following the introduction of Zr into the lattice. SEM study showed that with increasing ZrO_2 content, the crystallite size of the mixed oxide decreased. The specific conditions of cathodic deposition may cause specific distribution and coordination of the Ce and Zr ions in the deposited thin films. To study this effect we used the concept of Auger parameter (α) since in mixed oxides the Auger transitions involving only core level electrons can be used to interpret changes of α with composition in terms of changes in ground-state electronic structure, e.g. electron transfer and hybridization between different valence orbitals. This information can make an important contribution to the understanding of mixed-oxide formation at the electronic structure level.

P-4

ROLE OF MODIFIED Al_2O_3 SUPPORT ON THE FORMATION OF Cu-Co SPINEL PHASE – XPS INVESTIGATION

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The increasing environmental protection requirements provoke serious efforts for improvement of the emission control technology. Due to its excellent physicochemical characteristics, aluminum oxide is one of the most important supports in catalysis. Introduction of promoters as Mg, Ca, Cu and etcetera will improve mechanochemical parameters of the support (Al_2O_3) and increase it's catalytic activity on one side, and ensure the better formation of active phase on the other side. The purpose of the present study is to investigate the influence of the promoter on the formation of active Cu-Co spinel phase by X-ray Photoelectron Spectroscopy (XPS). The following samples have been prepared: γ-Al_2O_3-4 wt% MgO; γ-Al_2O_3-8 wt% MgO; γ-Al_2O_3-8 wt% MgO-3 wt% CuO and calcinated at 1000 °C for 3h. Then the active Cu-Co phase was deposited by impregnation in a mixture of $Cu(NO_3)_2{\cdot}3H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ in a respective stoichiometric quantity (1:2). After that they were calcinated at 550 °C for 3h. XPS results lead to the evaluation of the valence state of the constituent element at the surface of the samples. For the system γ-Al_2O_3 - X wt% MgO (X = 4, 8), XPS data indicate the formation of stoichiometric spinel (Cu:Co=1:2). In the case when the sample contain 4 wt% MgO additional CuO phase have been detected. For the other system γ-Al_2O_3-8 wt% MgO-3 wt% CuO the formation of separate Co_3O_4 and CuO have been observed. The results conformed the other obtained by X-ray Diffraction analysis as well as the catalytic activity towards NO_x for these systems. The highest activity has the sample with Cu:Co ratio approach to 1:2.

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CATALYTIC STUDIES OF NEW CHLORO AND TRIPHENYLSILOXY DERIVATIVES OF DIOXOMOLYBDENUM(VI) FOR OLEFIN EPOXIDATION

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Molybdenum(VI) complexes are versatile catalysts for the oxidation of organic compounds [1]. In recent years, complexes of the type $[MoO(O_2)_2(L_1)(L_2)]$ and $[MoO_2X_2(L_1)(L_2)]$ (X = Cl, Br, CH_3) with different combinations of base ligands L_1 and L_2 have been extensively investigated as catalysts for epoxidation reactions, usually employing *tert*-butyl hydroperoxide (TBHP) as the mono-oxygen source [2]. It is thought that the variable catalytic activities observed for these complexes are due, at least in part, to differences in the Lewis acidity of the metal centre as a result of the different donor properties of the ligands.

The high potential of substituted pyrazolylpyridines as supporting ligands for oxomolybdenum catalysts has already been well established for oxodiperoxo complexes of the type $[MoO(O_2)_2L]$ [3]. In this work, dioxomolybdenum complexes with substituted pyrazolylpyridines $[MoO_2X_2L_2]$ (X = Cl, $OSiPh_3$; L_2 = 2-(1-butyl-3-pyrazolyl)pyridine, ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate) were prepared and characterized by ^{1}H-NMR, IR and Raman spectroscopy. The catalytic performance of these materials was studied in the epoxidation of several olefins, such as 1-octene, 2-octene, limonene, cyclododecene and cyclooctene, using TBHP as the oxidant. The influence of the nature of the X and L ligands and of the reaction conditions on the catalytic results was investigated.

References

[1] K. A. Jörgensen, *Chem.Rev.* **1989**, *89*, 431.

[2] F. E. Kühn, M. Groarke, É. Bencze, E. Herdtweck, A. Prazeres, A. M. Santos, M. J. Calhorda, C. C. Romão, I. S. Gonçalves, A. D. Lopes, M. Pillinger, *Chem. Eur. J.* **2002**, *8*, 2370.

[3] W.R. Thiel, M. Angstl, N. Hansen, *J. Mol. Catal. A: Chem.* **1995**, *103*, 5.

P-6

SODIUM 30-TUNGSTOPENTAPHOSPHATE, $[NaP_5W_{30}O_{110}]^{14-}$, AS A REUSABLE AND ECO-FRIENDLY CATALYST IN SELECTIVE OXIDATION OF PYRIDINE CARBOXYLIC ACIDS

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In nanotechnology, industry and medicine, pyridine N-oxides are important. These compounds are also versatile synthetic intermediates and the chemistry and applications of them have recently received much attention [1,2]. Recently, pyridine N-oxide derivatives represented a new class of anti-HIV compounds [3]. In addition, in the nanotechnology field, has been shown that nanoshampo including carboxylic acid pyridine N-oxide is a very powerful hair growth stimulator with a high level of safety [4].

With respect to the pyridine N-oxides usually are prepared by oxidation of pyridines using peracids such as meta-chloroperbenzoic acid and peracetic acid, from the esters of N-hydroxy-2-thipyridone, by ring transformation of isoxazolesand through cycloaddition reactions and metal complex catalysts [5-10], there is still a good scope for research towards finding green and eco-friendly catalysts.

Recently, interest has been directed towards potential applications of heteropolyacids (HPAs). It was shown that HPAs exhibited interesting catalytic properties as catalysts for both redox and/or acid-base type reactions.

Until now, most of the research concerning catalytic properties of HPAs has been carried out using, Keggin structure and its derivatives. In the recent years, the interest in other HPAs, has been growing. However, the catalytic behavior of sodium-30 tungstopentaphosphate, so-called Preyssler's anion, has been largely overlooked.

In continuation of our researches on catalytic properties of HPAs [11], in this research, the catalytic oxidation of some pyridine carboxylic acids to the corresponding N-oxides has been studied using the Preyssler's catalyst in homogeneous and heterogeneous conditions. The effects of various parameters such as the solvent type, the substrate, catalyst type, temperature and reaction time have been studied. The results showed that Preyssler's catalyst with exclusive properties surpassing the Keggin HPAs, catalyze the reactions with good yields at especial positions of carboxylic acid to the nitrogen. The catalyst can be recovered and recycled.

References

[1] A. Albini, S. Pietra, "Heterocyclic N-oxide" CRC press, Boca Raton. 1991.

[2] C. J. Oconnor, E. Sinn, R. L. Carlin, Inorg. Chem. 16 (1977) 3314.

[3] J. Balzarini, M. Stevens, E. De Clercq, D. Schols, C. Pannecouque, J. Antimicr. Chem. 55 (2005) 135.

[4] Dr. Proctor,The world's best products at the world's best prices (online internet).

[5] (a) G. B. Payne, P. H. Deming, P. H. Williams, J. Org. Chem. 26 (1961) 651; (b) G. B. Payne, J. Org. Chem. 26 (1961) 668; (c) D. C. Edwards, Tetrahedron Lett. (1966) 4767; (d) E. Ochiai, Aromatic Suschitzky, J. Chem. Soc., Chem. Commun. (1971) 28.

[6] B. H. R. Derek, O. Nubar, V. Bernard, Tetrahedron Lett. 44 (1988) 7385.

[7] A. W. Chucholowski, S. Uhlendorf, Tetrahedron Lett. 31 (1990) 1949.

[8] R. Nesi, D. Giomi, S. Papaleo, S. Bracci, P. Dapporto, Synthesis. (1988) 884.

[9] R. Nesi, D. Giomi, S. Papaleo, S. Bracci, P. Dapporto, J. Org. Chem. 54 (1989) 706.

[10] K. Takabe, T. Yamada, T. Katagiri, Chem. Lett. (1982) 1987; (b) R. W. Murray, K. Iyanar, J. Org. Chem. 61 (1996) 8099; (c) A. Goti, L. Nannelli, Tetrahedron Lett. 37 (1996) 6027.

[11] a) M. M. Heravi, Kh. Bakhtiari, F. F. Bamoharram, Catal. Commun. 7 (2006) 373. b) M. M. Heravi, Kh. Bakhtiari, F. F. Bamoharram, Catal. Commun. 7 (2006) 499. c) M. M. Heravi, F. Derikvand, F. F. Bamoharram, J. Mol. Catal. 242 (2005) 173. d) M. H. Alizadeh, H. Razavi, F. F. Bamoharram, K. Daneshvar, J. Mol. Catal. 206 (2003) 89. e) M. H. Alizadeh, H. Razavi, F. Farrash Bamoharram, M. H. Hassanzadeh, Kinet. Catal. 44 (2003) 524. f) F. F. Bamoharram, M. M. Heravi, M. Roshani, M. Gahangir, A. Gharib, Appl. Catal. 302 (2006) 42. g) M. M. Heravi, R. Motamedi, N. Seifi, F. F. Bamoharram, J. Mol. Catal. 249 (2006) 1. h) F. F. Bamoharram, M. Roshani, M. H. Alizadeh, H. Razavi, M. Moghayadi, J. Braz. Chem. Soc. 17 (2006) 505. i) M. M. Heravi, F. K. Behbahani, F. F. Bamoharram, J. Mol. Catal. (2006) 1n press. j) F. F. Bamoharram, M. M. Heravi, M. Roshani, A. Gharib, M. Gahangir J. Mol. Catal. 252 (2006) 90.

P-7

ACID-FUNCTIONALIZED AMORPHOUS SILICA BY CHEMICAL GRAFTING WITH NAFION® GROUPS

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Esterification of carboxylic acids with alcohols belongs to classical chemical reactions, widely employed in the syntheses of many fine and specialty chemicals. Typical homogeneous acid catalysts are mineral inorganic acids, such as H_2SO_4, HCl, HI, and $ClSO_3OH$. The disadvantage of mineral acids is their miscibility with the reaction medium, which causes separation problems and equipment corrosion at higher catalyst concentrations. Therefore heterogenized acid catalysts provide an attractive alternative to homogeneous catalysts [1]. Organically modified silica has recently been exploited to prepare sulphonic acid modified solid catalysts [2]. The aim of this work is to study the preparation of silica containing perfluorinated sulfonic acid groups.

Samples of perfluorinated sulfonic acid groups were prepared by chemical grafting of a silica substrate with $C_3F_6O_3S$. Some of them were modified by treatment with $C_{10}H_{10}ClF_{13}Si$. The preparation of silica modified with perfluro sulfonic groups was the following. SiO_2 (1.4 ml/g, 213 m^2/g) and $C_3F_6O_3S$ was suspended in toluene under reflux for 4 h. The solid was filtered and washed with toluene. The silica modified sample was treated with $C_{10}H_{10}ClF_{13}Si$ to modify the hydrofobicity of the surface. Perfluorinated sulfonic silica was mixed with $C_{10}H_{10}ClF_{13}Si$ in toluene, this mixture was refluxed, filtered and washed. Another sample was prepared by adding simultaneously both functionalizating groups in toluene.

Thermogravimetric, IR and XPS analysis indicated that the incorporation of perfluorinated sulfonic acid groups was effective. Clear differences were observed between samples modified with $C_{10}H_{10}ClF_{13}Si$. When perflurosulfonic acid and sililant agent were consecutively added, only a very small amount of sulfonic groups were exposed (XPS) but the proportion of these sulphonic groups markedly increased when both agents were simultaneously added. The catalytic performance was assessed with the esterification of acetic acid with methanol. All the catalysts showed much higher conversion levels than in the absence of catalyst, pointing to the involvement of the surface acid groups of the heterogeneous catalyst produced by silica functionalization.

References

1. R. D. Badley and W. T. Ford, *J. Org. Chem.*, 54 (1989), 5437
2. L. Mercier and T. J. Pinnavia, *Chem. Mater.*, 74 (2000), 188

PHYSICAL PROPERTIES OF TITANIUM DIOXIDE BASED PHOTOCATALYSTS PREPARED BY SOL-GEL TECHNIQUE

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Titanium dioxide has been the prevailing photocatalyst in heterogeneous photocatalysis due to its being chemically and biologically inert, non-toxic, inexpensive and environmentally safe. Some metal sulfides may also be photocatalytic systems, but they have some drawbacks because of corrosion. Iron oxide may be inexpensive, but it can also be corroded. Zinc oxide is probably the closest competitor to titanium dioxide but its weaknesses are instability in some solutions and a tendency for its hydroxide to cover its surface, causing lower photocatalytic activities [1].

Later studies used titanium dioxide as efficient photocatalysts in the anatase crystal form [2,3]. Sol-gel synthesis is more perspective among all techniques of preparation of titanium dioxide because it can give titanium dioxides with desired properties. During sol-gel process it is possible to control a lot of factors such as rheology [4], porosity [5], structure [6] and it also allow to add the doping species with homogenous distribution in l titanium dioxide bulk. However the main titanium dioxide sol-gel precursors are titanium tetraalkoxides which are expensive enough to produce photocatalysts by this technique on industrial scale.

The influence of calcination temperatures on crystallinity was investigated by X-ray diffraction with Cu K_α irradiation. The average crystalline size for TiO_2 calcined at 450 °C, obtained from Scherer equation gives a value about 12 nm. Pore diameter distribution calculated from nitrogen physicosorption-desorption isotherm experiment shows that investigated photocatalysts has narrow mesoporous distribution with maximum at 7 nm. The BET surface area is about 230-250 m^2/g for samples calcined at 150 °C and about 130-140 m^2/g for samples calcined at 450 °C.

The photocatalytic properties were tested in reaction of photodegradation of methylene blue water solution. The synthesized photocatalysts doped with transition metal ions in micro amounts possess high photoactivity: in comparison with commercial available Degussa P25 they are five times more active if compare the same mass of photocatalyst loading. In recalculation per unit surface area, for Degussa P25 it is 35-50 m^2/g, the activities are similar. The investigation of kinetics of methylene blue photodegradation indicate that the extent of decomposition does not depend on rotating speed. This allows us to make a conclusion that process takes place in kinetic field and does not depend on diffusion.

1. A. Mills and S. Le Hunte, J. Photoch. Photobiol. A: Chem. **108**(1997)1.
2. V. Ahmed Yasir, P. N. Mohan Das, K. K. M. Yusuff, Int. J. Inorg. Mater. **3**(2001)593.
3. Q. Sheng, S. Yuan, J. Zhang, F. Chen, Microporous and Mesoporous Mater. **87**(2006)177.
4. A. Ponton, S. Barboux-Doeuff, C. Sanchez, Coloids and Surface A **162**(1999)177
5. H. Ding, H. Sun, Y. Shan, J. Photoch. Photobiol. A: Chem. **169**(2005)101.
6. S. Kobayashi, K. Hanabusa, M. Suzuki, M Kimura, H. Shirai, Chem. Lett. (1999)1077.

P-9

CPO ENCAPSULATION IN SILICA GEL FOR EPOXIDATION REACTIONS

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Chloroperoxidase (CPO) from *Caldariomices Fumago* is a heme-containing peroxidase that has been widely studied in recent years [1]. CPO could catalyse a great number of reactions, including epoxidation of olefins, with high conversion and enantiomeric excess [2]. Epoxides are useful intermediates in the preparation of optically pure bioactive compounds or products with biological activity. The main drawbacks related to the industrial-scale use of the free CPO are its high cost and the difficulties in separation from reaction mixture and reuse in new catalytic runs. The immobilization of enzymes into porous materials could overcome these drawbacks, allowing the easy separation of the catalyst and its recycling for new catalytic runs. In our laboratory CPO was successfully immobilized into silica gel [3] and used for the enantioselective oxidation of tioanisole with high conversion and excellent enantiomeric excess (ee >99 %). In this work, CPO immobilized in silica gel is used in the catalytic epoxidation of *cis*-2-heptene with H_2O_2. To our knowledge, the epoxidation of olefins with CPO immobilized in a solid matrix has never been reported before. The effect of different reaction parameters like: i) reaction temperature, ii) pH of the aqueous buffer (solvent), iii) H_2O_2 concentration, iv) *cis*-2-heptene/ H_2O_2 ratio v) quantity of catalysts on the catalytic activity and enantioselectivity has been examined in order to optimize the reaction conditions. After 5 h the conversion values are 70 % with an ee % near to 99 %. The as obtained ee % is comparable with that obtained with free CPO in the same conditions. We have observed that the CPO gel was recyclable, in fact both conversion and ee % in the second run were unchanged.

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[1] F. van Rantwijk, R. A. Sheldon, Curr. Opin. Biotechnol., 11 (2000) 554.

[2] V. M. Dembitsky, Tetrahedron, 59 (2003) 4701.

[3] V. Trevisan, M. Signoretto, S. Colonna, V. Pironti and G. Strukul, Angew. Chem. Int. Ed. 43, 4097 (2004).

INFLUENCE OF THE PREPARATION AND LIGHT SOURCE ON TiO_2 AND WO_3 PHOTOCATALYSTS FOR PHOTOELECTROCHEMICAL WASTEWATER TREATMENT

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The excitation of TiO_2 with visible light for wastewater treatment is a case of many investigations. Its poor activity in this wavelength range led to modifications of this catalyst and investigations of semiconductors, more active in the visible range [1]. In this work a comparison of the photocatalytic activity of TiO_2 is made with WO_3, a semiconductor that can absorb visible light up to 470 nm [2, 3].

In the treatment of wastewater the separation of the catalyst from the reaction process can be avoided by immobilization on a glass substrate. The optimum thickness of layers has to be found, that absorbs most of the incident light on the one hand and activates the whole surface on the other hand for irradiation of the catalyst through the glass substrate.

The preparation and the thickness of layers coated on a transparent substrate have a great influence on the crystallinity. This topic has not been investigated sufficiently up to now and will be presented here.

The excitation of a photocatalyst via irradiation generates electrons and holes. The holes are the driving force for oxidation of organic contaminants either by direct oxidation of the pollutant or by the generation of hydroxyl radicals via adsorbed water. The problem of excessive recombination of photogenerated charge carriers was solved by application of a small electric potential; oxidative and reductive reaction sites are thus separated, oxidations occurring on the working electrode (TiO_2 or WO_3 on electrically conducting support), reductions on a counter electrode. Photocurrent and the degradation rate of oxalic acid are monitored as indicators of catalytic performance.

The action spectrum maximum (photocurrent or degradation quantum yield vs. wavelength) of a photocatalyst can be shifted into the visible range of light upon replacing TiO_2 by WO_3. When irradiated with sunlight, WO_3 can completely mineralize organic waste.

[1] M. Grätzel, NATO ASI Ser., Ser. C, 1988, 237, 367-398

[2] N.S. Gaikwad; G. Waldner; A. Brüger; A. Belaidi; S.M. Chaqour; M. Neumann-Spallart, J. Electrochem. Soc., 2005, 152(5), G411-16

[3] G. Waldner, A. Brüger, N.S. Gaikwad, M. Neumann-Spallart, "WO3 thin films for photoelectrochemical purification of water", in preparation for submission to Journal of Applied Catalysis (2006).

P-11

SYNTHESIS OF CATALYSTS - ZEOLITE MATERIALS FOR PREFERENCIAL OXIDATION OF CARBON MONOXIDE APPLICATION

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One of the most promising methods of hydrogen production is the reforming of hydrocarbon fuels, such as natural gas, gasoline, or methanol, followed by a CO shift reaction to form H_2-rich fuel gases. However, such reformats still contain at least 1% of CO. Owing to the fact that the anode Pt catalyst in PEFC is very sensitive to poisoning by CO, the concentration of CO must be reduced to < 10 ppm level. CO levels in the off-gas of a water-gas-shift reactor typically lie between 0.5 and 2 vol % and not significantly more than 1 vol % is contained in the off gas of a methanol reformer [1].

Preferential oxidation (PROX) of CO by O_2 is advantageous over other technologies because it can operate at relatively low temperatures and atmospheric pressure. It means that the method result in a compact reforming system that can quickly response to load changes and frequent starting and stopping of the operation [1].

Zeolite was selected as the most suitable catalyst support for the present application due to its high specific surface area and uniform pore structure, which acts as a molecular sieve. Zeolite catalysts loaded with metal such us Pt, Ru or other alloys use the microporous structure as special reaction spaces. Furthermore, the physical fixation of metals within the micropores is expected to inhibit sintering, thereby preserving the high catalytic surface area required for effective operation conditions. Because zeolite have larger molecular weights and also higher chemisorbing properties than H_2, CO and O_2 are expected to remain longer and thus have a greater chance of being adsorbed on catalysts in the pores than do conventional alumina supported catalysts. Accordingly, zeolite-supported catalysts are expected to selectively promote CO oxidation.

A wide range of zeolite materials, such as MFI, FAU or MOR zeotypes, have been synthesised by hydrothermal synthesis under autogenous pressure. The preparation of metal catalysts in zeolite cages in a highly dispersed state was achieved by applying the ion exchange method, followed by calcination with air and reduction with H_2.

X-ray diffraction pattern performed over ion-exchanged sample, in which a pure zeolite phase is obtained without any new satellite peaks. TPR profiles for monometallic Pt catalysts show peaks at temperatures that indicate the probable position of the metal cations in the cavities of the zeolite. TEM photograph (see Fig 1) shows some minority large particles (2-3 nm) located in the zeolite surface and majority small particles supported in the zeolite cages (mordenite pore diameter is 0.65×0.70 nm).

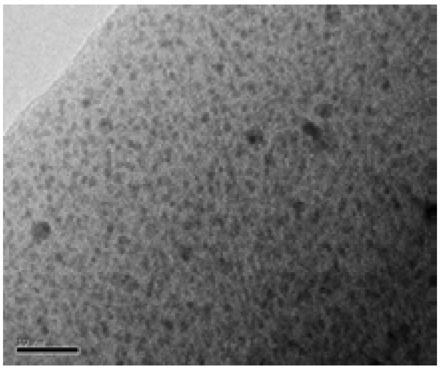

Fig 1. TEM photograph of a Pt-MOR H_2 reduced sample.

[1]. M. Kotobuki, A. Watanabe, H. Uchida, H. Yamashita, M. Watanabe. Journal of Catalysis 236 (2005), 262-269.

SONOCATALYSIS AND BASIC CARBONS: AN ECOFRIENDLY METHODOLOGY FOR THE SYNTHESIS OF CHALCONES

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The ultrasound combined with a solid catalyst based on activated carbons proves an efficient and eco-friend route for preparing chalcones in good yields. This organic solvent-free protocol is valuable since rapid reaction rate, low energy consumption, waste minimization and simple operation can be achieved. The members of Chalcone and Flavonoid family are attracting increasing attention due to their applications as antibacterial, antioxidant, anti-inflammatory and anticancer pharmacological activities [1].

They are commonly synthesized via Claisen-Schmidt condensation between acetophenone and benzaldehyde [2]. There are many hurdles for the reaction under homogenous conditions. In this context, heterogeneous catalysts are considered as an eco-friendly alternative. There is no report in the literature for the use of activated carbons as catalysts in combination with ultrasounds.

The present paper reports the experimental results for the condensation between benzaldehyde and acetophenone catalyzed by alkali-doped carbons under ultrasonic activation, in the absence of any solvent. Recently, activated carbons have been employed to catalyze fine chemicals reactions, because of their extended surface area, microporous structure and high degree of surface reactivity [3].

Two alkali-doped catalysts (Na-Norit and Cs-Norit) were used. The catalytic runs were carried out in a Selecta Ultrasound-H ultrasonic bath (40 KHz, 550 W). Under our experimental conditions, the corresponding chalcone is selectively obtained. It was found that there is a substantial enhancing effect in the yield when ultrasound was used. Enhancement effect on the reaction rate by combining the basicity of the carbon with ultrasound is presented as an alternative method for the production of chalcones and, in general, for the production of other fine chemicals due to the mild conditions that this systems offers.

References

[1] S.F. Nielsen, T. Boesen, M. Larsen, K. Schönning , H. Kromann, *Bioorg. Med. Chem.*, 12 (2004) 3047.
[2] M.J. Climent, A. Corma, S. Iborra, A. Velty, *J. Catal.,* 221 (2004) 474.
[3] C.J. Durán-Valle, I. Fonseca, V. Calvino-Casilda, M. Picallo, A.J. López-Peinado, R.M. Martín-Aranda, *Catal. Today,* 107-108 (2005) 500-506.

P-13

MWCNT's FOR LIQUID-PHASE OXIDATION. FUNCTIONALIZATION, CHARACTERIZATION, AND CATALYTIC ACTIVITY

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Replacing stoichiometric oxides such as $KMnO_4$, Ag_2O and CrO_3 by less environmentally noxious ones is self-evidently a sensible chemical strategy. Doing so catalytically, with alkylhydroperoxides or hydrogen peroxide as oxidants is an even better one, but best of all would be to develop catalysts that selectively oxidize hydrocarbons using either molecular oxygen or air under mild conditions.

Carbon Nanotubes represent a technologically important class of nanostructured materials. Their small dimensions and mechanical, electrical, and thermal properties put these mesoporous materials among the best candidates as catalyst supports. In this work, the morphology and characteristics of multiwalled carbon nanotubes (MWCNT) was modified with an acid treatment. The catalytic activity of the new structures was studied in liquid-phase oxidation.

MWCNT (Sunnano MWNT-A-P) were functionalized with HNO_3 under reflux for 12 h to generate functional groups. Then sodium was introduced by exchange of modified MWCNT with an aqueous solution of Na_2CO_3. The samples were characterized by chemical analysis (ICP-AES), N_2 adsorption-desorption at 77 K, IR of diluted samples in KBr, XRD, XPS TPD-MS analysis in Ar flow. These samples were employed in the oxidation of ethylbenzene with air. In a typical oxidation with air, 600 ml of ethylbenzene (0.4 wt% of ethylbenzene hydroperoxide), kindly provided by Repsol-YPF, was mixed with 1 g of the sample. The reaction temperature was fixed at 421 K, the absolute pressure was 3 bar and the oxygen concentration at the outlet was controlled at 3 %. The concentration of the main product was measured by standard iodometric titration, and other by-products were analyzed by GC.

The characterization data of modified samples showed that the functionalization was effective. A clear increase in CO and CO_2 profiles was revealed by TPD. The C1s and O1s spectra measured by XPS of functionalized samples showed the formation of several surface structures containing both C and O atoms. However, no structural changes of MWCNT were observed (XRD and N_2 isotherms). The introduction of the functional groups modifies the catalytic behaviour of MWCNT in the liquid phase oxidation of ethylbenzene.

LIQUID PHASE SELECTIVE OXIDATION OF SULFUR ORGANIC COMPOUNDS WITH H_2O_2 ON Ti HETEROGENEOUS CATALYSTS

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To eliminate undesirable sulfur compounds or to convert them into more innocuous forms, various processes different from HDS have been employed. These processes include physical extraction with a liquid, selective adsorption on suitable materials, reductive and oxidative microbial transformations and catalytic oxidation. In the latter case, oxidants such as nitrogen oxides, nitric acid, hydrogen peroxide, ozone, t-BuOOH, oxygen, air and peracids can be used. The liquid phase oxidation process with H_2O_2 produces oxidized compounds that can be physically separated and may be easily downstream processed. Within this frame, the aim of this study was two-fold. Firstly, we studied the oxidation with H_2O_2 of several model molecules in a two Liquid–Liquid (L–L) phase system under very mild reaction conditions with a titanium heterogeneous catalysts. Secondly, we expected to get information on the applicability of the oxidation method with hydrogen peroxide in the selective transformation of the organic sulfur compounds contained in kerosene and a light oils.

The supported titanium catalyst was prepared according to literature reports [1]. These catalysts were characterized by chemical analysis (ICP-AES), N_2-adsorption at 77 K, UV-Vis, IR, and XPS. The catalytic sulphoxidation of sulphur-containing organic compounds with hydrogen peroxide was carried out in a 250-mL glass batch reactor, equipped with a magnetic stirrer, a thermometer, and a condenser using acetonitrile as solvent [2]. The organic compounds were recovered by decantation and analyzed by GC–FID.

The influence of several reaction parameters such as the ratio between peroxide of hydrogen and sulphur compound (40 - 2.5), the sulphur compound concentration (5 - 0.2%), and the nature of the sulphur compound (benzothiophene, dibenzothiophene, 4-ethyl-6-methyl-dibenzothiophene) were studied. These catalysts showed a high activity at low reaction temperature (353 K). Under these conditions, no side reactions such as alkene epoxidation took place. As a consequence of the very high reactivity observed, this method could be employed in the deep desulphurization of middle distillate fuels

References

1. M. C. Capel Sánchez, J. M. Campos-Martín, J. L. G. Fierro, M. P. de Frutos and A. Padilla Polo, *Chem. Commun*., 2000, 855.
2. J. M. Campos-Martín, M. C. Capel Sánchez, J. L. G. Fierro Green Chem. 2004, **6** , 557

P-15

CATALYTIC ROLE OF α-SITES IN THE OXIDATION OF BENZENE TO PHENOL BY NITROUS OXIDE

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MFI zeolites of alumosilicate, borosilicate and titanosilicate composition were shown to be inert in the benzene to phenol oxidation by nitrous oxide, but exhibit high activity and selectivity in this important reaction after the introduction of Fe [1, 2]. The active sites of zeolite catalysts are extralattice complexes of bivalent iron Fe_{α}^{2+} (α-sites) stabilized in the zeolite matrix [3]. Upon N_2O decomposition, these sites generate the so-called alpha-oxygen represented by monatomic oxygen radical O_{α}^{-}, which is involved in highly selective oxidation of benzene to phenol.

The catalytic role of α-sites was studied previously in many works. However, a quantitative correlation between zeolite activity and α-sites concentration (C_α) under comparable conditions did not receive necessary attention. The present work considers the catalytic properties of Fe-containing zeolite catalysts of various composition with α-sites concentration varying within two orders of magnitude. The obtained linear dependence of the reaction rate on C_α (Fig. 1) reliably indicates that the reaction proceeds precisely on the α-sites. This dependence is probably the first example of this type in selective oxidation catalysis.

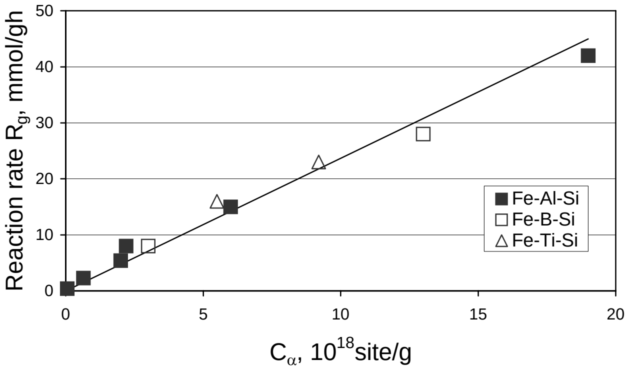

Fig. 1. Rate of benzene oxidation vs. α-sites concentration.

References:

1. L.V. Pirutko, A.K. Uriarte, V.S. Chernyavsky, A.S. Kharitonov and G.I. Panov, Microporous and Mesoporous Mater., 48 (2001) 345.
2. L.V. Pirutko, V.S. Chernyavsky, A.K. Uriarte and G.I. Panov, Appl. Catal. A: General, 227 (2002) 143.
3. K.A. Dubkov, N.S. Ovanesyan, A.A. Shteinman, E.V. Starokon and G.I. Panov, J. Catal., 207 (2002) 341.

OXIDATION OF ETHANOL TO ACETALDEHYDE OVER Na-PROMOTED VANADIUM OXIDE CATALYSTS

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Catalysts based on supported vanadium oxides are known to be active and selective for a number of industrially important reactions, in particular they have shown excellent performance for selective oxidation of ethanol to acetaldehyde [1]. On the other hand, siliceous mesostructured materials have recently attracted much attention as catalyst supports since they posses high surface areas, good thermal stability as well as controllable uniform pore sizes [2]. In the present work Na-promoted vanadium oxide catalysts supported on MCM-41 and TiO_2 (anatase) were investigated for the partial oxidation of ethanol to acetaldehyde. The catalysts were prepared by incipient wetness impregnation with vanadium content of 6 wt. % and Na was added to the catalyst at different Na/V molar ratios in the range of 0- 2. The catalyst characterization was performed by X-ray diffraction (XRD), N_2 adsorption, temperature programmed reduction (TPR), temperature- programmed oxidation (TPO) and diffuse reflectance (UV-Vis). Our results indicate that the presence of the Na plays a strong role in the reducibility of the vanadium species as detected by TPR analysis. Moreover, TPO from the spent catalysts after ethanol partial oxidation revealed that an increase in the Na loading decreased the amount of carbon deposited during reaction. UV-vis revealed that the Na affects the dispersion of the vanadium species on the supports as well. For the vanadium catalysts supported on MCM-41 an increase of the activity and selectivity to acetaldehyde was observed in intermediate Na loadings compared to the unpromoted catalyst. In contrast, in the VO_2/TiO_2 system the catalytic activity decreased monotonically as the Na content in the catalyst increased.

References

[1] I.E. Wachs , B. M. Weckhuysen, Appl. Catal. A 157 (1997) 67.
[2] G. C. Bond, Appl. Catal. A 157 (1997) 91.

P-17

PREPARATION AND CHARACTERIZATION OF SULFATED ZIRCONIA MODIFIED SBA-15 FOR METHANE ACTIVATION

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In a previous study, our group has investigated the thermodynamics and kinetics of homogeneous methane halogenation reactions for the purpose of using halogenated methane compounds in further methane coupling reactions[1]. It was observed that bromine was the most favorable halogen in terms of activity and selectivity. The objective of the work in progress is to demonstrate the methane coupling reactions in a two step process: (1) the bromination of methane followed by (2) a metathesis reaction over super acid catalysts. Sulfated zirconia on SBA-15 was selected as the potential super acid catalyst for methyl bromide methatesis reaction.

Sulfated zirconia on SBA-15 was prepared and characterized to be used in the methatesis of halogenated methane compounds. Zirconia modified SBA-15 was prepared by the introduction of zirconia during the SBA-15 synthesis and sulfation was carried out after the final oxide was prepared. Zirconia loadings were adjusted in the 5-20 mole % range. The catalysts were characterized by XRD and CO titration measurements. It was observed that the long range order of SBA-15 was preserved up to 20 mol % of ZrO_2. However, the sulfation step destroyed the long range orders as revealed by the low angle XRD. The number and strength of acidic sites of sulfated catalysts are being characterized by measuring the differential heats of CO adsorption data using a Tian Calvet microcalorimeter connected to a gas adsorption manifold. The effect of using SBA-15 templates on the acidic characteristics of sulfated zirconia will be discussed.

References:

[1] V. Degirmenci, D. Uner, A. Yilmaz, Catal. Today, 106 (2005) 252.

EFFECT OF NANOSIZE ADDITIVES ON DEHYDROGENATION OF CYCLOHEXANOL OVER METAL OXIDE CATALYST

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The cyclohexanol dehydrogenation is a very important reaction since it is an industrial reaction for caprolactam production and also a good model reaction.

Industrial catalysts of dehydrogenation of cyclohexanol to cyclohexanone are generally based on copper as an active component of catalytic system and usually are used in a temperature range from 220 to 260 °C. The conversion of cyclohexanol over these catalysts is close to equilibrium values (50-60%) and selectivity for cyclohexanone is close to 99%. While various catalysts for dehydrogenation processes of convert cyclohexanol to cyclohexanone are known generally, there still exists a need to provide catalysts with a superior conversion and selectivity properties.

A number of investigations have focused on catalysts preparation, determining the influence of support and active metal loading, influence of oxidation state of copper on the activity and selectivity of copper-containing catalysts [1-7].

In this communication we report the results of the investigation of catalytic properties of the systems being formed on the basis of $Cu\text{-}ZnO\text{-}Al_2O_3$ with nanosize additives of WO_3 and $CuO_x\text{-}WO_3$.

Catalysts were prepared by methods of coprecipitation and deposition of preformed metal oxide nanoparticles. The samples were characterized by X-ray diffraction analysis, electron microscopy, X-ray photoelectron spectroscopy. The catalytic properties were studied in a continuous flow-type reactor in temperature range 200-300 °C and at flow rates of cyclohexanol 0,21 mole h^{-1} and nitrogen 0,19 mole h^{-1}. Initially the samples were reduced by mixture 10-50%H_2-N_2 at 250 °C for 8 h.

It has been shown that modification of Cu-Zn-Al-oxide catalysts by nanosize additive $CuO_x\text{-}WO_3$ favor the cyclohexanone yield in the reaction of cyclohexanol dehydrogenation without decrease of the process selectivity.

References:

1. N.S.Kozlov, L.I.Mostovaya, M.A.Sedeltseva, V.I.Gupalo // Kinetika i kataliz, 27, 244 (1986)
2. N.N.Nikiforova, K.A.Gavrenko // Neftehimiya, 14, 116 (1974)
3. I.V.Orizarsky, L.A.Petrov, V.M.Petrova.// React.Kinet.Catal.Lett. 17, 427 (1981)
4. W.S.Chen, M.D.Lee // Appl.Catal. 83, 201 (1992)
5. H.F.Chang, M.A.Saleque, W.S.Hsu, W.H.Lin // J.Mol.Catal.109, 249 (1996)
6. C.Sivaraj, B.M.Reddy, P.K.Rao // Appl.Catal. 45, L11 (1988).
7. V.Z.Fridman, A.A.Davydov // J.Catal.195, 20 (2000).

P-19

SOLID ACID CATALYSTS FOR CYCLODEHYDRATION OF XYLOSE

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Furfural is a key derivative for the production of a wide range of non-petroleum-derived chemicals. It can be made from agricultural raw materials and surpluses rich in pentosan (in particular xylan). By aqueous acid catalysis, the xylan is hydrolyzed to xylose, and the latter is cyclodehydrated into furfural. Known industrial processes of furfural production use conventional mineral acids, such as sulfuric acid, as catalysts, which are extremely corrosive, highly toxic, not easily handled and recovered.

In this work we wish to report on the catalytic performance of several heterogeneous catalysts in the liquid phase cyclodehydration of D-xylose to furfural. Sulfonic acid-functionalized ordered mesoporous silicas were found to be effective catalysts for this reaction, using either dimethylsulfoxide as the solvent or a water-toluene mixture [1a]. However, a limitation of these catalysts is that the thermal removal of organic matter strongly adsorbed on the surface of used catalysts is not possible since it requires heating above the thermal stability limit of the surface-bound alkylsulfonic acid groups. Heteropolyacids supported on mesoporous silicas were also tested for this reaction, giving furfural yields that were comparable with those obtained using H_2SO_4, under similar reaction conditions [1b]. However, the supported heteropolyacids are partially leached into the aqueous phase during the catalytic reaction, which compromises the reusability of the catalysts. A microporous niobium silicate, designated as AM-11, was found to be more water-tolerant, and could be reused without loss of activity or selectivity between recycling runs, yielding more furfural than HY zeolite or mordenite [1c]. Mesoporous niobosilicates, [Si,Nb]-MCM-41, possess higher initial activity than AM-11, but lower stability in recycling runs. Mesoporous aluminosilicates possess lower initial catalytic activity than [Si,Nb]-MCM-41, but eventually lead to higher furfural yields, without significant loss of catalytic activity in recycling runs.

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[1] (a) A.S. Dias, M. Pillinger, A.A. Valente, J. Catal. 229 (2005) 414. (b) Microporous Mesoporous Mater., in press. (c) A.S. Dias, S. Lima, P. Brandão, M. Pillinger, J. Rocha, A.A. Valente, Catal. Lett. 108 (2006) 179.

NONBONDING INTERACTION ENERGY AND TEMPLATING POWER IN THE GENESIS OF AlPO-5 MOLECULAR SIEVES: AN EXPERIMENTAL AND COMPUTATIONAL STUDY

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Despite the great efforts made, the principles governing the formation of crystalline porous materials are not yet well understood because of the complexity of the hydrothermal crystallizations [1]. In this study, we monitored the genesis of AlPO-5 from gels of the same molar composition Al_2O_3: P_2O_5: 250 H_2O: R [R= methyldicyclohexylamine (MCHA), triethylamine (TEA), tripropylamine (TPA) or tetraethyl ammonium hydroxide (TEAOH)] in the range 130-190 ºC. The as-synthesized samples were characterized by XRD, TG&DSC, FT-Raman, and SEM. Moreover, the template-framework interactions were investigated using density functional theory (DFT) calculations on periodic models of AlPO-5 employing the Dmol^3 program [3].

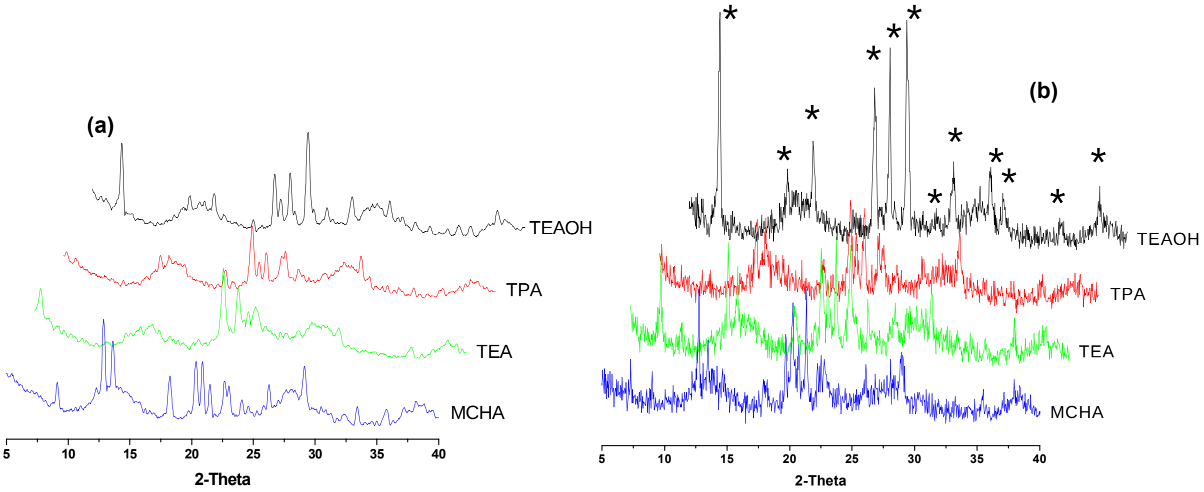

Fig. 1: AlPO-5 products from gel composition Al_2O_3: P_2O_5: 250 H_2O at 130 ºC (a), and at 145 ºC (b) for 20h using various templates: MCHA, TEA, TPA, and TEAOH. (*) reflections are due to AlPO-5 phase

Figure 1 shows that TEAOH has the best ability to form AlPO-5 structure when compared to other organic templates. This is explained, using computational density functional calculations on periodic models like the one shown in Figure 2, by the stronger nonbonding interaction between the tetraethylammonuim ion and the framework.

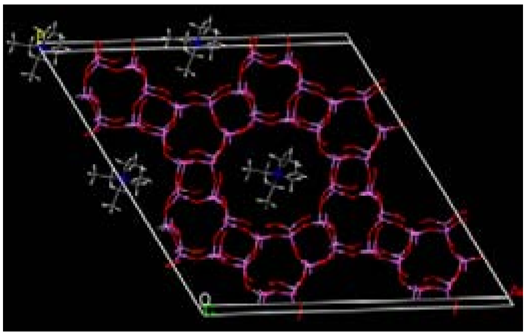

Fig. 2: TEA cation in periodic models of AlPO-5 framework.

References

[1] C.S. Cundy, P.A. Cox, Micropor. Mesopor. Mater. 82 (2005) 1.
[2] N.J.Tapp, N.B. Milestone, D.M. Bibby, Zeolites 8 (1988) 183.
[3] www.accelrys.com/

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P-21

SCALING THE ACIDITY OF ZEOLITES AND SAPOs USING PDFT METHODOLOGY

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Introduction

It is well known that the acidic properties of microporous molecular sieves play a crucial role regarding their applications in oil refining and petrochemical industries.[1] Early attempts by Lee, Parrillo, and co-workers[2,3] to scale the acidity of zeolites viz., H-MOR, H-ZSM-5, H-ZSM-12, and H-Y used a series of alkylamines rather than using a single reference basic molecule. It was shown that the relation between adsorption energies of some molecular bases and its proton affinities in the gas phase is interesting and important. Here we investigate this relation at the atomic scale using the periodic density functional theory (PDFT) level aiming first to analyze the interactions between alkylamines and mordenite framework and further to extend the application of this method to silicoaluminophosphate-5 (SAPO-5).

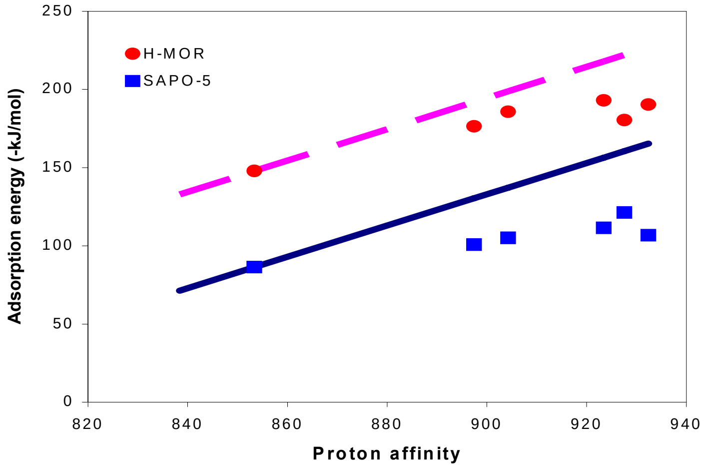
Computational method

The whole topology of a molecular sieve model is considered by applying periodic boundary condition. The method was applied reliably to measure and predict the strength of acidic sites in various sieves.[4] PDFT has been used to calculate the structural geometries and energies employing the Dmol^3 program.[5]

Results and Discussion

Table 1 illustrates the comparison between the calculated proton affinities of ammonia, some alkylamines, and the reported values. The very small differences between them indicate the accuracy of the computational method that has been used. Figure 1 shows the relation between proton affinity and adsorption energies for mordenite (H-MOR, red circles) and silicoaluminophosphate-5 (SAPO-5, blue squares). The dashed and solid lines have slope=1 and pass through the ammonia on H-MOR and SAPO-5, respectively. Not only the higher adsorption energies of all molecular bases on H-MOR can be observed but also the larger deviations of isopropyl, dimethyl, and trimethyl amines from the straight lines. Simply one can deduce that for applying the gas phase proton affinity-adsorption energy relation to scale the acidity of acidic molecular sieves, short chain primary amines would give a better fitting than branched or longer chain amines.

Molecular base	Calculated proton affinity in the gas phase (kJ/mol)	Reported values (kJ/mol) [3]
ammonia	853.4	858.3
methylamine	897.4	896.4
ethylamine	904.3	909.0
isopropylamine	923.4	918.6
dimethylamine	927.6	923.2
trimethylamine	932.4	939.1



References:

1. Weitkamp, J. *Solid State Ionics* **2000**, *131*, 175.
2. Parrillo, D. J.; Gorte, R. J. *J. Phys. Chem.* **1993**, *97*, 8786.
3. Lee, C.; Parrillo, D. J.; Gorte, R. J.; Farneth, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 3262.
4. Elanany, M.; Koyama, M.; Kubo, M.; Selvam, P.; Miyamoto, A. *Micropor. Mesopor. Mater.* **2004**, *71*, 51; Appl. *Surf. Science* **2005**, *246*, 96.
5. www.accelrys.com

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INFLUENCE OF THE SUPPORTED METAL OXIDE (Fe, $H_3PW_{12}O_{40}$) OVER SiO_2 FOR PARTIAL OXIDATION OF METHANE TO FORMALDEHYDE

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In the last years intensive efforts have been made for developing of heterogeneous catalytic process for the direct synthesis of formaldehyde *via* partial oxidation of methane (POM). Silica supported oxides are among the best heterogeneous catalysts for POM, especially the supported oxides of Mo, V, W and Fe. It was established that the performance of the silica surface is affected by the preparation method and loading of the supported metal oxide.

The aim of this study is to investigate the influence of supported phase on catalytic activity and selectivity in the reaction of POM.

In order to improve method of syntheses, the 12-tungstophosphoric acid ($H_3PW_{12}O_{40}\cdot 6H_2O$) was chosen as precursor of supported WO_x species. The impregnated amount was 60 wt% $H_3PW_{12}O_{40}$ and they were dried at 120 °C. Silica-supported Fe catalysts were prepared by sol-gel method, which allows obtaining high superficial area of the support facilitating a high dispersion of the iron on the amorphous surface of the silica. The catalysts contained different percentages of Fe (0.1-0.5 wt%) and were noted as “heterogeneous”. It was prepared one sample (Fe=0.5 wt%) with more homogeneous distribution of iron species due to improved preparation method and it was noted as “homogeneous”. The catalysts were characterized by XRD, BET, TPR measurement, TEM. The catalytic activity tests are carried out at atmospheric pressure, reaction mixture $CH_4/O_2/N_2 = 7.5/1/4$ and He is used as gas diluting.

The results show that a good methane conversion (8.60 mol%) with the catalyst Fe=0.5 “homogeneous” was obtained at 650 °C with selectivity to formaldehyde about 50 mol% in the temperature range 600-650°C. In the case of supported 12-tungstophosphoric acid the selectivity is almost 30 mol% at 700 °C but the conversion is lowest. The effect of preparation steps on metal dispersion and consequently on catalytic behavior will be discussed.

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P-23

QUANTIFICATION OF ESSENTIAL SOLVENT EFFECTS IN 2-SUBSTITUTED ANTHRAQUINONES HYDROGENATION OVER PALLADIUM SUPPORTED CATALYST

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The catalytic hydrogenation of anthraquinones has found an industrial application in the hydrogen peroxide production. The aim of this work was to study the hydrogenation kinetics of various substituted anthraquinones. In addition, the solvent effect in the hydrogenation of 2-ethyl-5,6,7,8-tetrahydro-9,10-anthraquinone was also studied.

Hydrogenations were performed in a stirred batch reactor at 313 K and 0.1 MPa in the presence of a commercial palladium supported catalyst MGS5-type. The substrates concentration in the reaction mixture was 84 $\mathrm{mmol \cdot dm^{-3}}$. The reaction kinetics was monitored by measurement of the hydrogen amount consumed in the course of hydrogenation. The substrates reactivity was expressed as the initial reaction rate. The reaction rates significantly differed and the differences were not connected with hydrogen solubility. For example, the rates in protic solvents were 10 times higher than the rates in aromatic solvents.

The solvent effect in the hydrogenation of 2-ethyl-5,6,7,8-tetrahydro-9,10-anthraquinone was quantified using multiple linear regression by applying linear free energy relationships[1]. The regression with two five-parameter models was compared. The Abraham-Kamlet-Taft's model showed a better close-fitting than the Koppel-Palm's model. The most significant factors influencing the reaction rate were found to be the solvent basicity and its cohesive energy density. The correlation coefficient was higher than 0.90 in both cases.

The substituent effect in the hydrogenation of 2–substituted anthraquinones (substituents were –H, –F, –Cl, –OH, –Me, –Et, –*tert*–Butyl, –*tert*-Pentyl) was successfully described by the Taft's equation[2] which separates the substituent effect into steric and polar contributions.

Acknowledgement

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References

1. Koppel I. A., Palm V. A., in: *Advances in Linear Free Energy Relationships*, Chap. 5, Plenum Press, London 1972
2. Taft R. W., in: *Steric Effects in Organic Chemistry*, Chap. 13, John Wiley & Sons, New York 1956

SYNTHESIS OF FRAGRANT LACTONES FROM CYCLIC KETONES AND ALIPHATIC ALDEHYDES BY USING MULTIFUNCTIONAL CATALYSTS

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This paper deals with the synthesis of fragrant lactones using acidic-basic catalysts obtained from layer double hydroxides (LDH) modified by metal (Pd, Sn). The synthesis consists of three reaction steps: aldolic condensation, hydrogenation and Baeyer-Villiger oxidation. To make the procedure simpler and faster the possibility of aldolic condensation and subsequent hydrogenation in a “one-pot” operation was studied. For the aldolic condensations and reactions “one-pot” were used Pd/LDHs. These catalysts were prepared by three different methods: coprecipitation, impregnation and intercalation (different properties). For Baeyer-Villiger oxidation the LDHs were modified by Sn. These catalysts were characterized by XRD, BET, TPR, TG and TEM methods. The mixed oxides obtained by calcinations of the precursor LDH lead to acidic-basic catalysts of the Lewis type. The activity exhibited by these catalysts for aldolic condensations is rather limited. Their performances could be improved by careful reconstruction of the lamellar structure by rehydration of the mixed oxides leading to a Broensted type catalyst likely active in condensation reactions.

The best result of the formation of 2-heptylidencyclopentanone (product of aldolic condensation) was achieved by using the intercalated catalyst with molar ratio cyclopentanone : heptanal 2:1 (100 % conversion of heptanal and 50 % conversion of cyclopentanone with 90 % selectivity after 1,5 h). The selectivity 72% of the product of one-pot reaction (2-heptylcyclopentanone) with 100 % conversion of heptanal and 50 % conversion of cyclopentanone was achieved. Baeyer-Villiger oxidations were carried out with the selectivity 100 %. The yield 60 % of δ-dodecalactone after 29 h was obtained.

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P-25

OXIDATION OF TERPENES OVER THE MOLECULAR SIEVES

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Active packaging employs a packaging material that interact with the internal gas environment to extend the shelf-life and improving food safety and quality [1].

The presence of oxygen in food packages accelerates the spoilage of many foods. Oxygen can cause change in color, nutrient loss and microbial attack. The promising application of oxygen scavenging systems in food package is to control mould growth and to delay an oxidation and subsequently a development of rancidity in products.

There are several technologies applied for scavenging the oxygen from inside of the package. The most conventional approach is the use of metal-based scavenger such as iron. Oxygen scavengers or absorbers can be included in packaging system as sachets, closures (crowns) and in polymer.

We have found that some terpenes such as R-(+)-limonene and α-pinene are susceptible for oxidation at ambient conditions and can be considered as potential oxygen scavengers. Terpenes are low-priced naturally occurring products widely used in flavor and fragrance additive in cleaning and cosmetic products, food and pharmaceuticals cause of their flavoring and antimicrobial properties.

The aim of the study is to investigate an efficiency of terpenes adsorbed on various zeolites [2] in a consumption of oxygen in sealed packages. Another target concerned the catalytic examination of various zeolites and its modifications in oxidation of terpenes.

The effects of research works are promising. Wide pore type of zeolites seems more efficient oxygen scavengers than the medium pore. The main products of oxidation of terpenes are oxides and compounds with hydroxyl and carbonyl group (e.g. carveol, carvone, verbenol, verbenone). The cation modification of zeolites with Fe, Cu increases reactivity with oxygen, while the hygrogen forms initiate also another reactions (e.g. isomerization).

References

[1] Brody, A.L., Kline, L., Strupinsky, G., *Active Packaging for Food Applications,* Technomic, Boca Raton, 2001,

[2] Szostak, R., *Molecular Sieves, Principles of Synthesis and Identyfication,* Van Nastrand Reinold, New York, 1989.

β-CYCLODEXTRIN INCLUSION COMPOUNDS OF A MOLYBDENUM TRICARBONYL COMPLEX AND THEIR USE IN CATALYTIC OLEFIN EPOXIDATION

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Tricarbonyl complexes $Cp'Mo(CO)_3X$ ($Cp' = \eta^5$-C_5R_5; X = Cl, alkyl, or ansa-alkyl) can be applied directly as catalyst precursors in homogeneous olefin epoxidation, being oxidized *in situ* by the oxidant *tert*-butylhydroperoxide to the Mo^{VI} catalysts [1]. During the *in situ* oxidation process, the expected products are $Cp'MoO_2X$ and/or $Cp'MoO(O_2)X$. The homogeneous Mo^{VI} catalysts derived from the parent tricarbonyl complexes can be recovered from the reaction mixtures and reused, although catalytic activities tend to decrease with recycling runs. One method to facilitate catalyst/product separation and to improve recyclability is heterogenization of the catalyst or catalyst precursor on a solid support [2].

An alternative, yet largely unexplored, method for the modification of the catalytic properties of oxometal complexes is their encapsulation in cyclodextrins (CDs). Metallo-organic complexes immobilized in CDs often exhibit markedly different physical and chemical characteristics compared to the bulk material. In the present work, the complex $CpMo(CO)_3CH_2CONH_2$ was immobilized in plain β-CD and permethylated β-CD (TRIMEB), and the resultant inclusion compounds were characterized by several solid-state techniques. The inclusion compounds can be used as precursors to homogeneous (TRIMEB as host) or recyclable heterogeneous (β-CD as host) catalysts for cyclooctene epoxidation.

References

[1] A.A. Valente, J.D. Seixas, I.S. Gonçalves, M. Abrantes, M. Pillinger, C.C. Romão, *Catal. Lett.* **2005**, *101*, 127.
[2] M. Abrantes, S. Gago, A.A. Valente, M. Pillinger, I.S. Gonçalves, T.M. Santos, J. Rocha, C.C. Romão, *Eur. J. Inorg. Chem.* **2004**, 4914.

P-27

MONO AND BI-METALLIC CATALYSTS BASED ON Au, Pd AND Pt SUPPORTED ON CARBON FOR THE SELECTIVE OXIDATION OF GLYCEROL IN AQUEOUS PHASE

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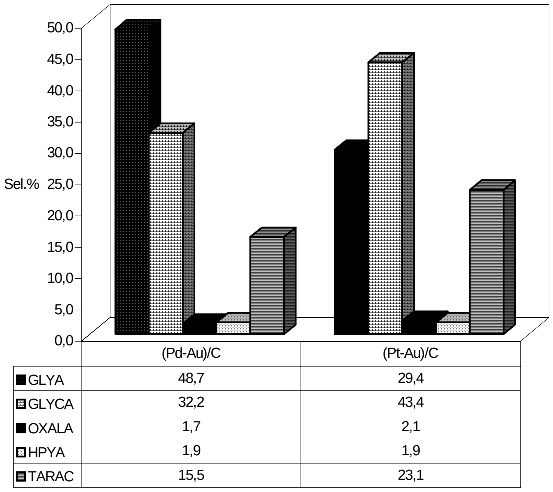
Glycerol has attracted attention since it is a highly functionalized compound and it is readily available from bio sustainable sources. However, in glycerol oxidation it is necessary to control the distribution of the products by tuning the reaction conditions and design the appropriate catalyst. Glycerol oxidation has been studied in aqueous phase at moderate temperature (50-60 °C) using Pt and Pd metals supported on carbon by Kimura [1,2], Gallezot [3,4], and Au/C by Hutchings [5,6] showing that the distribution of the products can be controlled from the nature of the catalyst. In particular, high selectivities to glyceric acid using a Au/C catalyst were obtained at basic conditions [5,6], and we recently have demonstrated [7] that by tuning reaction conditions it is possible to obtain glyceric acid, with selectivity closed to 100% at full conversion. Using preformed metallic sols, we were able to design different catalysts. Using this technique we prepared bimetallic catalysts (Au-Pd, Au-Pt) supported on carbon in order to study the effect and the role of Pd and Pt metals on Au metal. Bimetallic systems showed an enhanced activity and selectivity appeared to be ruled by Pd or Pt, being (Au-Pd) catalysts more selective toward glyceric and tartronic acids, and (Au-Pt) toward glycolic acid.



	(Pd-Au)/C	(Pt-Au)/C
■GLYA	48,7	29,4
▨GLYCA	32,2	43,4
■OXALA	1,7	2,1
□HPYA	1,9	1,9
▤TARAC	15,5	23,1

Table 1. **Comparison of different (Pd-Au)/C and (Pt-Au)/C catalysts at 90% conversion on glycerol oxidation at 50 ºC.**

References

[1] Kimura H., *Appl. Catal. A*, 105 (1993) 147.
[2] Kimura H., Tsuto K., Wakisaka T., Kazumi Y. and Inaya Y., *Appl. Catal. A*, 96 (1993) 217.
[3] Garcia R., Besson M. and Gallezot P., *Appl. Catal. A*, 127 (1995) 165.
[4] Fordham P., Besson M. and Gallezot P., *Appl. Catal. A*, 133 (1995) L179.
[5] Carrettin S., McMorn P., Johnston P., Griffin K. and Hutchings G.J., *Chem. Commun.*, (2002) 696.
[6] Carrettin S., McMorn P., Johnston P., Griffin K., Kiely C.J. and Hutchings G.J., *Phys. Chem. Chem. Phys.*, 5 (2003) 1329.
[7] Porta F. and Prati L., *J. Catal.*, 224 (2004) 397.

SYNTHESIS AND INVESTIGATION OF CARBON SUPPORTED ADSORPTIVE CATALYSTS FOR PROCESSING OF TOXIC CHLOROCONTANING ORGANIC COMPOUNDS

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In 80-s' years of 20 century it has been established, that polychlorinated aromatic compounds (PCAC) are very toxic substances. Processing and recycling of these compounds are complicated not only by their thermal and chemical stability, but also by formation of very hazardous pollutants - dioxines. The adsorption technologies developed for waste treatment of the industry do not solve a problem of the further recycling highly toxic PCAC. The analysis of various methods of processing PCAC has shown that the most perspective is the catalytic hydrogenolysis process. The combination of adsorption step and catalytic hydrogenolysis allows to considerably simplify the scheme of processing PCAC, preventing dioxines formation and increasing the durability of the equipment.

The goal of the research work is synthesis of the active and stable adsorptive catalysts, capable to adsorb highly toxic polychlorinated aromatic compounds from objects of an environment for the further processing.

During this research work the adsorption step of chlorobenzene (CB) from water solutions was studied and it was shown, that the quantity of adsorbed CB and a kind of adsorption isotherms are in a good accord with porous structure of carbon adsorbents. The most effective CB adsorbents are microporous carbons with the high surface area MeKS, FAS, AG-2000. On the basis of the given carbons, palladium catalysts were synthesized and their activity in liquid-phase hydrodechlorination of CB by molecular hydrogen was studied. Conditions of the process were optimized. As a result of the investigation of the prepared adsorptive catalysts in adsorption catalytic cycle, it was shown, that 1 % Pd/AG-2000 specimen possesses high adsorption capacity in relation to CB and has the highest catalytic activity under mild conditions (pressure 1 atm and temperature 50 °C).

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P-29

USE OF MODIFIED MESOPOROUS SILICA MATERIALS IN GAS- AND LIQUID PHASE REACTIONS

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The discovery of ordered mesoporous silica of M41s types[1] in the early 1990s has attracted a great interest in many areas of physical, chemical and engineering sciences. The synthesis of these materials involves the use of a self-assembled molecular array of surfactants molecules as structure-directing template. The removal of surfactants led to very ordered mesoporous molecular sieves with adjustable pore sizes ranging from 2 to 10 nm[1]. Owing to their special pore properties these materials has been best appreciate in systems where molecular recognition is needed: selective adsorption and separation process, chemical sensors, nanotechnology and shape-selective catalysis. In particular, the advantages of using ordered mesoporous solids in catalysis are the relatively large pores which facilitate mass transfer and the very high surface area which allows a high concentration of active sites per mass of material. In order to obtain a solid catalyst characterized by high surface area, ordered pore structure and active in acid catalyzed reactions, in this study ordered silica mesoporous materials have been modified with the introduction of sulphated zirconia (SZ)[2,3] in their structure[3]. The silica supports were prepared by the liquid-crystal template method (LCT); the active phase (SZ) was introduced by *incipient wetness impregnation* of $Zr(SO_4)_2$ in the as-synthesized supports, followed by thermal decomposition of precursor in flowing air. The obtained materials were characterized by ion chromatography (for the determination of sulphates content), nitrogen-adsorption measurements, X-ray diffraction, FTIR spectroscopy, TG-DSC analysis and TPR-MS measurements. The catalytic behaviour of the systems of interest has been investigated towards two different reactions: (i) the gas-phase isomerization of *n*-butane and (ii) the liquid-phase acylation of anisole and veratrole with benzoic anhydride.

A correlation between morphological and chemical physical features of the systems and their catalytic activity has been proposed.

[1] C.T. Kresge, M.E. Leonowicz, W. J. Roth, J. C. Vartuli, J.S. Beck, Nature, 359 (1992) 710.
[2] a) K. Arata, Adv. Catal. 37 (1990) 165; b) S. Melada, M. Signoretto, F. Somma, F. Pinna, G. Cerrato, G. Meligrana, C. Morterra, Catal. Lett., 94 (2004) 193.
[3] E. Ghedini, M. Signoretto, F. Pinna, G. Cerrato, C. Morterra, Appl. Catal. B:Enviromental, 67 (2006) 24.

INVESTIGATION OF NANOSIZE $NaBH_4$ – REDUCED SUPPORTED PALLADIUM CATALYSTS FOR HYDROGENOLYSIS OF CHLOROBENZENE

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The reduction of active component precursor is one of the crucial stages in catalysts synthesis. The traditional way considers reduction in a flow of hydrogen. However recently more and more attention is given to using sodium borohydride ($NaBH_4$) as an alternative and promising reducing agent. Advantages of this way consist in the possibility of sodium borohydride to reduce the supported precursors of an active component even at room temperature with formation of nanodispersed metallic clusters.

The goal of the present work is to investigate the physicochemical and catalytic properties of Pd and Pd-Pt supported catalysts reduced in water solution of sodium borohydride at room temperature. Catalysts were prepared by the impregnation method, using a carbonaceous material, called “Sibunit”, as the support. The state of the active component formed in sodium borohydride medium was studied by transmission electron microscopy (TEM), X-ray diffraction analysis (XRD), X-ray fluorescence and X-ray photoelectron spectroscopy (XFS and XPS).

It was determined, that the sodium borohydride solution at room temperature allows to reduce completely the supported precursors of active component of Pd/C and Pd-Pt/C catalysts up to metal state. The average size of supported metal particles was 2-5 nanometers. Investigation of catalytic activity of samples in liquid-phase hydrodechlorination of chlorobenzene showed, that bimetallic alloyed Pd-Pt clusters revealed maximal reactivity. Influence of additional temperature treatment in the reducing and oxidizing medium on a state of an active component of catalysts, their activity and stability in the hydrodechlorination of chlorobensene were studied.

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SYNTHESIS OF THE SILVER CATALYSTS USING MOLTEN NH_4NO_3

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Nowadays, one of the most important problems in catalysis is CO oxidation. Usually supported noble metals are used in this process as catalysts. Recently it was shown [1] by theoretically calculations that Ag in nanoparticle state is more active than Au. Also there are some recent experimental proofs of catalytic activity of supported Ag [2] and Ag-Co mixed oxides [3].

Six catalysts were synthesized in our work. Massive catalyst $AgCoO_2$ (sample **A**) was prepared by decomposition of nitrates in molten NH_4NO_3. Three supported catalysts with 5 wt. % $AgCoO_2$ were synthesized by coimpregnation of supports (SiO_2 – 185 m^2/g, SiO_2 – 320 m^2/g and γ-Al_2O_3 – 185 m^2/g) with aqueous solutions containing Ag, Co and ammonium nitrates (samples **B, C, D**). Two samples 5 % $AgCoO_2/\gamma$-Al_2O_3 were prepared by wet impregnation of γ-Al_2O_3 with aqueous solutions of Ag, Co and ammonium nitrates and decomposition in the sandy bath (sample **E**) or using microwave radiation (sample **F**). All catalysts were calcined at 600 °C (2 h) and were studied in CO oxidation reaction (gas mixture: 4.0 vol. % CO, 2.1 vol. % O_2, 93.9 vol. % He; gas rate was 10000 h^{-1}).

Samples **B** and **C** show almost no activity in CO oxidation (table 1). Difference in temperatures of 50 % and 100 % conversion for samples **A** and **D**, **E**, **F** probably originated from small specific surface area of $AgCoO_2$ and perhaps from the formation of $CoAl_2O_4$ which is also active in CO oxidation. The most active sample was **F** which was prepared using microwave radiation. Most likely microwave radiation treatment due to quick heating of the nitrate mixture results in the formation of catalysts with higher specific surface areas of active component comparing to conveniently prepared samples and as a result with higher catalytic activity in CO oxidation reaction.

Table 1. **CO oxidation over Ag-Co oxide catalysts**

catalyst	$T_{50\%}$, °C	$T_{100\%}$, °C	catalyst	$T_{50\%}$, °C	$T_{100\%}$, °C
A	288	400	**D**	200	430
B	550	> 650	**E**	224	448
C	370	> 570	**F**	155	260

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1. P.P. Dholabhai, X. Wu and A.K. Ray // J. Molec. Str.: THEOCHEM. 2005. V. 723. P. 139-145.
2. Zhenping Qu et al. // J. Molec. Catal. A: Chem. 2005. V. 239. P. 22-31.
3. Erdogan Gulari et al. // Appl. Catal. A: Gen. 1999. V. 182. P. 147-163.

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THE INFLUENCE OF SIZE FACTOR ON CATALYTIC PROPERTIES OF ZrO_2 IN CO OXIDATION

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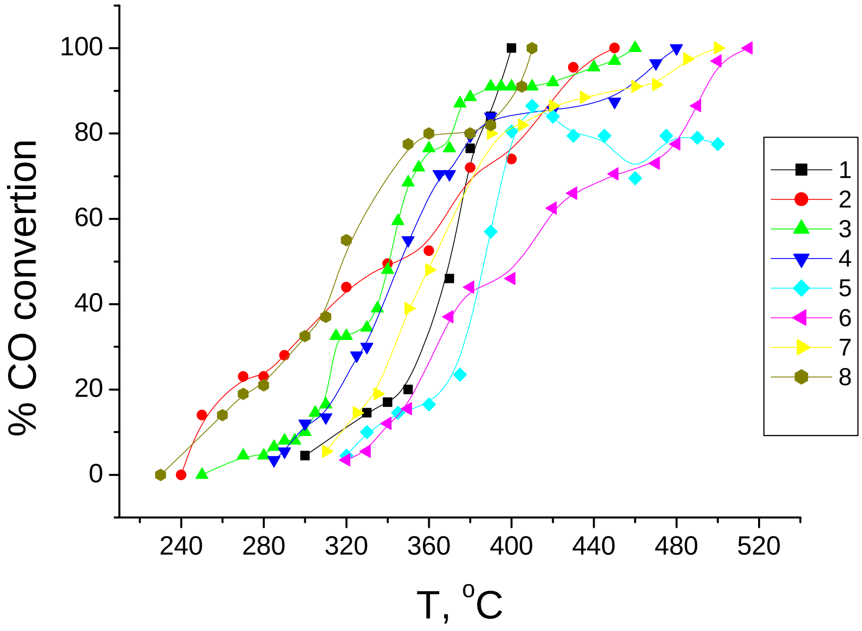
The nanosized zirconia polycrystals stabilized by yttria have worldwide interest in heterogeneous catalysis. The reduced particle size not only guarantees an increased specific surface area (quantitative change of surface reactivity) but also raises the fraction of low-coordinated surface sites. The aim of this study is the investigation of yttria-stabilized zirconia with different particle sizes in model reaction of CO oxidation. The characteristics of samples are presented in Table.

Samples, №№	**$T_{heating}$, °C**	**Phase composition, %**	**Particle's size, nm**
1	400	Tetragonal + amorph.	10
2	500	Tetragonal	8,9
3	600	Tetragonal	11,8
4	700	Tetragonal	14,4
5	700	Tetragonal	14,4
6	800	99% Tetragonal + 1%Monocline	18,5
7	900	98,5% Tetragonal + 1,5% Monocline	27,1
8	1000	99,2% Tetragonal + 0,8% Monocline	36,2

Fig. shows the light-off temperatures of zirconia catalysts with different particle sizes.



The catalytic properties of samples were found to be a function of particle size of ZrO_2. At low temperatures the most active was the sample of 10 nm. At high temperatures – 18,5 nm.

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THE DIFFUSION OF SIMPLE GASES ON CATALYSTS WITH FRACTAL STRUCTURE

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The most of heterogeneous catalytic processes take place in porous catalyst with the developed surface. During the studying of macrokinetic processes, that take place in these catalysts, their spatial structure should be taken into account. This structure could be described using fractal geometry.

We study the influence of fractal properties of silica gel in the diffusion of gases. The diffusion of gases (H_2, CO) is studied in the volume of catalysts with fractal surface according to diaphragm method. The fractal dimension of silica gel was calculated from adsorption isotherms of N_2 according to the BET theory and according to data of capillary condensation of methanol.

The silica gel samples, which were investigated by us, had fractal dimension in the range from 2,05 to 2,90. The diffusion dependence of diaphragm fractal dimension was revealed.

It was shown, that the fractal dimension influences not only the diffusion coefficient but also the type of diffusive equation.

SIMULATION STUDIES OF CATALYTIC MEMBRANE REACTORS FOR ENHANCED METHANE STEAM REFORMING

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Methane steam reforming (MSR) is an important technology for synthesis gas and hydrogen production. Synthesis gas is a key raw material for chemical products manufacturing, while hydrogen is seeing as a promising clean and efficient fuel for the 21's century. Current technologies for MSR are reaching a stagnant performance level. In this work two types of catalytic membrane reactors are considered for MSR: inert membrane reactor (IMR) and catalytic film coated membrane reactor (CCMR). Catalytic membrane reactors can enhance the needs of high hydrogen production, operate at lower temperature range compared to packed tubular reactors, and simultaneously lead to product separation in a single unit. Mathematical modeling includes multicomponent mass transfer, membrane flux characteristics, and the effect of non-infinite hydrogen membrane selectivity. In co-current operation, both types of membrane reactors can achieve higher conversion than fixed bed reactors, and overcome the thermodynamic limits of closed systems. In IMR, the sweep flow control makes possible to attain 100% conversion at equilibrated retentate-permeate pressure. Reactor performance highly depends on geometric configuration: shell/tube or monolithic. For some conditions IMR generates ca. 40% more conversion and 20% higher hydrogen recovery as compared to CCMR.

References

1. Barbieri, G.; Di Maio, P. "Simulation of the methane steam re-forming process in a catalytic Pd-membrane reactor". Ind. Eng. Chem. Res., 36 (1997) 2121-2127.
2. Fernandes, F.A.N.; Soares, A.B. Jr. "Methane steam reforming modeling in a palladium membrane reactor". Fuel, 85 (2006) 569-573.
3. Galluci, F.; Comite, A.; Capannelli, G.; Basile, A. "Steam reforming of methene in a membrane reactor: an industrial case study". Ind. Eng. Chem. Res., in press (2006).
4. Ritchie, J.T.; Richardson, J.T.; Luss, D. "Ceramic membrane reactor for synthesis gas production". AIChE J., 47 (2001) 2092-2101.

P-35

PREYSSLER CATALYST, $[NaP_5W_{30}O_{110}]^{14-}$, A MILD, GREEN AND EFFICIENT CATALYST FOR OXIDATION OF AROMATIC AMINES TO AZOXY COMPOUNDS

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The conversion of amines into oxygen containing compounds is an important reaction in industry and academia. Among the various reported methods, formation of nitro and nitroso compounds is common and has been most extensively studied while a limited number of methods have been reported for the preparation of azoxy compounds. The azoxy compounds are of interest because of their physiological activity, uses in liquid crystal displays and therapeutic medicines [1,2]. With respect to the most of the reported methods for preparing of azoxy compounds involves metal catalysts, and the majority of them are usually expensive, of limited environmental compatibility, and even toxic, there is a good scope for research and working with green catalysts.

In green chemistry, heteropolyacids (HPAs) as solid catalysts are very important. HPAs constitute a large class of compounds that are remarkable owing to their physicochemical properties. They include strong Bronsted acidity, reversible transformations, activation of molecular oxygen and hydrogen peroxide, high proton mobility and solubility in polar and nonpolar solvents. These properties have made them more and more popular in many fields, such as catalysis, biology, medicine, magnetism, photochemistry and material science [3-7].

Although, most of catalytic fundamental investigations used the Keggin HPAs, in recent times, interest in other HPAs has grown. Among them, the capability of Preyssler catalyst, $[NaP_5W_{30}O_{110}]^{14-}$, still has been largely overlooked and there still is a room to maneuver.

In continuation of our researches on HPAs to various reactions [8] and with the aim of extending of application of Preyssler catalyst, in this research we report our results on the oxidation of amines for synthesis of azoxy compounds as a major product in the presence of Preyssler catalyst. The effects of molar ratio of oxidant, solvent type, and catalyst type, reaction time and temperature were investigated. The results showed that the oxidation of anilines with H_2O_2 catalyzed by Preyssler catalyst proceeds with good yields. The catalyst can be recovered and reused again.

References

[1] S. Sakuae, T. Tsubakino, Y. Nishiyama, Y. Ishii, J. Org.Chem. 58 (1993) 3633.
[2] J. P. Snyder, V.T .Bandurco, F. Darack, H. Olsen, J. Am.Chem. Soc. 96 (1974) 5158.
[3] M. Kidwai, R. Venkatramanan, R. K. Garg, K. R. Bhushan, J. Chem. Res. (2005) 586.
[4] D. L. Tabern, E. H.Volwiler, J. Am. Chem. Soc. 57(1935) 1961.
[5] K. S. Atwal, G. C. Rovnyak, B. C. O'Reilly, J. Schwartz, J. Org. Chem. 54 (1989) 5898.
[6] C. O. Kappe, W. M. F. Fabian, M. A. Semones, Tetrahedron 53 (1997) 2803.
[7] A. D. Patil, N. V. Kumar, W. C. Kokke, M. F. Bean, A. J. Freyer, C. Debrossi, S. Mai, A. Truneh, D. J. Faulkner, B. Carte, A. L, Breen, R. P. Hertzberg, R. K. Johnson, J. W. Westly, B. C. M. Potts, J. Org. Chem. 60 (1995) 1182 .
[8] a) M. M. Heravi, Kh. Bakhtiari, F. F. Bamoharram, Catal. Commun. 7 (2006) 373.
b) M. M. Heravi, Kh. Bakhtiari, F. F. Bamoharram, Catal. Commun. 7 (2006) 499.
c) M. M. Heravi, F. Derikvand, F. F. Bamoharram, J. Mol. Catal. 242 (2005) 173.
d) M. H. Alizadeh, H. Razavi, F. F. Bamoharram, K. Daneshvar, J. Mol. Catal. 206 (2003) 89.
e) M. H. Alizadeh, H. Razavi, F. Farrash Bamoharram, M. H. Hassanzadeh, Kinet. Catal. 44 (2003) 524.
f) F. F. Bamoharram, M. M. Heravi, M. Roshani, M. Gahangir, A. Gharib, Appl. Catal. 302 (2006) 42.
g) M. M. Heravi, R. Motamedi, N. Seifi, F. F. Bamoharram, J. Mol. Catal. 249 (2006) 1.
h) F. F. Bamoharram, M. Roshani, M. H. Alizadeh, H. Razavi, M. Moghayadi, J. Braz. Chem. Soc. 17 (2006) 505.
i) M. M. Heravi, F. K. Behbahani, F. F. Bamoharram, J. Mol. Catal. (2006) 1n press.
j) F. F. Bamoharram, M. M. Heravi, M. Roshani, A. Gharib, M. Gahangir J. Mol. Catal. 252 (2006) 90.

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SELECTIVE OXIDATION OF METHANOL ON IRON-MOLYBDENUM CATALYST – STATE AND POSSIBILITIES FOR IMPROVEMENT

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Despite the high activity and selectivity of the employed in practice iron-molybdenum catalysts for selective oxidation of methanol, the quantity of residual methanol contained in formalyne is between 1,0 and 3,0 % (1). Lowering this quantity under 0,5 % requires introduction of a supplementary adiabatic layer situated under the main reactor. In spite of the wide usage of this approach in practice, the scientific literature has not registered any research in this direction. This requires intuitive work, involving the risk of serious losses resulting from the secondary oxidation of the obtained in the main reactor formaldehyde.

Very recently Casale Chemicals SA proposed a new, five-stage adiabatic reactor (1) for selective oxidation of methanol. The same company (2) offers a way of improving the work of the classic tube reactors by inputting the gas mixture, containing non-reacted methanol through second catalytic reactor of adiabatic type. However, in this case too there is no data on the conditions of performing the process.

The purpose of the present work is to define the limit values of the main parameters of the process of selective oxidation of methanol upon oxide catalysts in the main reactor and in the adiabatic layer or additional adiabatic reactor, which can guarantee a maximum rate of methanol conversion at high selectivity.

In performing the experiment a two-stage flow-line equipment is used, allowing for complete independence of the work of the catalyst in the main reactor and in the auxiliary reactor, functioning as an adiabatic layer. The composition of the gas mixture entering the main reactor, space velocity and temperature rate provide conditions for performing the experiment, which are maximally close to the industrial ones.

The range of the temperature, methanol concentration and space velocity for the obtaining of acceptable results is outlined. It has been found that besides on temperature, the limits of applicability of the adiabatic layer depend to a substantial degree on the composition of the entering gas mixture.

References:

1. K. Ivanov, Applied Catalysis A, General, 116, L1-L-3, (1994);
2. G. Sioli, US patent No 5959154, (1999);
3. G. Sioli, EP No 1166864A$_1$, (2002).

FTIR SPECTROSCOPIC STUDY ON FORMATION OF NEW TYPES OF CATIONIC IRIDIUM CARBONYLS IN Ir-ZSM-5

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In this work we report some new non-classical carbonyls of iridium formed after CO adsorption on Ir-ZSM-5. Mainly Ir^+ cations were found on sample activated at 523 K and reduced by CO at the same temperature. With CO they formed $Ir^+(CO)_2$ gem-dicarbonyls (2104 and 2033 cm^{-1}) which decomposed at 673 K without leaving a measurable fraction of monocarbonyls. The dicarbonyl structure was established by ^{12}CO-^{13}CO coadsortpion experiments. In the presence of CO in the gaseous phase and at ambient temperature the $Ir^+(CO)_2$ dicarbonyls were converted into $Ir^+(CO)_3$ species (2182, 2099 and 2033 cm^{-1}). At 100 K these complexes are able to accommodate a fourth CO molecule thus producing tetracarbonyls (2155, 2145, 2125 and 2105 cm^{-1}). The results are explained by the high coordinative unsaturation of the Ir^+ cations in the ZSM-5 matrix. This is also the reason for the formation of mixed $Ir^+(H_2O)(CO)_2$ species (2087 and 2015 cm^{-1}) after CO–H_2O coadsortion. Evacuation of the sample at 673 K, followed by reduction with CO at 523 K generates Ir^{2+} cations. With CO these cations form another kind of geminal complexes, namely $Ir^{2+}(CO)_2$ species (2173 and 2129 cm^{-1}). Here again, the structure was confirmed by ^{12}CO-^{13}CO coadsortpion experiments. These dicarbonyls are decomposed at 573 K (without producing monocarbonyls again) and are able to accommodate additionally neither CO nor water molecules. The results are explained by the smaller cationic radius of Ir^{2+} (as compared to Ir^+) which is associated with a decrease of the number of ligands required for coordinative saturation.

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CATALYTIC PROPERTIES OF THE ULTRAMARINE ANALOGS PREPARED FROM ZEOLITES

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The natural and artificial ultramarine is a sodium aluminosilicate sodalite that contains the sulfur anion-radicals combined with sodium cations encapsulated inside the β-cages. The anion-radicals play a role of chromophores, responsible for the intense coloration. The colored ultramarine analogs can be also obtained from synthetic zeolites (A, X, cancrinite) by means of thermal reaction with sulfur radical precursors. The color and structure of the products can be modified by altering the composition of the initial mixture, particularly its alkalinity and contribution of cations other than sodium. In many cases zeolite structure is transformed into sodalite upon thermal procedure, but the original zeolite structure can be maintained too. Some of the cations (eg. H^+, transition metal cations) or sulfur species can play a role of catalytic active sites, which could be especially noticeable in the products of opened structure of parent zeolites. Catalytic activity of potential pigments is undesired and it could cause unexpected effects during their application.

The colored samples obtained by thermal treatment of mixtures of zeolite A or cancrinite with sulfur and alkalis were examined as catalysts in propan-2-ol decomposition. The starting mixtures contained either the original sodium forms of zeolites or their modifications with cations such as K^+, Li^+, Co^{2+}, Ca^{2+}, Cu^{2+}, Fe^{3+}. The catalytic tests indicate that the pigment samples with SOD structure are inactive or show a negligible activity. The samples of more opened structures (e.g. LTA, CAN, nepheline hydrate) indicate some activity. The 12 member ring channels of cancrinite are accessible for the reagent molecules and even the sample prepared without contribution of any cations, but Na shows a noticeable activity. The modification of the colored samples with other cations (particularly with transition metal cations) brings about a substantial increase in activity. It is likely that metal sulfides formed inside the cavities during an ion-exchange procedure are responsible for the activity of the samples. It is interesting to notice a considerable contribution of acetone in the products obtained over Co and Zn modified samples.

The active sites should be eliminated if the samples are applied as pigments to avoid their interactions with polymers or solvents.

SYNTHESIS OF ZnO NANOPARTICLES STABILIZED IN MgO AND THEIR CATALYTIC PROPERTIES

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ZnO-based materials have considerable interest due to their possible applications in many technologies, such as optoelectronic devices, solar energy conversion, catalysis, etc.

We reported the method for the preparation of the nanostructured system ZnO/MgO with constant chemical composition and controlled size of ZnO nanoparticles. The method is based on a deposition of the ZnO colloidal nanoparticles on the MgO. The nanoparticles are obtained by mixing of isopropanol solutions of zinc acetate and sodium hydroxide. The size of ZnO nanoparticles is controlled by conditions of their growth: concentration of initial reagents, temperature, and time. The obtained ZnO/MgO solids contain the ZnO nanoparticles with diameters in the range of 6-10 nm. The nanoparticle size was obtained from the absorption edge in diffusion reflection spectra and TEM.

The catalytic properties of obtained solids were tested in the CO oxidation by molecular oxygen. The non-monotonic dependence of catalytic activity on the size of the ZnO nanoparticles is obtained. This dependence experimentally proves existence of quantum confinement effect in catalytic process.

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STRUCTURAL-FUNCTIONAL DESIGN OF NANO-DIMENSIONAL CATALYSTS OF DEEP OXIDATION OF METHANE

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The development of oxide catalysts of deep oxidation of methane with optimal structural, dimensional, redox- and acid characteristics will allow to resolve the task of ecologically pure and resource-saving hydrocarbon fuel combustion.

Catalytic properties of nano-dimensional alumina- and zirconia- supported oxide systems, nanocomposites with the structure of spinel $Me^{II}Fe^{III}{}_2O_4$ (Me-Mn, Co, Ni) in the reaction of deep oxidation of methane have been studied with the use of different techniques: X-ray powder diffraction, transmission electron microscopy, temperature-programmed reduction by H_2, temperature-programmed desorption of ammonia, X-ray photoelectron- and IR-spectroscopy. The method of preparation of supported nano-sized catalysts under non-equilibrium conditions providing high activity and thermal stability of alumina-manganese catalysts was proposed [1]. Low temperature nano-dimensional catalysts of spinel structure $MeFe_2O_4$ (Me = Mn, Co, Ni) synthesized by thermal decomposition of heterometallic trinuclear acetate complexes of iron (III), including in porous matrixes of carriers (Al_2O_3, ZrO_2) and in the presence of surface active agents have been developed [2]. As stated, dimensional factors (revelation of phase, internal dimensional effects) in complex oxide nanocomposites are the main reason for difference in their catalytic properties (activity and thermal stability). It has been shown that among supported ferrites and cobalt-zirconia nanosystems the most active low-temperature catalyst is characterized by the highest amount and reactivity of oxygen, as well as by presence of strong acidic centres on the surface.

On the basis of zirconia- and alumina- oxide systems with optimal physical-chemical characteristics (structural, dimensional, red-ox and acid) structured catalysts formed on the surface of ceramic honeycomb supports have been synthesized. These catalysts provide 100 % conversion of CH_4 to CO_2 at temperatures 700-750 °C and can be used for processes of neutralization of coalbed methane exhausts and combustion of gaseous hydrocarbon fuel in power installations (catalytic heat generators, gas turbines combustion chambers etc.).

References:

1. Kosmambetova G.R., Kantserova M.R., Orlyk S.N. / Patent of Ukraine № 65892 A, 15.04.2004, Bull. №4.
2. Kantserova M.R., Orlyk S.N., Gavrilenko K.S., et.al. / Patent of Ukraine № 71394 A,15.11.2004, Bull. №11.

OXIDATIVE DEHYDROGENATION OF PROPANE AND ETHANE OVER VANADIUM CATALYSTS SUPPORTED ON MESOPOROUS MATERIALS

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Catalytic oxidative dehydrogenation (ODH) of light alkanes provides a promising alternative route for the efficient production of C_2= - C_4= alkenes, which are widely used as raw materials in the chemical and polymer industry. Among the catalysts that have been studied, supported vanadium catalysts appeared to be the most active and selective ones for the oxidative dehydrogenation of propane and of ethane as well. The present work focuses on vanadium catalysts supported on mesoporous silicate materials with large surface areas and different pore structures. Mesoporous materials are usually being utilized as supports in order to achieve higher metal dispersion at relatively high loadings. The activity and selectivity in the oxidative dehydrogenation of propane and ethane of the catalysts based on mesoporous supports were related to their compositional, porosity and surface characteristics and were compared to the more classical $V/\gamma\text{-}Al_2O_3$ catalysts.

The mesoporous silicates tested as supports were the MCM-41 (with hexagonal channel-like pore structure and pore diameters of ~2.9 nm) and the HMS (with wormhole-like three-dimensional pore structure and pore diameters of 2.4 nm) type of materials and were synthesized based on previously reported methods. Mesoporous-supported vanadia catalysts were prepared following typical wet impregnation methods in order to obtain 2.5, 5, 10, 20% V_2O_5. For comparison, a $10\%V_2O_5/\gamma\text{-}Al_2O_3$ catalyst was also prepared by the same method. All the supported catalysts were calcined at 500 °C under air for 4 hrs prior to catalytic tests which were carried out in a fixed bed micro-reactor, at 350 – 625 °C and with a 1:1 propane or ethane to oxygen ratio, diluted with He. The catalytic results of ODH of ethane at 350-625 °C and of propane at 400-600 °C showed that the vanadium catalysts supported on both mesoporous silicates exhibited higher selectivity towards propylene and ethylene at high conversions, compared to the $\gamma\text{-}Al_2O_3$ based catalysts. No significant differences in activity and selectivity were observed between the two types of mesoporous supports, while lower V loadings afforded the most promising catalysts.

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INORGANIC ANALOGUES OF PORPHYRINS - TETRABUTYLAMONNIUM SALTS OF TRANSITION METAL MODIFIED MONOLACUNARY KEGGIN ANIONS. PROPERTIES AND APPLICATION FOR LIQUID PHASE PHENOL OXIDATION

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In recent years chemistry of heteropolyacids (HPAs), particularly their application as catalysts, attracted a lot of attention. Heteropolyacids are complex proton acids and have strong acidic properties. Structure of HPAs may be easily modified by exchange of addenda atoms, heteroatom or countercation. Heteropolyacids have well known structure and their acidic and redox properties are easily controlled. Due to their multifunctionality they can be useful catalysts in oxidation of organic compounds. Introduction of transition metal ion into heteropolyacid structure changes their oxidative properties. Those substituted monolacunary HPAs anions ligate the heterometal in pseudoporphyrin environment.

The most active metalloporphyrins applied in hydrocarbon oxidation are those including manganese, iron and cobalt. Due to this fact we assumed that HPAs modified with transition metal ions would be also active in those reactions. In our research we investigated tetrabutylammonium salts of tungstophosphoric acid with cobalt, manganese and iron as addenda atoms. We obtained monosubstituted Keggin anions with addenda atom substituted by cobalt, manganese or iron cation. Introduction of tetrabutylammonium (TBA) salt into the Keggin anions results in soluble in organic solvent catalysts.

Our catalysts were studied by means of FT-IR, UV-Vis, TG with DSC, and XRD. In the UV-Vis spectra of tetrabutylammoniumbromide (TBAB) dissolved in diethyl ether we observed band at 211 nm. After introduction of TBA cation into the structure of monosubstituted Keggin anions (TM-HPA) we observed red shift of the band to 235 nm. This band is absent in the potassium salts of TM-HPAs. FTIR spectrum of HPW demonstrates P-O stretching vibration band, at 1080 cm^{-1} which splits into 1073 and 1021cm^{-1}. Thus splitting of the P-O stretching vibration band is characteristic for lacunary anions. According to the TG/DSC analysis synthesized catalysts are thermally stable up to 500 K.

The catalytic activity of the TBA-HPA salts including cobalt as addenda atom, was studied in the liquid phase phenol oxidation reaction with a few oxygen donors. Reaction was carried out in the glass reactor with acetonitrile as solvent and hydrogen peroxide as oxygen donor. Reaction mixture was checked once per hour and analyzed with GC.

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STRUCTURAL EFFECTS OF P ON THE STABILIZATION OF SURFACE CHROMIUM SPECIES ON ALUMINA DURING PROPANE OXIDATIVE DEHYDROGENATION

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Introduction

Chromia/alumina catalysts are used in the dehydrogenation of light alkanes. However, the chromia/alumina catalysts undergo significant deactivation due to loss of dispersion of surface chromium oxide into aggregates of Cr_2O_3 crystallites. We report the use of operando Raman-GC to determine the effect of additives on the structure and stabilization of surface chromate species during propane oxidation to propylene.

Experimental

The Raman spectra were run with a Renishaw Micro-Raman System 1000 (514 nm Ar+). The operando Raman-GC spectra were run with a home-made operando reaction cell that consists of a fixed-bed quartz-microreactor contained by quartz wool plugs at both ends. During the operando Raman-GC study, the catalyst structure and its performance are analyzed simultaneously. Chromia/alumina catalyst was prepared by impregnation of alumina support, and P-doped chromia/alumina catalyst was prepared by sequential impregnation. Alumina was first impregnated with phosphorus, dried, calcined and subsequently impregnated with chromium solution.

Results and Discussion

The oxidation of propane on a $Cr(6+)/Al_2O_3$ catalysts shows very high activity, but the degree of catalyst dispersion rapidly decreases. Operando Raman spectra show intense reduction of surface chromate sites above 210 °C and the progressive formation of Cr_2O_3 (Raman band at 550 cm^{-1}). The addition of phosphorous shifts the Cr=O mode to lower frequencies (1010 to 992 cm^{-1}), which implies a weakening (activation) of the Cr=O bond. Interestingly, the catalyst becomes less active. It suggests that the Cr=O bond is not the active site for propane oxidation. The operando Raman-GC study of propane oxidation on P-doped chromia/alumina catalyst show a catalyst with lower activity, but significantly higher selectivity to propylene. The presence of P significantly limits the decreasing of dispersion degree of surface chromates. Formation of Cr_2O_3 is not observed up to 380 °C, i.e., at 170 °C higher than in the absence of P.

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INFLUENCE OF THE SUBSTRATE MOLECULAR STRUCTURE IN UNSATURATED NITRILES HYDROGENATION OVER RANEY-TYPE CATALYSTS

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Chemoselective hydrogenation is an important tool in fine chemicals industry. Compounds to be hydrogenated often contain several reducible groups and in many cases, only one of them has to be reduced. This work was focused on the hydrogenation of unsaturated nitriles of various structure (cinnamonitrile, 1-cyclohexenylacetonitrile, acrylonitrile, 3,3-dimethylacrylonitrile, geranylnitrile and 2- and 3-pentenenitrile) over Raney-type catalysts.

Hydrogenations were carried out under optimized reaction conditions for cinnamonitrile[1]. The influence of the substitution and the position of the double bond relative to the nitrile group on the selectivity to unsaturated amines were investigated.

It was found[2] that the molecular structure of the substrate crucially determined the selectivity to unsaturated amine. The highest selectivities were obtained when the double bond was not in conjugation with the nitrile group. Also the distance of the C=C bond from the C≡N influenced positively the selectivity. Another important factor was the substitution of the double bond. It was more difficult to hydrogenate a sterically hindered double bond. On the other hand presence of additional substituents at the C=C bond increased the selectivity to unsaturated amine. The selectivity was also influenced by stabilization of the double bond by additional conjugation. The molecular structure revealed a similar influence on the reaction rate. The reaction rate also depended on the conjugation of the C=C bond with the C≡N bond and decreased with a higher degree of substitution.

Acknowledgments

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References:

1. Kukula P., Struder M., Blaser H.-U.: Adv. Synth. Catal. 346, 1487 (2004).
2. Kukula P., Koprivova K.: J. Catal. 234, 161 (2005).

MESOPOROUS MESOPHASE THIN FILMS FOR GAS SEPARATION

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For existing at present moment gas chromatography sorbents typical is chaotic labyrinth of pores of various sizes and forms of narrowings and widenings, as well as sorbents in chromatography columns have low means of surface area about 200 – 500 m^2/g. Therefore, existing columns show specific effectiveness not sufficient for many separations. Also, irregular structure of pores is the reason for strong dependence of effectiveness on gas-carrier rate. These factors increase characteristic time of analysis of complicated mixtures to tens minutes.

In order to improve the parameters of retention we used mesoporous molecular sieves (MMS) with regular structure of pore space and high surface area. The synthesis of MMS like MCM-41 [1] involves ionic surfactants as structure directing agents. Precursors of solid phase (SiO_2) concentrate on the surface of micelles which form 2D and 3D hexagonal or cubic permolecular structures. After condensation of solid phase the surfactants can be deleted by calcinations, extraction or ion exchange. As a result one obtains solid MMS, which replicate the removed organic phase.

Typical chromatogram for the mixture of C_1-C_4 hydrocarbons in capillary column covered with a film of silica MMS is shown on Figure 1.

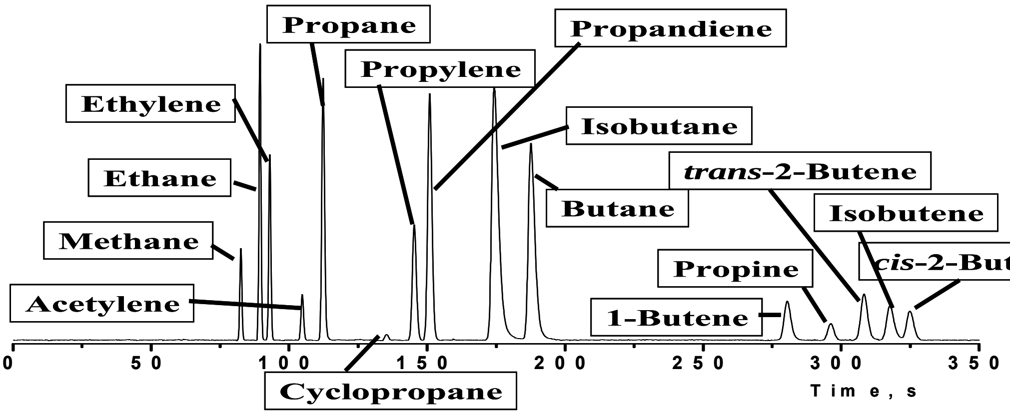

Figure 1. Chromatogram of C_1-C_4 hydrocarbons mixture separated on the silica mesoporous molecular sieve film.

[1] *C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.C. Beck. Nature.* ***1992****, 28, 57-72.*

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FROM HOMOGENEOUS TO HETEROGENEOUS CATALYSIS: HYDROGENATION WITH SUPPORTED Rh(I) METAL COMPLEXES

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The preparation and application of heterogenized metal complexes is a relatively new field of research resulting in a new way of catalysis. The heterogenized metal complexes can successfully combine the excellent performance (high activity and selectivity) of homogeneous catalysts with the easy separation and recycling of the heterogeneous catalysts. Additionally, in the several cases the immobilization of metal complexes leads to enhanced stereo-, chemo- and enantioselectivity.

Hydrogenation reactions play an important role in chemical industry. The fact that homogeneous catalyst is present in the reaction mixture along with products can be main disadvantage for much wider use of the homogeneous catalysts. One of the effective routes to solve this problem is immobilization of homogeneous (Wilkinson, etc) catalysts on solid supports [1]. The main goal of this work on the one hand is the synthesis of different immobilized Rh(I) metal complexes and their use in hydrogenation reactions and on the other hand to establish mechanisms of reactions by hydrogenation of suitable substances with para-hydrogen. The $RhCl(PPh_3)_3$, $RhClCO(PPh_3)_2$, $Rh_2Cl_2(CO)_4$, $RhCl(P(OCH_3)_3)_3$ were impregnated on the different supports (silica gel, alumina, modified silica gel) with the aim of producing the working catalyst. When $RhCl(P(OCH_3)_3)_3$ supported on silica gel [2] was used in the reaction of heterogeneous hydrogenation of styrene (liquid medium) and propylene (gaseous medium) the products of hydrogenation have been observed. It was shown, that $RhCl(PPh_3)_3$ supported on 2-diphenylphosphinoethyl functionalized silica gel is effective catalyst of heterogeneous hydrogenation of alkenes in liquid phase.

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[1]. Shin-Guang Shyu, Sheau-Wen Cheng, Der-Lii Tzou, “Immobilization of $Rh(PPh_3)_3Cl$ on phosphinated MCM-41 for catalytic hydrogenation of olefins”, Chem.Commun.,1999, 2337-2338

[2]. M. Tada, T. Sasaki, Y. Iwasawa, "Novel SiO2-attached molecular-imprinting Rh-monomer catalysts for shape-selective hydrogenation of alkenes; preparation, characterization and performance", Phys. Chem. Chem. Phys., 2002, V. 4, pp. 4561-4574.

TRANSITION METAL MODIFIED ZEOLITES AS CATALYSTS FOR LIGHT PARAFFINS OXIDATION

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Much research effort is currently devoted to the chemical conversion of light alkanes to valuable chemicals [1]. Especially, oxidative dehydrogenation (ODH) of light paraffins into olefins has been widely searched during the last few decades, because this process is an alternative route to production of important base chemicals of the economic benefits [2]. Among the different catalysts which have been examined for this process, the transition metal ion species exchanged in zeolites has been discovered as very active and selective oxidation catalysts [3].

The presented study is focused on the research of ethane and propane oxydehydrogenation over iron modified zeolites of different structure (ZSM-5, zeolite-Y, mordenite). Commercial zeolites were modified with iron (III) ions by means of ionic exchange from aqueous solution, followed by calcination at 600°C (Fe-ZSM5, Fe-Y, Fe-mordenite) or 900°C (Fe-ZSM5). Hydrocarbons ODH reaction was carried out in the presence of N_2O as an oxidant. Acidity of applied samples was estimated on the grounds of FT-IR spectra of adsorbed pyridine. Iron concentration was calculated from ICP measurement. The catalytic tests in ODH reaction were performed at 400°C, in continuous flow reactor.

Fe-ZSM-5 showed high activity in ethane ODH reaction performed in the presence of N_2O and the only products were ethene and COx. Selectivity towards ethene was 75-85%, whereas selectivity towards COx did not exceed 20 %.

In ODH of propane selectivity towards propene was lower (45-60%), whereas selectivity towards COx still did not surpass 20 %. However, besides of propene and CO_x, the lower hydrocarbons (C_1 and C_2) being the products of the cracking process have appeared. Selectivity towards the cracking products reached almost 35%. Selectivity towards mentioned products in propane oxydehydrogenation reaction was very sensitive to the catalysts acidity and to previous thermal treatment of the samples.

References

1. O. V. Buyevskaya, D. Wolf, M. Baerns, Catalysis Today 62 (2000) 91.
2. E. Heracleous, M. Machali, A. A. Lemonidou, I. A. Vacalos, J. of M. Catalysis. A: Chem. 232 (2005) 29.
3. K. Novoveská, R. Bulánek, B. Wichterlová, Catalysis Today 100 (2005) 315.

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PHOSPHORUS POISONING OF Pt/BETA ZEOLITE AND Pt/ZSM-5 DIESEL CATALYST COMPONENTS

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Pt-containing zeolite catalysts are effective in reducing NO_x with hydrocarbons in diesel exhaust gas with high oxygen content [1]. Zeolites have an ability to adsorb HC, which also improves NO_x conversion with increasing temperature [2,3]. Deactivation of diesel catalysts is a problem that has not been solved with the current catalyst technology, and knowledge about effects related to deactivation of zeolites is still narrow. Deactivation of zeolite containing catalysts can occur at both low and high temperatures especially in moist conditions. Contaminants found in aged catalysts include depositions of P, S, Zn, Ca, N, HCs, and coke. Depositions of P, Zn, Ca, and S are very hard to remove, and therefore they are associated with irreversible deactivation [4].

In this study, powdered Pt/beta zeolite (Pt 0.85 wt-%, $Si/Al_2 = 300$) and Pt/ZSM-5 (Pt 0.85 wt-%, $Si/Al_2 = 29$) catalysts were studied as fresh and after two treatments: hydrothermal ageing and phosphorus poisoning in hydrothermal conditions. The aim was to evaluate effects of phosphorus on catalytic activity and characteristics of the catalysts at laboratory-scale. Simplified model components were used in order to obtain detailed knowledge on poisoning phenomena of these zeolites. The results showed that the deactivating effects of phosphorus were stronger than the effects of hydrothermal treatment alone. Phosphorus had accumulated in the samples during the ageing. The decrease in the specific surface area indicated the possible reason for deactivation.

References

[1] J. Guo, M. Konno, T. Chikahisa, T. Murayama and M. Iwamoto, JSAE Rev. 16 (1995) 21.
[2] H. Shinjoh, J. Alloys Compd. 408–412 (2006) 1061.
[3] R.J. Farrauto and K.E. Voss, Appl. Catal. B: Environ. 10 (1996) 29.
[4] W.E.J. van Kooten, H.C. Krijnsen, C.M. van den Bleek and H.P.A. Calis, Appl. Catal. B: Environ. 25 (2000) 125.

STRUCTURAL, TEXTURAL AND THE ACID-BASE PROPERTIES OF ALUMINA, PREPARED FROM A HYDRATED PRODUCT OF THE CENTRIFUGAL THERMAL ACTIVATION OF HYDRARGILLITE (CTA-PRODUCT)

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Introduction

Technical alumina (hydrargillite – HG) is known to be the raw material for production of aluminium hydroxide and alumina. The thermoactivation process of HG in a centrifugal flash-reactor (TSEFLAR) [1] leads under certain conditions to practically full destruction of the HG crystal structure to give an X-ray amorphous CTA-product [2]. In comparison to HG, the CTA-product possesses a higher catalytic activity, a large specific surface area and an X-ray amorphous structure.

The aim of work is study of formation features of aluminium hydroxide with pseudoboehmite structure (prepared by hydration of the CTA-product) and aluminium oxide on its basis.

Results and discussion

Aluminium hydroxide samples were prepared by hydration of CTA-product at certain conditions. Alumina was obtained by thermal treatment at 600-900°C for 4 hours. Physical-chemical properties of these hydroxides and oxides were studied using atomic absorption spectroscopy, DTA/TG, XRD, nitrogen adsorption isotherm, HRTEM, FTIR spectroscopy.

It is shown that hydration of the CTA-product in the acid medium allow to prepare a fine pseudoboehmite. Depending on hydration conditions of the CTA-product formed pseudoboehmite is more crystallized also can be refer to “finely crystalline”; or less crystallized and it properties comes nearer to pseudoboehmite, synthesized by precipitation. Textural characteristics of CTA-oxides are defined by temperature of treatment and the nature of initial aluminium hydroxide prepared by hydration of the CTA-product. Total concentration of surface Lewis acid sites of CTA-oxides is essentially higher than for γ-Al_2O_3. Distinctive feature of CTA-oxides is that on their surface strong Lewis acid sites are present. Total concentration of basic sites of CTA-oxides is lower in comparison with γ-Al_2O_3, however in contrast to γ-Al_2O_3 they contain the strong basic sites.

References

1. Patent RF 2186616 (2002).
2. Yu.Yu Tanashev, L.A. Isupova, A.S. Ivanova et al.: *16th International Congress of Chemical and Process Engineering (CHISA),* 22 – 26 August 2004, Praha, Czech Republic. Abstracts. P. 214.

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THE OBTAINING OF THE LIGHT OLEFINS FROM NATURAL GAS VIA METHANOL AND DIMETHYL ETHER ON ZEOLITE CATALYSTS

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The natural gas is alternative source to oil to obtain of synfuel and other valuable products of the petrochemical synthesis. One of the most rational ways of converting natural gas is its conversion to syngas with the following conversion to the hydrocarbons. The process of obtaining of olefins and liquid hydrocarbons from the dimethyl ether and methanol seems to be more efficient in comparison with Fisher-Tropsch method. The technology of obtaining of olefins in industrial scale is not realized in Russia.

The purpose of this work was to study of the influence the type of zeolites, molar ratio SiO_2/Al_2O_3, the nature of the active metals in the composition of zeolite catalysts on their activity and selectivity in conversion of dimethyl ether and methanol diluted by nitrogen, and also influence of reaction conditions, for obtaining mainly light olefins.

Catalytic properties of synthesized laboratory samples of metal-containing zeolite catalysts were studied in the pilot setup of high pressure with twenty-four-hour running, providing uninterrupted supply of dimethyl ether. The catalyst testing was carried out at pressure 3 MPa, temperatures from 300°C to 450°C, gas mixture (% vol.): 24 DME, 76 N_2, WHSV=1300 $l/l_{kat.}h$. A sampling of products of the reaction was carried out after 5 and 23 hours of catalyst run at each temperature. Conversion of methanol was carried out at 0,1 MPa on SAPO-34 (Zeolyst International) catalyst. All the catalytic materials were characterized by XRD, IRS, TPD NH_3.

It was found that the activity and selectivity of studied catalysts depend on the nature of metals in the composition of catalysts, molar ratio SiO_2/Al_2O_3 and conditions of a reaction. On ZSM-5 zeolite (ZAO Nizhnegorodskie Sorbenty) catalysts wide range of hydrocarbons is observed. There is a wide spectrum of C_1-C_8 hydrocarbons both paraffins and olefins of n- and iso-structure in gas product.

Composition of liquid products is characterizes by a wide range of hydrocarbons to C_{12} n- and iso-paraffins, olefins, aromatics and naphthenes. Both metal nature and temperature of experiment influences on distribution of hydrocarbons in gas product. Liquid hydrocarbon product is characterized by high octane number (RON) 90-98.

Conversion of DME reaches maximum values at 350°C, however, a further increasing of temperature results in gradual decreasing of conversion, which, probably, is conditioned by partial deactivation of a catalyst. Content of CH_4 in hydrocarbon gas was about 5-10%, of ethylene about 14-16% and of propylene about 10-12% on the best samples of catalysts. For all catalysts it is observed decrease in catalyst activity after 23 hours, which, probably, is caused by forming of high-weight molecular products, blocking the access of reactants to the active sites of catalysts. On SAPO-34 catalysts narrow range of hydrocarbons $C_1 – C_5$ is observed. The SAPO-34 is characterized by high conversion (96%) and high yield of $C_2 – C_4$ olefins (about 84% wt). However, with the exception of ZSM-5, it is deactivated rapidly due to coke formation. Increasing of zeolite molar ratio leads to enlargement of stable catalyst run and decreasing of coke-formation probably due to decreasing of the number of weak acid sites and increasing of the number of strong acid sites in zeolite.

The explanation of a different behavior of catalysts in the process requires further researches.

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Ru-COMPLEX IMMOBILIZATION USING IONIC EXCHANGE

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One of the leaf alcohol cis-hex-3-en-1-ol represents interesting and important substance in fragrance and flavour industry. Many ways for its preparation were tried, but the most promising could be the selective hydrogenation of sorbic acid with consecutive chemical reduction. The sorbic acid hydrogenation represents a very complex problem because of the large amount of different products (unsaturated acids). Lately, the successive system for sorbic acid hydrogenation to cis-hex-3-enoic acid was found[1]. This system uses ruthenium “naked” pentamethylcyclopentadienyl half sandwich complex with the second ligand presented by the sorbic acid as catalyst.

In general homogeneous and heterogeneous catalysis differ in many aspects - selectivity and easiness of re-use of the catalyst are the best-known. By a choice of optimal catalyst and process conditions, it is possible to obtain very high selectivity in homogeneous catalytic reactions but catalyst recovery is a serious problem especially in industrial practice. Promising way is combining the advantages of both catalysis types. This process is the immobilization of homogeneous complex onto the solid surfaces referred to as “heterogenization of homogeneous catalyst”. Such operation is not easy because of strict demand on keeping the structure of the complex unchanged due to binding onto heterogeneous support.

One type of the immobilization of used catalyst could be ionic exchange using smectite group clays as supports. Cationic part of catalyst can be exchanged with solvated cations in the clay layers. Different types of support and solvents were used for immobilization. Immobilized catalyst was then used for sorbic acid hydrogenation using different reaction conditions and its reuse was realized.

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References

1. S. Steines, U. Englert, B. Driessen-Hoelscher: Chem.Commun., 3 (2000) 217.

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OPTIMIZATION OF THE SYNTHESIS OF PEROXYPROPIONIC ACID BY USING ZEOLITE AND MESOPOROUS MOLECULAR SIEVE CATALYSTS

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Peroxypropionic acid (PPA) is important from an industrial viewpoint. Because of its oxidative properties, it can be used in the destruction of organophosphorus (as paraoxon) and of sulfurated pollutants. One way to produce this peroxycarboxylic acid is the oxidation of the parent carboxylic acid by H_2O_2 in presence of an acidic catalyst:

$$CH_3CH_2COOH + H_2O_2 = CH_3CH_2COOOH + H_2O$$

The catalyst generally used for this reaction is sulfuric acid, but the solution is very acidic leading to several drawbacks including catalyst separation. For these reasons we have investigated heterogeneous zeolite and mesoporous molecular sieve catalysts. The selected catalysts were H-ZSM-5, H-beta and H-MCM-41.

They were synthesized and characterized using XRD, nitrogen adsorption, FTIR, X-ray fluoroscopy and scanning electron microscopy.

Since there are no reports in the literature on application of heterogeneous catalysis to PPA synthesis one of the main challenges is to find the optimum conditions (initial concentration, temperature and rotating speed) for this reaction over zeolites. In the presentation activity of tested catalytic materials will be discussed and related to the catalyst structure.

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NOVEL CATALYSTS IN BIODIESEL SYNTHESIS

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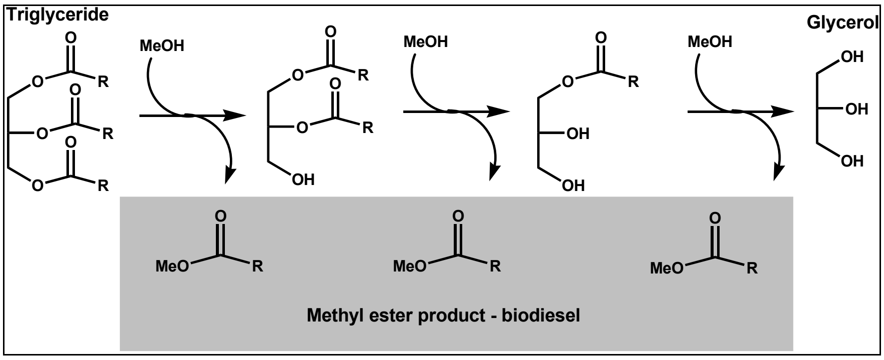
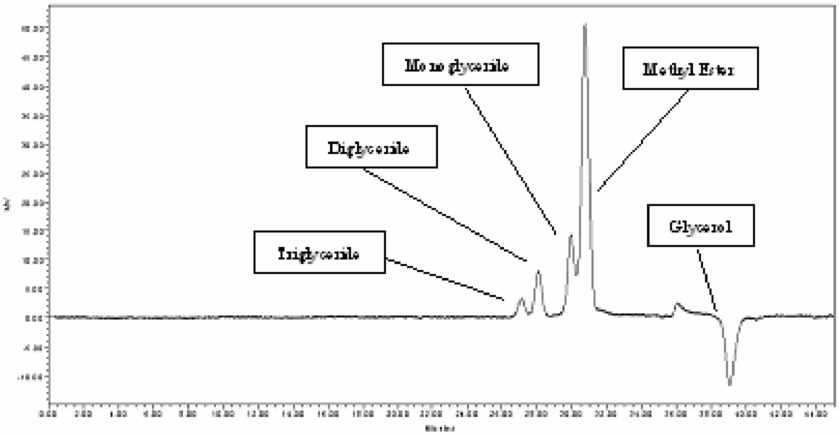
Biodiesel is a renewable fuel formed by transesterification of triglycerides with a short chain alcohol, typically methanol (Fig.1 below).[1] Biodiesel can be used as a direct replacement for diesel in engines and the market has grown rapidly over the last 10 years due to both legislation and environmental concerns. This growth looks set to continue worldwide and in particular in Europe where EU legislation has a target of 5.75% of all fuel to be biofuel by 2010.[2]





Strong acid or base catalysts can catalyse this process with base catalysis by sodium or potassium hydroxide or methoxide being the most common industrial method.[3] The use of these alkaline catalysts can however lead to problems of saponification, which manifest themselves as costs due to the need for pure starting materials and purification of the products.[4] There is, therefore, a desire to have an improved catalyst for this process that will simplify the purification step and allow use of less expensive feedstocks.

This paper describes the development of novel biodiesel catalysts at Johnson Matthey Catalysts. In particular the use of a heterogeneous catalyst to replace the homogeneous base will be discussed.

1. L.C. Meher, D. Vidya Sagar, S.N. Naik, Renewable and Sustainable Energy Reviews; (2004); 1-21.
2. Directive 2003/30/EC of the European Parliament; (May 2003).
3. F. Ma, M.A Hanna.; Bioresour. Technol.; 70; (1999):1–15.

STUDY OF THE SORPTION PROPERTIES OF THE REGENERATED CO_2 SORBENTS BASED ON LIME

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The development of the autonomous fuel cell generators poses the problem concerning the production of the pure hydrogen gas, where CO concentration should be less than 10 ppm [1]. Sorption–enhanced reaction process is one of the best solutions. This process includes steam reforming of the hydrocarbons in the presence of a CO_2 sorbent, which increases the methane and CO conversions, thus allowing the production of hydrogen gas with low CO_x concentration [2].

In this work the routine synthesis and studies of the lime-based CO_2 sorbents were performed. The dynamic CO_2 capacity and stability of CaO in the cycles of CO_2 sorption/$CaCO_3$ decomposition were studied. The influence of the lime additives (like alkali and barium carbonates, metal oxides etc.) on the capacity and stability of the sorbents was examinated. Tests of our materials in the sorption–enhanced reaction process showed the fast deactivation of the catalysts mixed with the sorbents having high content of alkali carbonates. Although non-promoted CaO has lower CO_2 capacity, its usage seems to be more preferable due to the higher stability of CaO. It was shown that the sorption properties of CaO are determined by its texture and worsening while the dispersion decreases. The sintering of the monodisperse model CaO system was studied in the cyclic conditions. It was shown that in isothermal conditions the dynamic capacity (y) of monodisperse CaO depends on the number of cycle (x) as follow:

$$y = \frac{p_1}{(p_2 + x)^{p_3}} + p_4 .$$

The influence of the temperature, CO_2 pressure and cycling time on the sorbent capacity was studied by thermogravimetry. The results obtained can be explained by the formation of two CaO phases: a highly reactive surface and a core phase, the latter being forming a rigid frame of the sorbent. We developed a method of preparation of the mechanically stable CaO sorbent with dynamic capacity more than 10 wt.%, which is maintained for several thousands of cycles.

Preferences

1. *Fuel Cell Handbook*. Seventh ed. 2004, EG&G Technical Services, Inc.
2. Hufton, J.R., S. Mayorga, and S. Sircar, *Sorption-Enhanced Reaction Process for Hydrogen Production*. AIChE J., 1999. **45**(2): p. 248-256.

P-55

MICROREACTORS FOR THE METHANOL STEAM REFORMING: INFLUENCE OF DESIGN ON HYDROGEN PRODUCTION

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Microreactors for the methanol steam reforming has many advantages in comparison with traditional catalytic systems, for example, high heat- and mass-transfer velocities, high value of the volume to surface ratio and other. The work is aimed at studying the reaction of methanol steam reforming in a microchannel microreactor and elucidating the effect of microreactor and microchannel plates design on the microreactor efficiency. We investigate two types of the microreactors: cylindrical microreactor with disk microchannel plates and rectangular microreactor with different microchannel plates. This microchannel plates were made from porous nickel and porous stainless steel. In the all experiments we use CuO/ZnO catalyst. The microreactors work more efficiency than traditional fixed-bed reactors. Our experiments revealed that the optimal diameter of the channels in the microchannel plates is 0,2 mm. The most effective was rectangular modular microreactor (the volume of all microchannel plates is 18 cm^3). At the 80% methanol conversion and the W/F= 1.8 g·min/mmol(MeOH) hydrogen production reaches 52 l/h.

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PRODUCTION OF KETONES FROM C_3-C_4 SATURATED HYDROCARBONS OVER MoCrGa-POLYOXIDE CATALYSTS

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Supported polyoxide catalysts on the basis of Mo, Cr, Ga, Bi, and Ce as well as natural clays of Kazakhstan, were tested in the process of oxidative conversion of propane-butane mixture. The influence of reaction temperature, contact time, composition and content of active component of catalyst were determined. The experiments were carried out at atmospheric pressure in a continuous-flow unit with a fixed-bed quartz-tube reactor. The gas mixture used for oxidation contained C_3H_8–C_4H_{10} from 14 to 80% and oxygen from 4 to 18% in different ratios at 300-700°C and W=330-15000 h^{-1}. Analysis for the reactants and products was carried out chromatographically with an "Agilent Technologies" instrument. The catalysts were characterized by XRD and EM analysis, and their surface area, porosity, and elemental composition were determined.

It was found that the partial oxidation of propane-butane mixture with varying the catalytic mixture composition and the contact time yielded acetone, methyl ethyl ketone, methanol, acetaldehyde, crotonic aldehyde, butanol, and acetic acid, as well as C_2–C_3 unsaturated hydrocarbons. It was shown that conversion proceeds with the formation of gaseous and liquid products. Important petrochemicals, such as acetone (500-550°C) and acetaldehyde (300-350°C) are main liquid products. Ethylene is the main product of gas phase. Yield of ethylene increases beginning from 450°C. Ternary catalyst is more active than two-component samples. Optimal space velocities for catalysts with different content of active phase over carriers were determined. Up to 23% of acetone and 35% of methyl ethyl ketone on 1%MoCrGa/Clay were produced at W=1350 h^{-1}. Increase of content of acetone up to 31% in catalysate was observed at reduction of propane-butane in reaction mixture. The determination of the product composition showed that the process follows a complex mechanism including oxidation, oxidative dehydrogenation, and cracking.

This screening study aimed at searching for appropriate compositions and technological parameters of the oxidative conversion of propane-butane mixture show that the chosen line of research is promising and makes it possible to obtain good results in the synthesis of hydrocarbons and oxygenated compounds.

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Pd-BASED THIN FILMS IN CATALYTIC MEMBRANE REACTOR APPLICATIONS

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Palladium-based membranes can be used for separation of hydrogen from gas mixtures with 100 % selectivity, or directly in catalytic membrane reactors for removal or addition of hydrogen. Pd alloyed with Ag or Cu may have hydrogen permeation rates that surpass pure Pd, and the mechanical strength is significantly improved compared to pure Pd.

From a technological point of view, such membranes are relevant in large-scale as well as miniaturized applications. The separation of hydrogen from carbon containing product mixtures (fossil or biomass) offers a stream high in CO_2 concentration as an additional benefit. Membranes with 100% hydrogen selectivity are especially suited for feeding low temperature proton exchange membrane fuel cells that have high demands with respect to impurities in general and CO in particular.

Hydrogen may be produced from various fuels in one step or by consecutive catalytic reactions. Methanol is a uniform, liquid fuel that can be converted at moderate temperatures by the steam reforming reaction (1). Depending on the conditions and the catalyst, the water-gas shift reaction (2) will play a role in the reactant/product mixture given by (1).

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \qquad \Delta H_{298K} = +49.4 \text{ kJ/mol} \qquad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2; \qquad \Delta H_{298K} = -41.3 \text{ kJ/mol} \qquad (2)$$

For application in separation of product mixtures or in membrane reactors, the composition of the gas mixture as well as process conditions such as temperature and pressure will influence the membrane performance. Molecules present may adsorb and block sites for hydrogen adsorption and dissociation. The adsorption of CO on Pd is strongly dependent on temperature, and even small amounts of unconverted methanol are reported to considerably reduce hydrogen transport.

The impact of surface processes increases with decreasing membrane thickness, where the transport is not necessarily limited by bulk diffusion. A unique technique for fabrication of free-standing Pd-based membranes of thickness down to 1 μm has been developed at SINTEF Materials and Chemistry. Permeances of more than 7×10^{-6} mol/(m^2 s Pa) have been reported for such Pd/Ag membranes at 300°C.

The performance and stability of < 2 μm thick Pd/Ag and Pd/Cu membranes under water-gas shift (WGS) and methanol steam reforming (MSR) reaction conditions have been investigated in a flat, self-supported configuration. By studying thin, unsupported membranes, surface process influences are enhanced while effects from a support, such as pore diffusion, are eliminated. Model reaction/product mixtures have been used to identify and isolate effects on the membrane transport.

LOW TEMPERATURE NITROGEN THERMODESORPTION: PROSPECTS AND INSTRUMENTAL REALIZATION

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Thermoprogrammable desorption (TPD) is widely used to characterize surface properties of heterogeneous catalysts for decades. H_2, O_2, nitrogen oxides, ammonia, CO and some other gases are used for measuring the accessible surface areas of active components, strength and concentration of surface active sites, etc. Although, thermodesorption studies in low-temperature region are not as elaborated as that for high-temperature region.

We constructed a special instrument for low-temperature TPD of N_2 and argon. Additionally to adsorption isotherms in a range of 77 – 373 K and 10 – 700 torr, the instrument allows measuring adsorption isobars and isosteres. Besides, the kinetics of thermodesorption can be measured in the named range of temperatures and pressures. As a result in our contribution we present the kinetic thermoprogrammable desorption of N_2 on mesoporous and microporous (active carbons and zeolites) adsorbents. Mesoporous materials show only one peak in a range of 90 – 150 K insignificantly dependent on the chemistry and geometry of adsorbent surface. Zeolites have at least 3 peaks, which we attribute to desorption from the external surface (90-150 K), from micropores (150-250 K) and from the sites of N_2 strong adsorption (exceeding 250 K). The latter sites are known binding N_2 due to its strong quadrupole moment. Active carbons show relatively wide distributions of desorption temperatures due to disordered system of micropores.

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COORDINATION AND OXIDATION STATE OF COBALT IONS IN Co-CONTAINING BEA ZEOLITES: XRD, FTIR and TPR INVESTIGATIONS

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The state of cobalt in two cobalt-containing BEA zeolites was studied by XRD, TPR and FTIR spectroscopy using CO and NO as probe molecules. One of the samples, CoAlBEA (0.4 wt % of Co), was prepared by conventional ion exchange and the other, CoSiBEA (0.7 wt % Co), by two-step post-synthesis method using dealuminated SiBEA zeolite. The introduction of Co to SiBEA led to an increase in unit cell parameters of the BEA structure and to consumption of silanol groups in vacant T-sites of dealuminated BEA. In contrast, no structural changed were observed after incorporation of cobalt into AlBEA by ion-exchange as AlBEA and CoAlBEA have the same unit cell size. The much higher reduction temperature of Co^{2+} ions in CoSiBEA zeolite (1100 K) than that found for CoAlBEA (780 and 630 K) indicates a strong interaction of Co^{2+} with SiBEA.

Low-temperature CO adsorption on CoAlBEA results in (i) species formed with the support (H-bonded CO showing bands at 2174, 2165 and 2156 cm^{-1}), (ii) Co^{3+}-CO species (2208 cm^{-1}) and (iii) a small amount of Co^{2+}-CO complexes (2188 cm^{-1}). In agreement with these results, NO adsorption leads to the appearance of (i) NO^+ (2133 cm^{-1}, formed with the participation of the zeolite acidic hydroxyls), (ii) Co^{3+}-NO (1932 cm^{-1}) and (iii) a small amount of $Co^{2+}(NO)_2$ species (ν_s at 1898 and ν_{as} at 1814 cm^{-1}).

Low temperature CO adsorption on CoSiBEA leads to formation of only one type of hydrogen bonded CO (2156 cm^{-1}, on the silanol groups). In addition, two kinds of Co^{2+}-CO species are found (carbonyl bands at 2185 and 2178 cm^{-1}). No Co^{3+} cations have been detected. Adsorption of NO confirms the absence of Co^{3+} ions and acidic hydroxyls (NO^+ and Co^{3+}-NO species have not been formed). Instead, two kinds of $Co^{2+}(NO)_2$ species are detected (ν_s at 1888 + ν_{as} at 1808 cm^{-1} and ν_s at 1878 and ν_{as} at 1799 cm^{-1}, respectively).

SYNTHESIS OF MODIFIED Al_2O_3 AEROGELS AND THEIR ACTIVITY IN DEHYDROCHLORINATION OF 1-CHLOROBUTANE AND (2-CHLOROETHYL)ETHYL SULFIDE

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A series of nanoscale aerogel-prepared (AP) alumina, carbon-coated alumina and sulfated alumina samples have been synthesized and their reactivity in dehydrochlorination of 1-chlorobutane and (2-chloroethyl)ethyl sulfide has been studied. The effects of solvent and gel modification with several organic and inorganic acids, and β-diketones on the textural properties of nanocrystalline alumina synthesized by modified aerogel procedure have been studied. The highest specific surface areas exceeding 1000 m^2/g were obtained for samples prepared with an ethanol-toluene mixture used as the solvent. Addition of different agents limiting the growth of alumina nanoparticles in small concentrations had a positive effect on the surface areas of the aerogels. Carbon-coated alumina samples with high surface areas were prepared after high-temperature evacuation of alumina aerogels modified with organic agents.

The activity of high surface area nanocrystalline alumina materials in dehydrochlorination of (2-chloroethyl)ethyl sulfide and 1-chlorobutane compares favorably with that of other nanocrystalline metal oxides. For example, the temperature of 1-chlorobutane decomposition could be decreased by ca. 100°C in comparison with AP-MgO extensively studied earlier while maintaining 98% selectivity to butenes. The initial reaction rates over alumina-based aerogels could be further significantly increased by surface modification with sulfate groups achieved by addition of sulfuric acid before gelation. Sulfated-doped alumina aerogels had high surface areas ca. 600 m^2/g after calcination at 600°C and showed excellent acidic properties typical for sulfated alumina. For instance, (2-chloroethyl)ethyl sulfide conversion in pentane solution at room temperature over sulfated aerogel alumina was 3 times higher than on AP-Al_2O_3 and 8 times higher than on AP-MgO.

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NANOCRYSTALLINE AEROGEL VO_X/MgO CATALYSTS FOR OXIDATIVE DEHYDROGENATION PROCESSES

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Nanoscale aerogel-prepared (AP) alkaline-earth metal oxides are known for more than a decade as effective sorbents for neutralization of toxic compounds and wastes [1]. The high reactivity of AP-MgO is related to high concentration of various active sites on the surface of 3-5 nm oxide nanocrystals with high surface area (~ 500 m^2/g). AP-MgO has been recently reported as a promising support in preparation of VO_X/MgO catalysts for oxidative dehydrogenation of butane in the presence of molecular iodine [2].

AP-VO_x/MgO catalysts containing various loading of vanadium with high surface area and good stability were obtained by co-gelation using $VO(OC_3H_7)_3$ added to $Mg(OCH_3)_2$ solution prior to hydrolysis and gelation. The resulting materials were extensively characterized by physicochemical methods and used as catalysts for oxidative dehydrogenation of propane (ODP) in the presence of iodine vapor and without it.

Materials after supercritical drying in the autoclave had surface areas as high as 1000-1300 m^2/g. After calcination in air at 600 °C required for synthesis of active catalysts it decreased to 250-340 m^2/g that is still far superior to those obtained by other methods [2]. According to high-resolution TEM data, this synthesis method allowed us to obtain catalysts with rather small particle size and the most uniform vanadium distribution on the surface.

The catalysts prepared by co-gelation also proved to have high activity and C_3H_6 selectivity in ODP reaction at temperature range of 400-600 °C. Their propylene selectivity at 400-450 °C was close to 100% with optimum vanadium concentration 5-10 wt.% V.

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[1] K. J. Klabunde, J. Stark, O. Koper, C. Mohs, D. G. Park, S. Decker, Y. Jiang, I. Lagadic, D. J. Zhang, *J. Phys. Chem.*, **100** (1996) 12142.
[2] V. V. Chesnokov, A. F. Bedilo, D. S. Heroux, I. V. Mishakov, K. J. Klabunde, *J. Catal.*, **218** (2003) 438.

ISOBUTANE SELECTIVE OXIDATION ON V-Mo-O MIXED OXIDE CATALYSTS

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The selective oxidation of isobutane in order to obtain C_4 oxygenated compounds is an important reaction from theoretical and practical point of view.

For this oxidation the nature of catalyst and the strength of the M-O bond are very important.

Four catalysts V_2O_5-MoO_3 (10,30,50,90 % V_2O_5, wt) were prepared from $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and NH_4VO_3 precursors.

A solution of 15% $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was added to a solution of 2% NH_4VO_3, and the obtained solution was heated at 90°C and stirred until water was evaporated.

The precipitate was dried at 100°C for 15h, followed by calcination in air at 200°C for 2h, 400°C for 2h and 600°C for 4h.

The obtained catalysts were characterized from structural and textural point of view by XRD and BET, respectively.

The phases observed for those catalysts are presented in table 1.

Table 1.**The phases observed on MoO_3-V_2O_5 catalysts**

% V_2O_5	Phases observed					
10	MoO_3	V_2MoO_8	-	-	VO_2	-
30	MoO_3	V_2MoO_8	$Mo_6V_9O_{40}$	V_2O_5	VO_2	-
50	MoO_3	V_2MoO_8	-	V_2O_5	VO_2	Mo
90	-	V_2MoO_8	-	V_2O_5	-	-

It can be observed that V_2MoO_8 phase is present in all samples, MoO_3 is present in the first three samples, while V_2O_5 is present in the last three. The specific area, average pore diameter and pore volume were determinated by BET.

The results are showed in table 2.

Table 2. **The specific area, average pore diameter and pore volume for V-Mo-O catalysts**

% V_2O_5	SSA (m^2/g)	Average pore diameter (nm)	V_p (cm^3/g)
10	1.81	11.09	0.0056
30	1.63	11.97	0.0052
50	0.94	15.27	0.0025
90	2.66	15.38	0.011

It is observed that the specific area for all samples is small, and decreases until 50% V_2O_5 in the catalyst, then increases for the 90% V_2O_5 catalyst. The average pore diameter increases from the 10% V_2O_5 to the 90% V_2O_5 catalyst.

The four catalysts have been tested in the selective oxidation of isobutane. The catalytic properties were determined between 350-550°C.

For all catalysts, an increase in the conversion of isobutane was observed when the temperature increases. For the 10% V_2O_5 catalyst, conversions were between 6.7 and 14% and, for the 30% V_2O_5 catalyst, between 1.5 and 14%, with smaller conversions at the same temperature compared with the 10% V_2O_5 sample. For the 50% V_2O_5 and 90% V_2O_5 catalysts, conversions are much higher, between 8 and 30%. For the 10 and 30% V_2O_5 catalysts, the selectivity in partial oxidation products is higher (60-95), (the selectivity in isobutene decreases with increased temperature), while for the 50 and 90% V_2O_5 catalysts the selectivity in total oxidation products is high (60-80%).

The high selectivities for total oxidation products for the 50 and 90% V_2O_5 catalysts can be explained by the fact that V_2O_5 prevails for these samples, and this is a powerful oxidation agent in comparison with MoO_3, which is predominant in the samples with 10 and 30% V_2O_5.

NEW SUPPORTS FOR Au PROMOTED Co BASED CATALYSTS FOR HYDRODESULFURIZATION

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The ever increasing amounts of heavier feeds and the severe restrictions imposed on the allowed percentage of sulphur-containing compounds, as well as aromatics in the different distillates make the hydrodesulfuration (HDS) of petroleum fractions one of the most important process in the refening industry. The synthesis of more active HDS catalysts are required [1].

One of the major factors that affect the activity of a HDS catalyst is the interaction between the active components of the catalyst and the support. Generally, the catalytic activity rises with increasing active species area. The use of a new family of mesoporous materials (MCM and HMS) as catalyst support gives possibilities to have the combination of high surface area and regular pore structure, which enables greater control over catalyst activity and uniformity of active sites.

In this work mesoporous materials (MCM-41 and HMS) [2-3] were used as supports of Co and gold promoted Co catalysts. The supports and catalysts were characterized by N_2 adsorpition-desorption (S_{BET}), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The catalysts were tested in the reaction of hydrodesulfurization (HDS) of thiophene. The results showed that the high catalytic activity is related to the degree of oxidation/sulfidation of the Co species. For the single cobalt catalysts the catalytic activity measured in the HDS of thiophene depended strongly on the cobalt oxide dispersion and on the Co^{3+}/Co^{2+} atomic ratio. The effect of gold is discussed in terms of increased cobalt dispersion and reducibility.

1. K.G Knudsen, B.H. Cooper, H.Topsøe, Appl. Catal. *A*, 205, 1999, 189
2. C.T.Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Bech, Nature, 3591992, 710
3. N.M.-Astorga, G. Pecchi, T. J. Pinnavaia, G. A.-Manoli, P. Reyes, J. Mol. Catal. Chem. *247, 2006, 145*

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NANO-SIZE GOLD BAZED CATALYSTS FOR COMPLETE BENZENE OXIDATION: INFLUENCE OF PROMOTER AND SUPPORT NATURE ON THE CATALYSTS REACTIVITY

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The detoxification of the hydrocarbons pollutants is one of the global environmental problems. High and stable activity in the reaction of complete benzene oxidation (CBO) over gold-vanadia catalysts supported on titania and zirconia [1], mesoporous titania and zirconia [2] and ceria [3], have been already established. One crucial factor for the selection of highly active gold catalysts is nature of the support. The important role plays the promoter used. The aim of the present study is to clarify the role of the support nature and the effect of the promoter on the catalytic activity in CBO over supported gold catalysts. Two series of gold catalysts, supported on ceria and titania (anataze), were prepared by deposition precipitation method. Then vanadia or molybdena (4 wt. %) were introduced as promoters via impregnation. The samples were denoted as AuMoTi, AuVTi, AuMoCe and AuVCe. The catalysts were characterized by XRD, Raman spectroscopy and TPR measurements. The catalytic tests have showed that the catalyst supported on ceria exhibit higher activity than that on titania. These results are explicable in regards to the high ceria oxygen storage capacity. The interesting result obtained was that the catalytic activity of AuVTi was much more higher comparing to AuMoTi catalyst but when ceria is used as support the situation is completely different – the AuVCe sample is less active than AuMoCe one. The lowest temperature of 100% conversion of benzene (190 °C) is achieved in the presence of AuMoCe catalyst. For all samples studied the average size of gold particle is < 5 nm. By Raman data the presence of hepta-molybdate and molybdate in traces was detected in MoTi sample. Less amount of hepta-molybdate and the coexistence of molybdate were registered for AuMoTi. The predominant presence of molybdate species was characteristic for MoCe and AuMoCe catalysts. For the VTi sample the presence of metavanadate was observed while for AuVTi the strong decrease of metavanadate and pyrovanadate formation is seen. The predominant part of VOx species in the case of VCe and AuVCe were the distorted metavanadate. The comparison of the TPR profiles of the samples on titania, promoted by vanadia and molybdena, showed differences in the reduction activity depending on the promoter. Three peaks are recorded in the TPR profile of MoTi sample (T_{max} at 410, 590 and 710 °C). In the presence of gold (AuMoTi) only the first peak was shifted towards significantly lower temperatures (125 °C) while the position of the other peaks was fast the same. The conclusion is that only a part of MoO_x species loaded are influenced by gold and available for the low temperature CBO. In contrast to these results one main peak of VT sample with T_{max} was observed at 445 °C and in the presence of gold the reduction of VO_x species was shifted to lower temperatures (T_{max} 120 °C). By this way, the H_2 consumption (e.g. the oxygen capacity) in the low temperature interval was significantly higher for the catalysts promoted by vanadia then that promoted by molybdena. This result can satisfactory explain the observed much higher activity in CBO of AuVTi catalyst compared to AuMoTi one. The situation with the catalysts supported on ceria was different. One complex TPR peak connected to the reduction both of ceria surface layers and molybdena or vanadia species was shifted toward lower temperatures in the presence of gold. The H_2 consumption of AuMoCe is higher than that of AuVCe which is in agreement with the higher catalytic activity in CBO of gold–molybdena catalyst supported on ceria.

References:

1. D. Andreeva, T. Tabakova, L. Ilieva, A. Naydenov, D. Mehanjiev and M. V. Abrashev, *Applied Catalysis A:General* 209 (2001) 291-300
2. V. Idakiev, L. Ilieva, D. Andreeva, J.L. Blin, L. Gigot, B.L. Su, *Applied Catalysis A: General* **243** (2003) 25–39.
3. D. Andreeva, R. Nedyalkova, L. Ilieva and M. V. Abrashev, *Applied Catalysis A: General* 246 (2003) 29-38.

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SYNTHESIS AND CHARACTERISTIC OF METHACRYLIC SUPPORTS FOR TRANSITION METAL CATALYSTS

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Functional polymers revolutionized organic synthesis and catalysis at the end of the twentieth century. Transformations of functional groups in such polymers (often multi-step) can lead to immobilization of metal complexes, on the one hand, or certain intermediate products, on the other one. Other advantages of using polymer matrices are rapid product purification and ability to complete the reaction through the use of an excess of reagents. Thanks to these characteristics they can be widely used as supports for catalysts or solid matrices for organic synthesis (*solid phase organic synthesis SPOS*) [1,2].

In our presentation new three-components, cross-linked glycidyl methacrylate or 2-hydroxyethyl methacrylate copolymers obtained by a suspension polymerization procedure are shown. Good swelling characteristics in common organic solvents and loading capacity (an epoxy or hydroxyl groups content) in range of 1-1.5 mmol per gram of a resin, made obtained materials (after further chemical modification) interesting as it comes to catalytic applications. Therefore, the construction of chelating ligands on the polymers was performed. Series of imine-bound resins were obtained which were then used to complex with cobalt ions. The catalysts prepared in this way were tested in the reaction of carboxylic acids with epichlorohydrin. The catalytic activity of mono and diimine systems was compared.

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References:

1. Hartley F. R., *Supported Metal Complexes,* London, 1985.
2. Dörwald F.Z., *Organic Synthesis on Solid Phase*, Weinheim, 2002.

Pt,Fe-CONTAINING HYPERCROSS-LINKED POLYSTYRENE AS CATALYST FOR WET AIR OXIDATION OF PHENOL

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Phenol contaminants of industrial wastewaters are very dangerous for aquatic organisms and the problem of dephenolization is of vital importance for basins of many rivers. Most methods of dephenolization boil down to sorption of pollutants by various sorbents. In this case, the pollutants are extracted from water, however to completely remove phenols from biosphere the extract should be afterwards buried or additionally processed for degradation of the contaminants. Direct degradation of phenols in wastewaters may help to resolve the problem. Catalytic wet-air oxidation (CWAO) is a prospective method for transformation of phenols to non-toxic products. CWAO consists in complete oxidation of organic compound to carbon dioxide and water using “pure oxidizers” (ozone, oxygen, etc) in presence of catalyst. A two-zone filter-reactor will be developed for CWAO of phenols. The first zone will serve for partial oxidation of phenols (up to 95%), whereas the second zone containing a biocatalyst will help to completely remove phenols from water.

Pt,Fe-containing polymer composites were chosen as catalysts for partial phenol oxidation. The catalysts were prepared by impregnation of hexachlorplatinic acid and iron (II) chloride in porous hypercross-linked polystyrene (HLP). Pt-impregnated HLP beads were dried in vacuum to obtain Pt-containing clusters of nanometer size. Fe-impregnated HLP beads were dried in vacuum, subsequently treated with sodium hydroxide and hydrogen peroxide to obtain nanoparticles of iron (III) oxide. The catalysts obtained were characterized by transmission electron microscopy (TEM). The TEM studies showed that the catalysts contained particles of Pt and iron (III) oxide sizing to 2-4 nm. The catalysts were tested in the processes of CWAO of phenol. The use of the catalysts containing iron (III) oxide nanoparticles (4,5 wt%) only resulted in 10% phenol conversion. The metal content in the catalysts containing Pt was varied from 0.1 to 5 wt%. The best results (conversion of 95% and turnover frequency of 0,64 1/s) were detected for catalysts with metal content of 0.1 wt%. The Pt-catalysts are prospective for testing in the first zone of the two-zone filter-reactor.

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PRODUCTION OF HIGHLY OCTANE GASOLINE HYDROCARBONS BY ISOMERIZATION ON ZEOLITE CATALYSTS

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Influence of nature and the content of zeolite in composition of Pt-catalysts on isomerization and cracking activity in modeling reaction of isomerization of n-hexane and C_5-C_{10} gasoline fraction of Fischer-Tropsch synthesis are investigated. It is shown, that isomerization activity of bifunctional catalysts are determined substantially by zeolite nature, its content in catalyst, temperature of experience and acid properties of zeolites.

Now isomerization is the most important octane boosting process for the gasoline.

In this work influence of nature and the content of zeolite in Pt-catalysts on isomerization and cracking activity in reaction of isomerization of n-hexane and hydrocarbons of C_5-C_{10} gasoline fraction in conditions of industrial process are investigated.

Catalysts based on zeolites (Y, β, ZSM-5, USY, Mordenite) were obtained by formation of zeolite with Al_2O_3, then dried up and calcinated at 500°C and then impregnated by solution $Pt(NH_3)_4Cl_2$. Zeolites were investigated by XRD, IRS, TPD NH_3. As a result of the researches of catalytic properties of Pt-zeolite samples, it was showed, the conversion of n-C_6H_{14} increases with growth of zeolite content and temperature in the order Y<MOR<β<ZSM for all samples of catalysts. Selectivity to i-C_6 increases in the order ZSM<β<MOR<Y for catalysts with the same content of zeolite. Higher isomerization activity of Y, β catalysts in comparison with ZSM catalysts may be explained by various structural and acid properties of these zeolites. Y-to-USY zeolite modification leads to increasing of n-hexane conversion and i-C_6 selectivity.

Catalyst such as Pt-loaded Al_2O_3 shows isomerization activity only for C_5-hydrocarbons in hydroisomerization of C_5-C_{10} fraction. Pt-loaded zeolite (Y, USY, β) catalysts show isomerization activity for all gasoline hydrocarbons.

So isomerization activity of bifunctional catalysts is determined by zeolite nature, content in catalyst and temperature.

ALUMINA SUPPORTED THIOCUBANE CLUSTER AS A CATALYST FOR LOW TEMPERATURE DECOMPOSITION OF HYDROGEN SULFIDE

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The problem of utilization of wastes, which negatively affect on national health, environment ant cultural heritage, is a complex worldwide task, which is stipulated by the requirements of environmental protection and the necessity of rational approaches, from the viewpoint of both economy and safety. Large amounts of H_2S are produced worldwide, mostly from natural gas production (yearly tonnage are 14.4 million tons) and oil refining (9.6 million tons). Most of the hydrogen sulfide is processed in a Claus plant where the sulfur is recovered, but hydrogen is jettisoned as water. As an alternative to this method, a new catalytic reaction for the hydrogen sulfide decomposition is proposed in the report with obtaining two marketable products instead of one: hydrogen and sulfur

$$2\ H_2S \Leftrightarrow 2\ H_2 + \tfrac{1}{4}\ S_{8(ads)}\ ,\quad \Delta_rH^0_{298} = -\,23.0\ \text{kcal/mol}\ .$$

The reaction occurs over typical sulfide HDS catalyst at ambient temperature in two steps (thermodynamics of the reaction is considered in frame of the DFT method [1]). The first step, stoichiometric reaction of two H_2S molecules adsorbed on two adjacent Co atoms with formation of S-S bond and release of first hydrogen molecule in gas phase, occurs spontaneously at room temperature. The second stage, catalytic decomposition of surface intermediate via release of second hydrogen molecule and recombination of molecular S_2 sulfur into cyclooctasulfur S_8, occurs very slowly at room temperature (days). To accelerate this step, new catalyst is proposed. The catalyst consists of thiocubane cluster with $Co_2Mo_2S_4$ core [2] supported on the alumina surface. In the cluster a short Co-Co distance 2.52 A is realized (instead of 3.16 A in the sulfide HDS catalysts). It was shown that activity of the alumina supported cubane cluster catalyst is much higher in comparison with the typical HDS catalysts. Material balance on hydrogen sulfide decomposed and hydrogen and elemental sulfur formed have been calculated.

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1. A.N. Startsev, I.I. Zakharov, O.V.Voroshina, A.V. Pashigreva, V.N. Parmon, Docl. Phys. Chem., 2004, v.399, 1, 283-286.
2. T.R. Halbert, S.A. Cohen, E.I. Stiefel, Organometallics 1985, 4, 1689-1690.

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EVALUATION OF ALUMINA-BASED CATALYSTS FOR N_2O ABATEMENT

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Nitrous oxide is an important greenhouse gas (270 times higher greenhouse potential than CO_2) with a long lifetime of about 150 years in the atmosphere. Due to its long life time it can be decomposed in the stratosphere by photolysis and oxidation producing nitrogen oxides which are leading to stratospheric ozone depletion. N_2O is produced by both natural (soils, oceans, atmospheric chemistry) and anthropogenic sources (agriculture, nitric acid and adipic acid production, power plants). Several technologies have been developed for the abatement of N_2O which involve thermal decomposition, non selective catalytic reduction, catalytic decomposition and selective catalytic reduction.

A series of metal (noble and transition) based catalysts supported on γ-alumina were used to decompose catalytically N_2O. All catalysts (Table 1) were prepared using the dry impregnation technique. Evaluation of activity and stability of the prepared catalysts was taken place in a quartz (U-shape tube) fixed bed reactor over a wide range of temperatures (200-600 °C) in the absence (P_{N2O}= 0.12 kPa, balance He, Figure 1) and presence of oxygen (mixtures of P_{N2O}= 0.12 kPa, P_{O2}=4.4 kPa, balance He) and by adding reducing agents on the reacting mixture (P_{N2O}=0.12 kPa, P_{O2}=4.4 kPa, P_{CH4}= 0.45 kPa or P_{C3H8}= 0.23 kPa, balance He).

Table 1: List of catalysts

Catalyst	Precursor	Calcination
γ-Al_2O_3	γ-Al_2O_3	600°C, 4h
2%Ru/γ-Al_2O_3	$RuClxH_2O$	500°C, 4h
2%Rh/γ-Al_2O_3	$RhCl_3x3H_2O$	600°C, 6h
2%In/γ-Al_2O_3	$In(NO_3)_3x5H_2O$	600°C, 6h
2%Cu/γ-Al_2O_3	$Cu(NO_3)_2x3H_2O$	600°C, 6h
2%Pd/γ-Al_2O_3	$Pd(NO_3)_2x2H_2O$	600°C, 6h
2%Ni/γ-Al_2O_3	$Ni(NO_3)_2x6H_2O$	600°C, 6h
2%Fe/γ-Al_2O_3	$Fe(NO_3)_3x9H_2O$	600°C, 6h

Figure 1: Activity Tests in the presence of N_2O

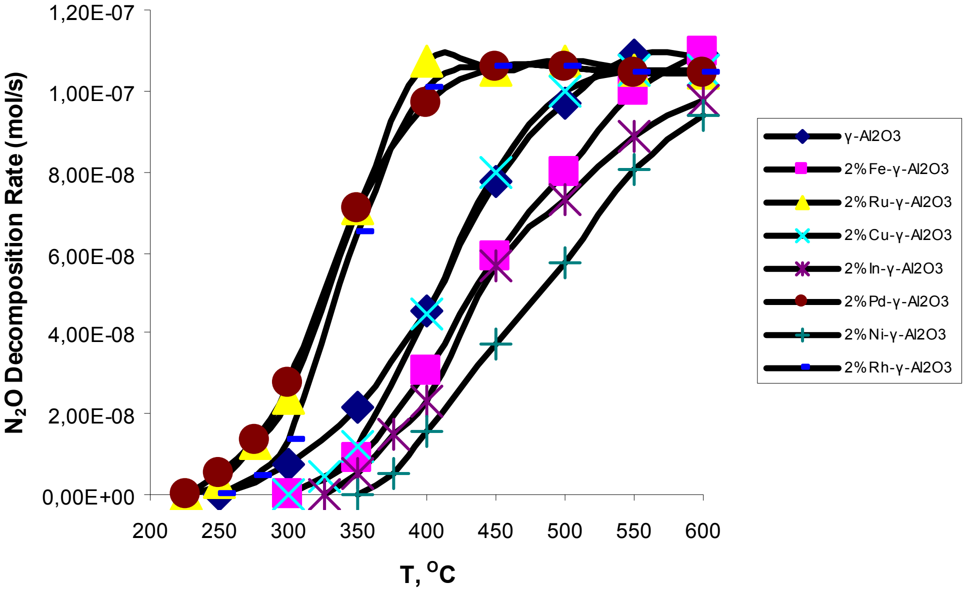

Figure 1 shows that the most active catalysts by far were Ru, Rh and Pd. Similar behaviour was observed for all gas mixtures (e.g. presence or absence of oxygen and reducing agents). It was clarified that oxygen inhibited the N_2O decomposition rate since the corresponding activity curves were shifted to higher temperatures, while the presence of a reducing agent shifted the curves to lower temperatures. C_3H_8 was more active compared to methane. Finally, and in order to get a better insight on the most active catalysts, stability tests (12 hours) and various characterization techniques (e.g. XRD, BET, ICP) were performed only in the case of Pd, Ru (noble metals) and Cu (transition metal) alumina based catalysts.

The proposed mechanism for N_2O decomposition in the presence and absence of oxygen seems to involve the following reaction paths: reversible N_2O adsorption on the catalyst surface followed by irreversible decomposition of adsorbed N_2O, with the simultaneous formation of gas-phase molecular nitrogen and an adsorbed atomic oxygen species. In the following gas-phase oxygen was then formed via reversible recombination of the adsorbed oxygen species. However in the presence of reducing agents, it was clarified that N_2O did not directly interact with propane or methane, but their contribution was targeted to the clean up of the catalyst surface from the adsorbed oxygen species, which were originated from N_2O decomposition or gas phase O_2.

P-70

CHROMIUM NITROSYL COMPLEXES IN Cr-ZSM-5: AN FTIR SPECTROSCOPIC STUDY

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Chromium-containing catalysts are widely used in industry, e.g. the famous Phillips catalysts (Cr/SiO_2) are applied to the polymerization of ethylene at relatively low pressures to produce high-density polyethylene (HDPE). Other important reactions with chromium-based catalysts are hydrogenation–dehydrogenation (e.g. production of dibutadiene from *n*-butane, methanol synthesis, WGS reaction), oxidation, isomerization, aromatization and selective catalytic reduction (SCR) of nitrogen oxides with hydrocarbons. In particular Cr-ZSM-5 has been reported to be a promising catalyst for SCR with hydrocarbons, dehydrogenation of propane to propylene, oxidative dehydrogenation of ethane to ethylene with CO_2, selective photocatalytic partial oxidation of propane to acetone, toluene disproportionation, neutralization of VOCs and chlorinated VOCs, etc.

The species formed after adsorption of NO on a Cr-ZSM-5 sample pre-subjected to different red-ox treatments have been studied by FTIR spectroscopy. Only NO+, occupying cationic positions in the zeolite, is formed on a non-reduced sample. Adsorption of NO on samples reduced by hydrogen at temperatures between 473 and 773K leads mainly to formation of different mononitrosyl (1890 and 1815 cm^{-1}) and dinitrosyl species (1910 + 1780 cm^{-1}). The latter are decomposed without producing a measurable fraction of the corresponding mononitrosyls. The dinitrosyl complexes are likely produced with the participation of Cr^{3+} cations. Some Cr^{2+} sites are created after reduction of the sample with hydrogen at 873 K or with CO at 773 K. These sites form another kind of dinitrosyl species (bands at 1902 + 1768 cm^{-1}) which are converted during evacuation to mononitrosyls (band at 1782 cm^{-1}). The assignments of the different bands are supported by ^{14}NO–^{15}NO co-adsorption experiments.

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ALKYLATION OF IMIDAZOLE ON BASIC-SEPIOLITE SUPPORTS ACTIVATED BY FOCALIZED MICROWAVE IRRADIATION: A CONTRIBUTION TO GREEN CHEMISTRY

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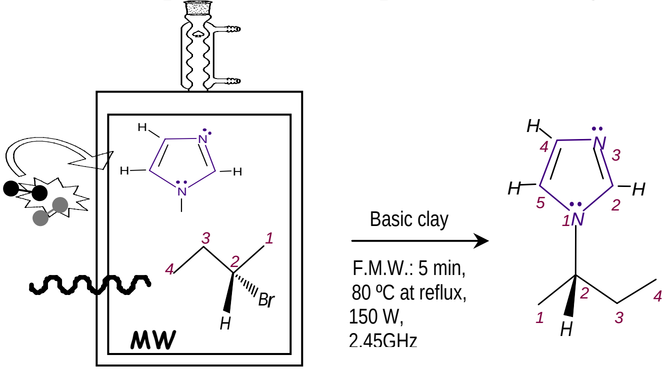
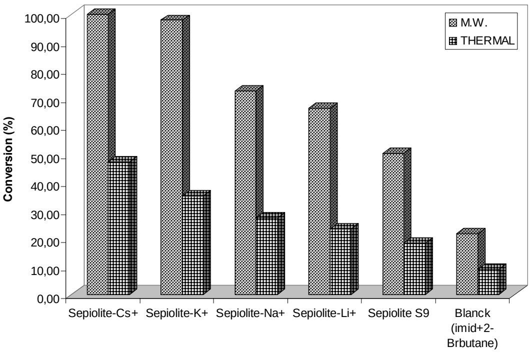
Introduction

The development of solid base catalysts for fine chemicals production is nowadays a subject of increasing interest [1,2]. Hydrotalcites [3], zeolites [4] and sepiolites [5], among others have shown interesting behavior as base catalysts. Moreover, new technologies are being employed to accelerate such catalytic reactions under mild conditions. Microwave irradiation is an alternative heating system to conventional heating methods, which affords interesting reactivity under mild conditions and very short reaction times [6,7].

Several alkaline sepiolites (doped with alkaline acetates) have been tested as basic catalysts in the alkylation of imidazole under solvent-free and wasteless conditions, by using focalized microwaves oven (FMW). The reaction in completed in few minutes, compared to hours when carried out under conventional heating, affording conversions and selectivities that can reach 100%, by careful choice of catalyst. The N-alkylated products, are key intermediates in the synthesis of pharmaceutically important anticonvulsant [8], bactericidal, fungicidal and protozoacidal compounds [9].

The experiments under FMW irradiation were carried out in a monomode microwave (PROLABO Synthewave 402) device, provided with a reflux condenser attachment, that can be used to keep temperature, time or power in a programmed mode, with accurate measurement of temperature at the surface of the sample by IR detection. Thermally activated experiments were performed using a batch reactor system under stirring.





The products were isolated by standard procedures and characterized by FT-IR and GC-MS. Previously to any experiment blank runs were carried out, which showed that the reaction in absence of the catalyst when used thermal heating was negligible.

In this work, the influence of external parameters (temperature, catalyst amount, time of reaction, type of alkali-metal promoter and power of FMW) on the microwave irradiation reaction is studied.

The Figure (% conversion of product in 5 minutes) shows the comparison between thermal effect and microwave heating during the alkylation of imidazol with the 2-bromobutane, (in both cases 80 ºC and 0,02 g of catalyst).

CATALYST	Conversion (%) of the only product formed, N-alkylated imidazole. Reaction temperature: 80ºC	
	M.W. / 5min	**THERMAL / 5min**
Sepiolite-Cs$^+$	100.00	47.24
Sepiolite-K$^+$	97.92	35.26
Sepiolite-Na$^+$	72.60	27.29
Sepiolite-Li$^+$	66.55	23.33
Sepiolite S9	50.33	18.26
Blank (imid + 2-BrButane)	21.78	8.99

From these results it can be said that the order of activity is:
Sep-Cs$^+$ > Sep-K$^+$ > Sep Na$^+$ > Sep-Li$^+$ > SepS9 > Blank (imidazol + 2-Bromobutane).

The basicity of alkali-doped sepiolites increases with the size of the alkali-metal cation, which parallels the order of activity under thermal and focalized dielectric heating activation at the studied temperature (80 ºC).

The conversion is greater for the Sepiolite-Cs$^+$ (more active catalyst), which affords the highest yields towards N-alkylated imidazole. This is mainly due to the significant increase of the number of basic sites on the surface of the catalyst. For comparative purposes, focalized microwaves activation (100% conv. with 100% sel. for 5 min, 0.02 g cat. at 80 ºC) leads to much better results than thermal activation (100% conv. with 100% sel. to 210 min, 0,02 g cat. at 80 ºC).

Conclusions

The combination of focalized dielectric heating with alkaline sepiolites as catalysts in absence of any solvent has been studied during the alkylation of imidazole with 2-bromobutane. The results demonstrate than it is possible to obtain efficient, mild and effective synthesis of N-substituted imidazole with excellent selectivity (100%). This method thus offers a practical alternative to conventional heating and traditional base catalysts. The process itself is environmentally friendly with minimal waste.

Acknowledgements

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References

[1] J. Weitkamp, M. Hunger, U. Rymsa, Microp. Mesop. Mater. 48 (2001) 255.
[2] H. Hattori, Appl. Catal. A: Gen., 222 (2001) 247.
[3] B. F. Sels, D. E. De Vos, P. A. Jacobs, Catal. Rev. 43 (2001) 443.
[4] W. F. Hölderich, G. Hetmann, Catal. Today 38 (1997) 227.
[5] A. Corma, R. M. Martín-Aranda, J. Catal. 130 (1991) 130.
[6] P. J. Kooyman, G. C. A. Luijkx, A. Arafat, H. van Bekkum, J. Mol Catal. A: Chemical 111 (1996) 167.
[7] L. Seyfried, F. Garin, G. Maire, J.M. thiébaux, G. Roussy, J. Catal. 148 (1994) 281.
[8] D.R. Hirschfield, eur. Patent. Appl EP 91 286 (1983), to Synthex.
[9] K.A.M. Walker, US Patent US 4.059.705 (1977), to Synthex.

P-72

CATALYTIC INCINERATION OF CHLORINATED VOLATILE ORGANIC COMPOUNDS

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Low temperature catalytic oxidation of CVOC to desired reaction products such as CO_2, H_2O and HCl appears to be the most promising and effective technology for the CVOC emission abatement [1]. This technology is especially preferable when emissions contain mixtures of several compounds and low concentrations of halogenated VOCs [2]. In this work the activities of 16 different Pt, Pd, and Pt/Pd catalysts supported on four different washcoats were studied with the aid of laboratory scale light-off tests. DCM (dichloromethane), PCE (tetrachloroethylene), DMF (dimethylformamide), and EGEE (oxitol) were used as model compounds alone and in mixtures. The concentration of an individual VOC was 500 ppm, thus the total concentration in the two component mixture tests were 1000 ppm. The gas hourly space velocity (GHSV) used was ~28 000 h^{-1}. The effect of additives such as water, ethanol, and ethylene were also tested. In general, Pt-catalysts showed better activity than Pd- or Pt/Pd-catalysts in DCM oxidation. On the most active catalysts, the DCM light-off was achieved at significantly lower temperatures ($T_{50} \approx 290$ °C) than the PCE ($T_{50} \approx 480$ °C) light-off. The total conversion (T_{100}) in DCM oxidation was achieved at 330°C, however, the maximum conversion of PCE remained at 98% at 700 °C. At moist conditions DMF affected the DCM conversion positively, e.g. the T_{50} of DCM was decreased by ~140 °C. Both, ethanol and EGEE decreased slightly the conversion of DCM. Any of the compounds or additives tested did not have an impact on the PCE conversion. The activity of the Pt/Pd-catalyst was not decreased during of running the CVOC experiment for ten hours. Removal of the water from the inlet feed decreased slightly the conversion of DCM, but it affected the yield of HCl significantly. It was observed that water is needed in CVOC oxidation as a hydrogen source promoting the selectivity towards HCl.

References

1. Everaert, K. & Baeyens, J. 2004. Catalytic combustion of volatile organic compounds. Journal of Hazardous Materials B109 (2004), pp. 113-139.
2. Centi G. 2001. Supported palladium catalysts in environmental catalytic technologies for gaseous emissions. Journal of Molecular Catalysis A: Chemical 173 (2001), pp. 287-312.

P-73

METHANE COMBUSTION OVER M-Ce-O BASED CATALYSTS (M = Fe, Ni)

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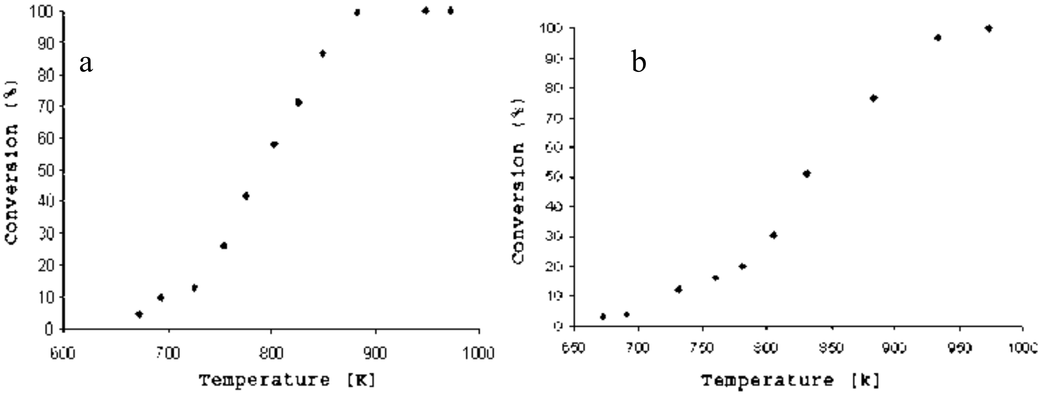
We have studied two ceria based mixed oxide catalysts in total oxidation of methane, from a mixture CH_4-air. We chose ceria-like basic oxide because of its properties generated by surface oxygen species and anionic vacancies.

The M-Ce-O catalysts (M = Fe, Ni) were prepared with an M/Ce atomic ratio equal to 20/80. The preparation method consisted in impregnation of ceria with $Fe(NO_3)_3$ and $Ni(NO_3)_2$, respectively, using a solution volume equal to the absorption capacity of ceria. A paste was obtained in each case. Pastes were dried 1 h at 80°C and 2 h at 120°C. The obtained solids were calcined under air at 200, 300, 400 and 500°C for 1 h at each temperature, and, finally, at 700°C for 4 hours. All the solids were grinded and sieved to 2-3 mm before catalytic test.

Powder X-ray diffraction (XRD) patterns of the catalysts were obtained using Cu Kα radiation. The diffraction patterns shows the formation of a homogenous mixture of two oxides, without formation of any compound. The specific surface areas of the two catalysts, CeO_2-Fe_2O_3 and CeO_2-NiO, measured by the BET method using nitrogen adsorption, are small, and their values are: 4,93 m^2/g and 4,11 m^2/g, respectively. The two catalysts were characterized by measurements of electrical conductivity and the type of semiconductor was established.

The samples were tested in the catalytic complete oxidation of methane. The catalytic activity for each catalyst was evaluated as a function of reaction temperature and gas flow rate. The two catalysts show a higher catalytic activity than other oxide catalysts in the catalytic complete oxidation of methane.

Figure shows the methane conversion as a function of reaction temperature over the two studied catalysts, CeO_2-Fe_2O_3 and CeO_2-NiO, respectively, in the catalytic complete oxidation of methane.



Influence of temperature on the conversion of methane over CeO_2-Fe_2O_3 (a) and CeO_2-NiO (b).

P-74

DEACTIVATION OF THE FCC CATALYSTS IN THE LABORATORY CAUSED BY THE CONTAMINANT HEAVY METALS OF THE FEED

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The irreversible deactivation of FCC catalysts due to deposition of heavy metals (Ni, V) from the FCC feed[1] was investigated in order to develop a more realistic laboratory procedure for examining the FCC catalyst's performance and its tolerance to metal deactivation. Two fresh and the corresponding equilibrium catalysts were the samples under study. The fresh FCC catalysts were submitted to the standard protocols of laboratory metal deactivation (Cyclic Deactivation Unit (CDU) and the Cyclic Propylene Steaming (CPS)). As expected, both CDU and CPS overemphasized the metal effects. Thus, improvement was attempted by variation of operating parameters crucial for oxidation state of poisonous metals.

Standard characterization techniques were applied on fresh and deactivated catalytic samples so as to find the correlation between changes in their properties and their catalytic activity. Unit Cell Size (UCS) of the catalyst was measured with XRD, surface areas and the micropore volume was measured with N_2 physisorption, while bulk concentrations of metals were determined with ICP. Distribution of the elements throughout the catalyst particles was additionally examined applying SEM-EDS method. Furthermore, development of a new chemical method is attempted for the determination of the oxidation state of vanadium, which is a most crucial factor leading to deleterious metal effects.

All catalytic samples were evaluated in both an SCT-MAT unit using a fixed bed configuration and an AUTOMAT unit using a fluid bed configuration in order to examine metal effects on FCC catalysts' activity and selectivity[2]. The scope is to determine the best laboratory evaluation procedure for FCC catalysts, which would retrace their different tolerance to metal deactivation.

References

1) P. O'Connor, A.C. Pouwels, Stud. Sur. Sci. Cat. 88, (B. Delmon and G.F. Froment, eds.) Elsevier, (1994) 129-144
2) D. Wallenstein, A. Haas, R.H. Harding, Appl. Catal. A 203 (2000) 23-36.

P-75

SELECTIVE HYDROGENATION OF BUTADIENE-1,3 AND ACETYLENE OVER SUPPORTED GOLD CATALYSTS

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It was recently found (Haruta *et al.*, 1993) that nanosized gold particles supported on metal oxides may reveal the significant catalytic activity for various reactions, although bulk gold metal has been long considered as a poor active catalyst. The catalytic performance of gold in oxidation processes is extensively studied. The properties of Au nanoparticles towards the catalytic reactions with participation of dihydrogen are much less known.

In this study, the selective hydrogenation of acetylene and butadiene-1,3 which is employed in industry to purify the alkene polymerization feed has been investigated over supported Au/Al_2O_3 and Au/Sibunit catalysts. The dispersion and chemical state of supported gold were characterized by XRD, TEM and XPS. The Au/Al_2O_3 catalysts exhibit the monomodal Au particle size distribution with the mean diameter in the range of 2-13 nm depending on preparation conditions. The Au/Sibunit samples contain gold mainly on the outside of support granule and show the bimodal Au particle size distribution. The gold nanoparticles (d=3-5 nm) are formed from Au(III) complexes fixed by the oxygen-containing groups on the carbon surface, whereas the larger particles (d=20-50 nm) are produced as a result of electrochemical reduction of Au(III) complexes by the surface of Sibunit during the deposition procedure.

The Au/Al_2O_3 catalysts demonstrate the significant catalytic activity for hydrogenation of acetylene and butadiene-1,3 in a flow reactor at 60-300 °C and at $H_2/C_2H_4/C_2H_2$=5/1/0.005 or H_2/C_4H_6=5/1, which increases with a decrease in the mean diameter of Au particles size, and high selectivity (~100 %) for alkenes (ethene or butenes). For hydrogenation of butadiene-1,3, the distribution of isomer products obtained with the Au catalysts differs from that obtained with Ni and Pd catalysts in the raised content of buthene-1 with respect to the content of buthenes-2. The Au/Sibunit catalysts even those contain the significant amount of Au nanoparticles show much lower activity for hydrogenation of butadiene-1,3 as compared with the Au/Al_2O_3 catalysts.

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P-76

METHANOL SYNTHESIS FROM CO_2 AND H_2 OVER THE CO-PRECIPITATED Cu/ZrO_2 AND $Cu/ZnO/ZrO_2$ CATALYSTS

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Industrial production of methanol is based on the use of synthesis gas. CO_2 is added to the feed only to adjust the stoichiometric requirements of the reactions. This process was commercialized already in 1923 and today several companies including Imperial Chemical Industries, Lurgi Corporation and Mitsubishi Gas Chemical Company offer technology solutions [1]. Despite that, mainly because of increased CO_2 emissions, methanol synthesis from CO_2 and H_2 has attracted wide interest during the last decade. Since the industrial methanol synthesis catalysts that are effective for the CO-rich feed are not so effective for the CO_2-rich feeds under the similar operation conditions [2], catalyst development work is very important part of research. The present study reports the performance of Cu/ZrO_2 catalysts precipitated with different agents and $Cu/ZnO/ZrO_2$ catalysts with different suspension aging times in the methanol synthesis from CO_2 and H_2. Catalyst samples have been characterized using different methods; ICP-OES, nitrogen physisorption and XRD. Activity measurements have been carried out in a continuous laboratory scale stirred tank reactor. The results indicate that the used precipitation agent in Cu/ZrO_2 preparation and aging time in $Cu/ZnO/ZrO_2$ preparation influenced greatly the characteristics of these catalysts as well as their activity in methanol synthesis (see Table 1).

Table 1. Summary of the results from characterization and activity tests (T = 250°C and p = 30 bar).

Catalyst samples		Metal contents				Nitrogen physisorption	Activity tests	
Sample	Precipitating agent or aging time	Cu (wt%)	Zn (wt%)	Zr (wt%)	Na (wt%)	BET (m^2/g)	CO_2 conversion (%)	Selectivity to methanol (%)
Cu/ZrO_2	Na_2CO_3	27.4	-	32.9	4.7	19	10.6	5.8
Cu/ZrO_2	NaOH	31.9	-	35.3	< 0.5	164	18.2	38.2
Cu/ZrO_2	NH_3	31.3	-	45.1	-	136	9.3	49.6
$Cu/ZnO/ZrO_2$	0.5 h	32.7	30.2	6.5	3.4	42	7.7	14.9
$Cu/ZnO/ZrO_2$	12 h	31.8	29.4	7.7	1.3	74	19.6	23.8
$Cu/ZnO/ZrO_2$	24 h	34.1	31.6	6.9	0.8	99	19.4	29.3

References

[1] S. Lee, Methanol synthesis technology, United States 1990, CRC Press, Inc. 236 p.
[2] T. Inui, H. Hara, T. Takeguchi and J.-B. Kim, Cat. Today 36 (1997) 25-32.

Acknowledgements

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THEORETICAL STUDIES OF Cu(I) SITES IN FAUJASITE: STRUCTURE, DISTRIBUTION AND INTERACTIONS WITH CO MOLECULE

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Copper exchanged zeolites attracted great attention due to their excellent catalytic properties in NOx decomposition,[1] as well as due to the catalytic activity they show in many organic reactions.

We focus on Cu(I) exchanged faujasite (FAU). Cu(I) sites alone and interacting with CO molecule have been investigated. The combined quantum mechanic/interatomic potential functions method (QM-Pot)[2] is applied. Within this approach lattice is divided into the cluster, conveniently small for advanced methods of the quantum mechanic (QM) – Density Functional Theory in our case, and the periodic environment, treated at less computationally demanding methods of the molecular mechanic (MM). Calculations are performed using the QMPOT[3] program, which couple Turbomole[4] package in QM part with the GULP[5] program in MM part. QM-Pot gives more reliable results than free cluster models with less computational effort than periodic QM calculations.

Our calculations shows that Cu(I) positions with threefold coordination (sites I' and II) are more stable then these ones with twofold coordination (site III). CO binding is the stronger the weaker is Cu(I) binding. Reliable CO frequencies can be obtained using semiempirical scaling based on the CO bond lengths.[6] CO frequencies in FAU are site specific, as well as they depend on the number of Al atoms in the nearest neighborhood of the adsorbed molecule. All results are in well agreement with experimental data.[7]

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References:

[1] Centi, G., Perathoner, S. *Appl. Catal. A* **1995**, *132*, 179
[2] Sauer, J., Sierka, M. *J. Comp. Chem.* **2000**, *21(16)*, 1470
[3] Sierka, M., Sauer, J. *J. Chem. Phys.* **2000**, *112*, 6983
[4] Ahlrichs, R., Bär, M., Häser, M., Horn, H., Kölmel, C. M. *Chem. Phys. Lett.* **1989**, *162*, 165
[5] Gale, J. D. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 629
[6] Bludský, O., Silhan, M., Nachtigallová, D., Nachtigall, P. *J. Phys. Chem. B* **2003**, 107, 10381
[7] Datka, J., Kozyra, P. *J. Mol. Struct.* **2005**, *744-747*, 991

DEVELOPMENT OF APPROACHES TO DESIGN BENZTIAZOLYLFORMAZANATES OF NICKEL (II) FOR OXIDATION-REDUCTION CATALYSIS

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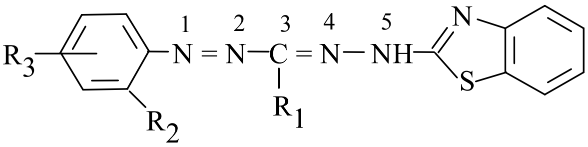
The directed synthesis of monomeric and hard-phase complexes of nickel (II) with multifunctional polynuclear ligands - benztiazolylformazanes was realized:



R_1: CH_3, C_6H_5, $CH{=}CH{-}CH_3$,
$CH(CH_3)_2$, C_4H_9;
R_2: H, OH, COOH;
R_3: H, 4-COOH, 4-SO_3H, 5-SO_3H,
5-NO_2, 4-$N(CH_3)_2$.

The high flexibility of formazan molecules and an unlimited opportunity of a variation of fine structure (control of a nature of donor atoms, character of heterocyclic fragments and substituents R_1, R_2 and R_3) provides firm coordination of metal in compound and makes possible to conduct directed synthesis of metalcomplexes with designated composition and a structure.

The carried out spectral researches of complex formation in a solution benztiazolylformazanes with nickel (II) ions have allowed to reveal participation of *o-COOH* or *o-OH* - groups in formation of complexes with composition L:Ni=1:1 involving coordinately-active oxygen at additional coordinating group in the nearest environment of nickel ion. In the case of not substituted formazanes formation of complexes is observed significantly with structure L:Ni (II) =2:1.

The immobilization of sulfurcontaining formazanates of nickel by the ionic mechanism on anionints AN-18×10 and AN-20×6 provides to retain composition and structure of metal complex coordination unit.

The catalytic activity of monomeric and hard-phase nickelcontaining complexes are investigated on an example of decomposition of hydrogen peroxide aqueous solution and liquid-phase oxidation of sodium sulfide (at 0, 20, 40 and 60^0C). The greatest activity and stability in investigated processes wasobserved for the nickel complexes with mixed nitrogen–oxygen containing coordinate unit and composition L:Ni=1:1.

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TRANSITION METAL COMPLEXES WITH SCHIFF BASE LIGANDS AS CATALYSTS FOR THE OXIDATION OF ORGANIC COMPOUNDS

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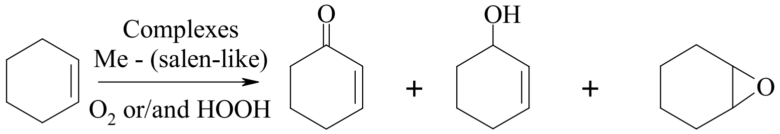
Interactions of transition metal complexes with dioxygen, hydrogen peroxide or hydroperoxides give various products with incorporated dioxygen named Reactive Oxygen Species (ROS). Understanding of dioxygen activation mechanism to produce ROS will lead to developing many fields connected with „Green Chemistry", waste products management, and biochemical reactions occurring in living organisms. Moreover, ROS can lead to replacing classical oxidants e.g. heavy metal salts and oxides.

Catalytic properties of manganese (III) complexes with different salen-like ligands in oxidations of organic compounds with hydrogen peroxide are broadly described in literature. However, iron-salen complexes were rarely applied as catalysts of above reactions.

In this work we present the results of oxidation of cyclohexene by dioxygen and hydrogen peroxide catalyzed by metal-salen-like complexes. Products of this reactions are mainly 2-cyclohexen-1-one and 2-cyclohexen-1-ole (in molar ratio 2:1). Cyclohexene oxide is formed in trace amounts.



The product profiles after 24 and 48 h reaction time indicate that 1.0 mM Fe(salen)/O_2 (0.2 atm)/1 M substrate combination is the most reactive (81 and 110 products/catalyst turnovers, respectively).

Presented results point out that metal-salen-like complexes (especially Fe^{III}(salen)) are useful as catalysts in oxidation of unsaturated hydrocarbons by dioxygen. These complexes can also catalyze oxidation of limonene by dioxygen.

OXIDATIVE DEHYDROGENATION OF PROPANE OVER BASIC OXIDES. THE ROLE OF Nd_2O_3 AS A PROMOTER

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Three catalyst samples of MgO, CaO, and SrO promoted with 5 mol% Nd_2O_3 have been studied for the oxidative dehydrogenation of propane. They were prepared from nitrate solutions of the corresponding metals by evaporation and decomposition of the nitrates to form intimate oxide mixture of neodymium and alkaline earth (AE) metals. Pure MO oxides (M=Mg, Ca or Sr) were also prepared to compare catalytic performances. The samples were calcined at 650 °C for 3h before being put in the reactor and activated at 600 °C in air flow for 1h before catalytic testing.

The specific surface areas equaled: 11 m^2/g for MgNd–O, 2.0 for CaNd–O, and 0.5 for SrNd–O samples. IR spectra showed that the starting nitrates have been decomposed to form oxides. Lattice M–O vibrations, carbonate species, OH groups, and water were detected. According to XRD analyses well crystallised MgO, CaO and SrO were formed together with solid solutions of Nd in AE oxides and of AE metals in Nd_2O_3. XPS data, before and after catalytic reaction, showed no appreciable element segregation toward the surface.

Fixed bed flow reactor, with its free volume filled with quartz particles, was used to study the reaction. The feed gas composition equaled $C_3H_8/O_2/N_2$ = 20/10/70 vol.%, catalyst weight: 30–110 mg, total gas flow: 30–90 cm^3 min^{-1}. At low conversion of propane at 500 °C the highest selectivity to propene (20%) was obtained with SrNd–O but it dropped very fast with increasing conversion. At propane conversion between 6 and 15% CaNd–O manifested the best selectivity (between 17 and 9%), whereas for MgNd–O the conversion reached the highest values (47%) but with low selectivity (about 10%). In general, the selectivity follows the surface basicity (i.e. Sr>Ca>Mg) and the conversion oppositely. In conclusion, it appears that pure AE oxides lead the high selectivity and low conversion while the Nd_2O_3 contributes to higher conversion.

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FRACTAL APPROACH TO THE ANALYSIS OF MORPHOLOGY AND PROPERTIES OF CATALYSTS

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Approach of fractal geometry has been used for the analysis of a few related problems of chemistry of surface and heterogeneous catalysis. The effects of complex morphology of catalysts, adsorbents and surfaces of electrodes on different molecular processes have been determined theoretically and experimentally. It was shown that fractal geometry can be used for finding out dependencies between geometry of the surface and functional properties of the heterogeneous catalysts.

On the basis of developed theoretical approach of fractal analysis the morphology of surface of polycrystalline gold and carbon nanotubes was studied. Carbon nanotubes were synthesized in a CVD catalytic process in atmosphere of ethylene in the presence of water vapors. We have used atomic-force microscopy (AFM), transmission electronic microscopy (TEM) and cyclic voltammetry (CV) for analysis of details of fractal structures on micro- and nanoscale level. We have developed the method for determination of roughness of surfaces based on the calculation of fractal dimension of images of AFM and TEM. The method based on CV cathode peak current dependency of scan rate was used for calculation of active surface area of the electrode as well as for determination of its fractal dimension. Application of fractal analysis in combination with these methods is the useful tool to control the state of fractal structures of catalysts and their functional properties.

EFFECT OF Ce CONTENT ON THE THERMAL BEHAVIOR OF NANOSTRUCTURED Ce-TiO$_2$ (ANATASE) OXIDES

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Introduction

Titanium dioxides are used as adsorbents, supports and catalysts for different catalytic reactions. The low thermal stability of titania with anatase structure is the main disadvantage. The present work is devoted to the study of thermal stability of Ce-doped TiO$_2$ (anatase) during thermal treatment.

Experimental

Ce doped TiO$_2$ (3-15% вес. CeO$_2$) samples were prepared by incipient wetness impregnation of TiO$_2$ (anatase) with cerium nitrate solution, followed by the air calcinations at 300-900 °C for 4 h. Samples were investigated by XRD, HREM and adsorption methods.

Results

Fig. 1 shows the sharp decrease in the specific surface area of pure TiO$_2$ while the heating temperature is increased. In Ce-doped TiO$_2$ the specific surface area remains nearly constant up to 400 °C and than decreases with growth of the heating temperature.

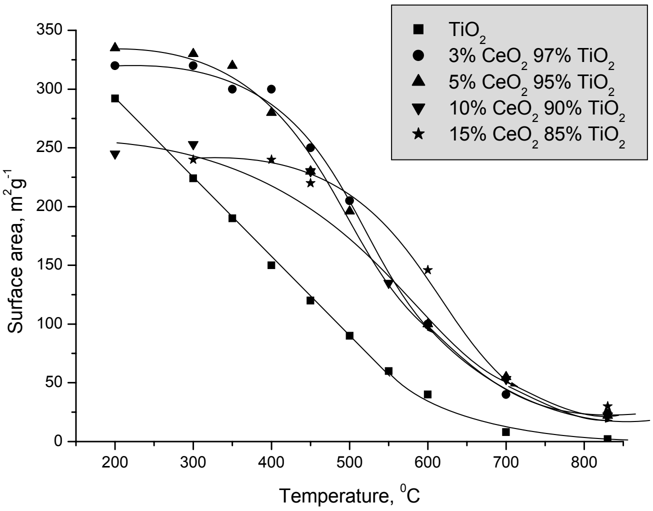

Fig.1. Effect of the heating temperature on the specific surface area of TiO$_2$ and Ce-Ti-O samples.

Noncoherent agglomeration of TiO$_2$ nanocrystals with formation of intergrain boundaries between them is observed when the calcination temperature is increased above 400 °C. Cerium ions are stabilized in the vicinity of intergrain boundaries. In the wide range of calcination temperatures the specific surface area of Ce-Ti-O samples is higher than that of pure TiO$_2$. The presence of cerium in Ce-Ti-O mixed oxides results in the stabilization of anatase structure and high specific surface area during the thermal treatment up to 900 °C.

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EFFECTS OF PREPARATION CONDITIONS ON THE CHARACTERISTICS OF CARBON-SUPPORTED PALLADIUM CATALYSTS PREPARED BY ALKALI HYDROLYSIS METHOD

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There are two main, thoroughly studied, approaches for Pd/C catalyst preparation based on the H_2PdCl_4 hydrolysis and palladium hydroxide precipitation onto a carbon surface: method (1) where an alkali is introduced directly into the H_2PdCl_4+C suspension [1], and method (2) where an alkali is gradually added into the aqueous solution of H_2PdCl_4 up to pH 5-6 followed by aging the mixture and contacting it with the support [2]. Another promising way, but unstudied till now, (method 3) means the solution of H_2PdCl_4 to be mixed with an excess of alkali followed by aging during a period of τ (0.25 – 24 h) before the contact with carbon or it is introduced directly into alkali+C suspension without aging (τ=0). At the same time, it is known that the higher pH of the catalyst precursor solution contacting with the support grain, the more palladium is located on its periphery [2]. So, it was of interest of studying the catalyst formation according to the method 3.

In this work an attempt was made to prepare a set of samples of 1%(wt)Pd/C catalysts by the method 3, with carbonaceous material Sibunit (S_{BET} = 350 m^2/g, grain size 0.09-0.18 mm) being chosen as support and Na_2CO_3 solution being used as the alkali agent at Pd/Na ratio of 1:5 - 1:21. For comparison, samples of 1%(wt)Pd/C catalyst were prepared by methods 1 and 2. Catalyst samples were washed, dried and reduced by hydrogen at 423 K. Dispersion of Pd was determined by the pulse CO chemisorption method and found to be 0.3-0.54. Catalytic activity and efficiency of the catalyst grain were estimated in liquid-phase hydrogenation of cyclohexene at 286 K, which is known as a structure-insensitive reaction.

Increasing in the aging time (τ) of H_2PdCl_4+Na_2CO_3 solution was shown to decrease Pd dispersion. While τ=0.25 h, the increase of the Pd/Na ratio from 1:5 to 1:9 gives a rise of catalyst dispersion from 0.05 to 0.30, but further increase of the Pd/Na ratio doesn't affect the dispersion of Pd/C. Comparison of the efficiencies of the catalyst grain of the Pd/C catalysts prepared by method 3 with the reference to those prepared by methods 1 and 2 indicates that the method 3 provides egg-shell distribution of Pd throughout the support grain.

1. P.A. Simonov, V.A. Likholobov. Physicochemical aspects of preparation of carbon supported noble metal catalysts, in: *Catalysis at Nanoparticle Surfaces* (A. Wieckowski, E.R. Savinova, C.G. Vayenas, eds.), 2003, Marcel Dekker, Inc., New York, 379-407.
2. P. A. Simonov, S. Yu. Troitskii and V. A. Likholobov, *Kinet. Catal.* (Russ. Ed.) **41**, 281 (2000).

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HOMOGENEOUS PYROLYSIS OF C_2-C_3 HYDROCARBONS UNDER CO_2-LASER-INDUCED HEATING

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A dehydrogenation of C_2-C_3 hydrocarbons is an important field of chemical technology's development. Reaction investigation in such situation is connected with distinguishing between homogeneous reactions of hydrocarbons in the reactor's volume and heterogeneous processes on the reactor's walls.

In order to analyze homogeneous reactions dehydrogenation of C_2-C_3 hydrocarbons was investigated under conditions of a wall-less reactor when heterogeneous processes are excluded. Reactor was 6.5 cm^3 in volume and had a design feature - the heat energy was supplied directly to the gas at atmospheric pressure using a continuous CO_2 laser with the radiation power up to 120 W at the power density up to 10^4 W/cm^2. Since ethane does not absorb radiation of the CO_2 laser, it was mixed with ethylene or propylene which are characterized by a strong absorption band at 10.6 μm. The reactor design ensured the gas flow to be bifunctional, i.e. a part of the high-dense mixture behave as a heat insulator between the quartz walls at the temperature not higher than 125 °C and the reaction zone at the temperature not higher than 1000 °C.

Conversion from C_2-C_3 hydrocarbons to ethylene in a wall-less reactor was studied theoretically and experimentally. It was designed a mathematical model of homogeneous pyrolysis of C_2-C_3 hydrocarbons mixed with ethylene or propylene. In proposed model power of adsorbed radiation is increased during reaction process with reaction product's accumulation. Hence according to this model energy catalytic process takes place in the reactor.

Compare of numerical results with experimental data shows that proposed model sufficiently describes chemical kinetics in reactor.

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MICROKINETIC MODELING AS A TOOL IN CATALYST DISCOVERY

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We propose a new approach for catalyst development that combines different scientific disciplines: experimental design, surface science, reaction kinetics and simulations with the objective of accelerating catalyst development.

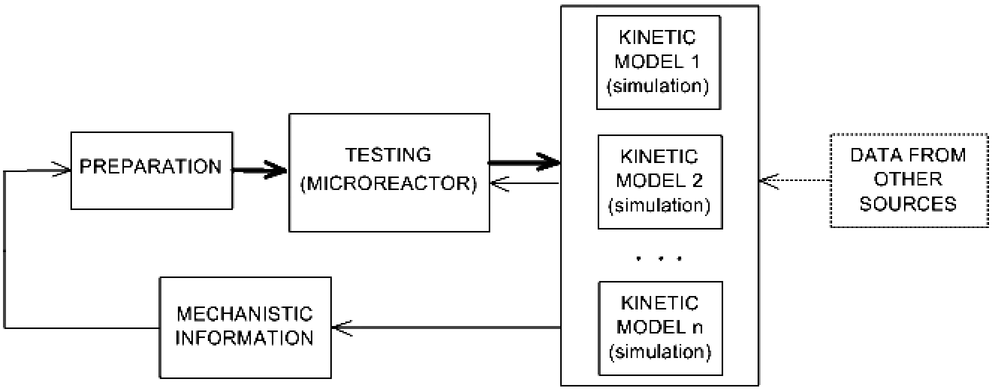

Figure 1. New approach for catalyst development

Figure 1 presents the scheme of the approach; the thicker arrows illustrate the information flow in the traditional approach. In the new approach information will flow along all the arrows: Exploration of a new catalyst starts with the proposal of a series of reaction mechanisms. Microkinetic models are derived for each mechanism [1, 2] and data from other sources such as spectroscopy, isotopic labeling and DFT calculations are incorporated. Afterwards a small library of catalysts is tested at a limited number of reaction conditions. After each measurement, all available information is analyzed, and a new measurement is proposed in order to rapidly uncover the properties of the catalyst. After several catalysts have been explored, the observed relation between catalyst composition, structure and activity is used as a source of inspiration for new preparations.

In this paper we present a study of the possibilities of using small kinetic data sets in microkinetic modeling, and studies of the required precision of temperature measurement.

References

[1] Stoltze P., Microkinetic simulation of catalytic reactions, Progress in Surface Science 65 (2000) 65-150
[2] Lynggaard H., Andreasen A., Stegelman C., Stoltze P., Analysis of simple kinetic models in heterogeneous catalysis, Progress in Surface Science 77 (2004) 71-137

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COPPER-CERIUM MIXED OXIDE CATALYSTS FOR HYDROGEN PRODUCTION

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Dimethyl ether steam reforming is one of promising method for hydrogen production. Preferential oxidation of carbon monoxide is used for conditioning of hydrogen-containing fuel for PEMFC fueling.

This report presents the results on the development and studies of cupper-cerium mixed oxide catalysts prepared by different methods for dimethyl ether steam reforming and preferential oxidation of carbon monoxide in hydrogen-rich gas mixtures. The catalyst performance was studied in a flow setup with on-line chromatographic analysis of the reaction products. The dependencies of the catalyst performance on the temperature, inlet composition and feed rate of the gas mixture have been determined. The experiments were performed at GHSW = $5000 \div 20000\ h^{-1}$ and temperature 150-400 °C for dimethyl ether steam reforming and $50 \div 200$ °C for CO preferential oxidation.

The effect of CO_2 and H_2O in the feed on the catalysts activity and selectivity was also studied. Prepared fresh and spent cupper-cerium oxide systems were characterized by means of TPR, TPO, TPD, XRD, XPS and TEM techniques. The FTIR spectroscopy *in situ* was applied for deep characterization of the functioning catalysts.

Based on the results obtained, the nature of active center, reaction mechanism and potentials of cupper-cerium oxide catalysts for practical application for hydrogen production in two-stage reactors have been discussed.

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CATALYTIC ACTIVITY OF NOBLE METALS SUPPORTED ON MESOPOROUS MATRICES

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In recent years, a growing amount of attention has been paid to noble metals-supported catalysts due to their potential applications in industrially important chemical reactions and environmental protection. However, the catalytic activity of supported Pt- and Au nanoparticles is remarkably sensitive to the nature of the matrix, as well as on the pre-treatment conditions of the sample [1,2]. Mesoporous molecular sieves of MCM-41 type are new supports for Au and Pt. Therefore, the aim of this study is the preparation of Pt/ or Au/MCM-41 and Pt/ or Au/NbMCM-41 catalysts (by the impregnation) and the characterisation of their catalytic properties in the methanol oxidation and SCR-NOx.

The state of Pt and Au in MCM-41 materials was studies by XRD, UV-VIS and FTIR with NO adsorption techniques. The results clearly indicated the presence of metallic Pt and Au on the catalysts surface already after calcination. However, contrary to Au/MCM-41, in the case of Pt/MCM-41 samples cationic form of Pt was also identified. Moreover, it was also concluded from the TEM results, that the presence of Nb in MCM-41 affects the properties of Pt-species. Higher dispersion and smaller particle size of Pt was obtained on NbMCM-41 than SiMCM-41. The interaction of Pt with Nb protects from Pt migration during heating. It is not a case of Au/NbMCM-41. The effect oxidation state of the metal and chemical composition of the matrix was took into account in the consideration of the catalytic activity in the CH_3OH oxidation and SCR-NOx by C_3H_6. At lower temperatures Pt-containing samples were more active than Au-modified ones in methanol oxidation. However, the positive effect of NbMCM-41 matrix on the conversion and selectivity to formaldehyde was clearly seen for Au-materials. The FTIR studies combined with NO and C_3H_6 coadsorption clearly indicated the effect of Nb in Pt/ or Au/MCM-41. NbO^- species present in NbMCM-41 enhance the oxidative activity of the catalyst in NO to NO_2 step during HC-SCR process. Pt-species is responsible for C_3H_6 activation, whereas metallic gold seems to be not active in SCR-NOx.

One can conclude that the catalytic activity of Pt- or Au/MCM-41 strongly depends on the nature of the matrix and the oxidation state of noble metal. Pt- or Au- supported MCM-41 seems to be attractive catalysts for the potential applications in redox processes. However, in the case of Au/MCM-41 further studies are needed to obtain high catalytic activity.

[1] I. Sobczak, M. Ziolek, M. Nowacka, Microporous Mesoporous Mat., 78 (2005) 103.
[2] G.J. Hutchings, M. Haruta, App. Catal. A: General 291 (2005) 2.

INTERACTION OF ATOMIC OXYGEN WITH THE SURFACE OF POLYCRYSTALLINE GOLD FOIL STUDIED BY XPS AND TPD

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The metals of Ib group (copper, silver) are widely used as active components of catalysts in the processes of complete and partial oxidation. Till recently gold was not used since it was believed totally inactive. However recently it was surely showed that nanosized gold particles supported on the reducible metal oxides possess high activity in many catalytic reactions. The pathways of oxidation are determined to a great extent by oxygen species, so their nature is a key factor in the understanding of the reaction mechanisms. Unfortunately the coordination and state of oxygen are not established because of certain difficulties in the application of the surface analysis methods (XPS, UPS, AES etc.) in the investigation of oxygen species on the surface of the supported gold catalysts. The investigation of the oxygen species on the gold surface can be used on the surface of massive samples (foils, single crystals, films) using atomic oxygen, produced on the hot Pt filament.

The experiments were performed using electron spectrometer equipped with XPS and TPD methods. The polycrystalline gold foil (99,99%) was used as a sample. No contaminations presence was found during the experiments. The adsorbed surface oxygen was characterized by means of XPS (Au4f and O1s spectra) and TPD, the reactivity was tested "*in situ*" using gas flow of CO, C_2H_4, H_2 by means of dynamic-XPS at different temperatures. It was found that interaction of gold surface with atomic oxygen produces two-dimensional gold oxide layer. Increasing of the time of interaction leads to formation of three-dimensional Au_2O_3. The reactivity of adsorbed oxygen in CO oxidation reaction at room temperature was found to be $\chi \approx 0{,}05$. While the reactivity towards H_2 was observed to be much lower ($\chi \approx 2*10^{-4}$). This fact is proposed to be important in the mechanism of the preferential CO oxidation in CO+H_2 mixtures.

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MECHANISM OF α-OXYGEN FORMATION AND ITS SECONDARY TRANSFORMATIONS ON FeZSM-5 SURFACE AT N_2O DECOMPOSITION. INFLUENCE ON THE SELECTIVITY OF OXIDATION REACTIONS

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It is known that decomposition of nitrous oxide (N_2O) on FeZSM-5 zeolites leads to the formation of a special form of surface oxygen (called α-oxygen), which has been shown to be anion-radical $O_\alpha^{\bullet -}$ adsorbed on iron (III) complexes stabilized in the zeolite matrix [1, 2]:

$$\mathrm{Fe^{II}(\quad)_\alpha + N_2O \longrightarrow Fe^{III}(\dot{O}^{-})_\alpha + N_2} \tag{1}$$

α-Oxygen has a very high reactivity and exhibits unique oxidation chemistry providing, in particular, selective oxidation of hydrocarbons into hydroxylated products. The most known example is direct oxidation of benzene to phenol over FeZSM-5 zeolites, which proceeds at nearly 100% selectivity and suggests a potential alternative to the three-step cumene process. Because of its remarkable features, α-oxygen is a subject of many theoretical and experimental studies, which results in some cases lead to significant discrepancies related to the formation mechanism, reactivity, and concentration measurements of $O_\alpha^{\bullet -}$.

The present work is a thorough mechanistic study of α-oxygen using isotopic, adsorption and spectroscopic techniques. We discovered that under some conditions typical especially of the experiments conducted with flow units, α-oxygen, in the absence of reductant, can interact further with N_2O, transforming successively into NO, NO_2 and NO_3 groups. These secondary transformations dramatically change the chemistry of α-oxygen and explain most contradictions accumulated in the literature, which in more detail will be discussed in our presentation.

References

1. E.V. Starokon, K.A. Dubkov, L.V. Pirutko, G.I. Panov // **Topics in Catal.**, 23 (2003) 137.
2. S. Malykhin, I. Zilberberg and G.M. Zhidomirov // **Chem. Phys. Lett.**, 414 (2005) 434.

IRON(II)- AND MANGANESE(II)-CATALYZED OXIDATION OF LIMONENE BY DIOXYGEN

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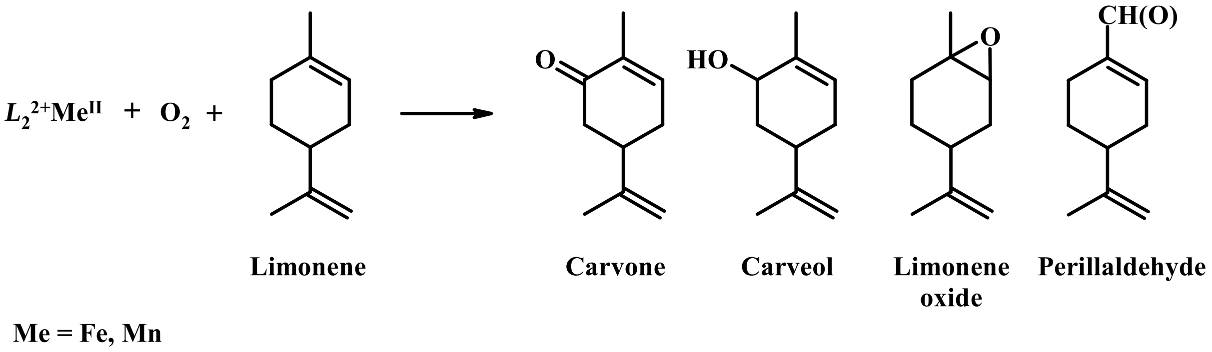
Monoterpenes are widely used in flavor and fragrance industry. Among these compounds R-(+)-limonene is the most abundant, low priced, naturally occurring product, which is suitable feedstock for production of important compounds.

We have found that labile iron(II) and manganese(II) complexes activate dioxygen for oxidation of limonene to produce carvone, carveol, limonene oxide, and perillaldehyde.



The product profiles after 24 h reaction time indicate that 1 mM $[Fe^{II}(bpy)_2^{2+}]_{solv}/O_2$ (1 atm)/2 M substrate and 1 mM $[Mn^{II}(bpy)_2^{2+}]_{solv}/O_2$(1 atm)/2 M substrate combinations are the most reactive (156 and 270 products/catalyst turnovers, respectively), whereas in the absence of the catalyst no products are formed.

Voltammetric measurements show that limonene reduces Fe(III) complexes to Fe(II) ones, which are active catalysts. This is confirmed by the fact that under argon atmosphere the use of 50 mM of catalyst and 1 M substrate gives no products in the case of $[Fe^{II}(bpy)_2^{2+}]_{solv}$, whereas in the presence of $[Fe^{III}(bpy)_2^{2+}]_{solv}$ small amounts of oxidation products were observed.

P-91

ACTIVITY AND SURFACE PROPERTIES OF MOLYBDENUM SULPHIDES-BASED CATALYSTS

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The metal-sulfur bond energy is supposed to be one of the key parameters in the desulfurization process because it determines the number of sulfur vacancies. It is reported that support can play a significant role in transformation of oxide forms to an active sulfided state.

The support may accelerate or slow down the sulfidation process. During activation, the support may react with molybdenum oxides, so their transformation into sulfides might depend on the strength of Mo-O-X bond. Moreover, the shape and orientation of MoS_2 particles may have an influence on HDS activity.

The aim of this work was to find correlation between activity of the catalyst, studied in hydrodesulfurization of thiophene and the type of support used.

Nickel-molybdenum catalysts, loading 3 and 10 wt % respectively, were prepared by a "repeated" wetness impregnation of silica, alumina, zirconia and ceria, first with aqueous solutions of ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) and next with nickel (II) nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$).

Scanning electron microscopy (SEM-EDS), temperature-programmed reduction (TPR) of oxides forms and TPR of sulfides were used for characterization of molybdenum catalyst. HDS activities of the systems were measured in a continuous flow reactor at atmospheric pressure. The catalyst samples were presulfided in situ with a stream of $10\%H_2S/H_2$ for 1 hour at 370°C before the catalytic test. The conversion of thiophene was calculated from the analysis data obtained after a two hour run.

Catalysts activity decreased in the order $NiMo/SiO_2 > NiMo/Al_2O_3 >> NiMo/ZrO > NiMo/CeO_2$. The sulfided $NiMo/SiO_2$ and $NiMo/Al_2O_3$ showed much easier reducibility than their oxide counterparts. In the case of $NiMo/ZrO_2$ and $NiMo/CeO_2$ any reduction peaks were observed in the temperature reaction range (25-370°C) during TPR oxide and sulfide forms.

The financial support of this work by the Polish Scientific Research Council (grant 4 TO9 B 057 25) is gratefully acknowledged.

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SYNTHESIS AND STUDIES OF THE CATALYTIC ACTIVITY OF THE Mn(III) – SCHIFF BASES COMPLEXES

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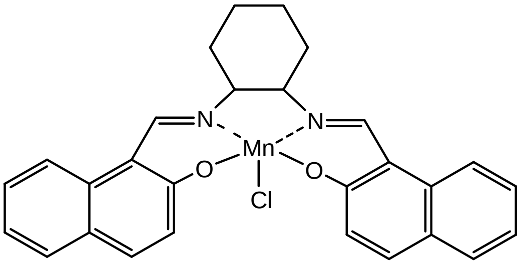
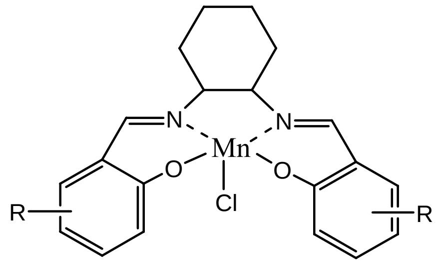
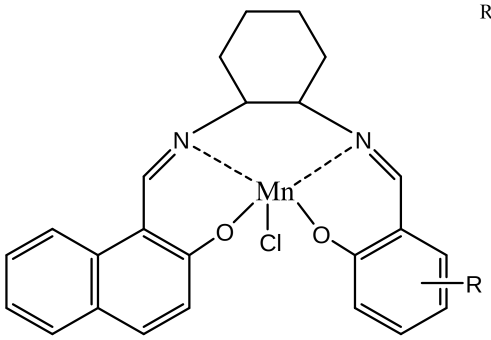
Optically active epoxides are key intermediates in organic chemistry because they can undergo reactions giving a wide variety of biologically and pharmaceutically important compounds [1]. Mn(III) – salen complexes have been reported as versatile catalysts for enantioselective epoxidation of non-functionalized alkenes [2,3].

In this communications we report on the synthesis of series of symmetric and asymmetric chiral Mn(III)–salen complexes prepared by refluxing manganese(II)-acetate and the respective Schiff bases in the presence of lithium chloride in ethanol.





R=H, 3,5-diCl, 3,5diBr



R=H, 3,5diCl, 3,5diBr,3,5diOCH$_3$

The catalytic activity of these complexes has been tested in the reaction of epoxidation of cyclohexene using hydrogen peroxide as an oxygen donor in the presence of imidazole.

References:

[1]. A.Martinez, C.Hemmert, H.Gornitzka, B.Meunier, *J.Organomet.Chem.***690**, 2005, 2163;
[2]. W.Zhang, E.N.Jacobsen, *J.Org.Chem.*, **56**, 1991, 2296;
[3]. R.Irie, K..Noda, Y.Ito, N.Matsumoto, T.Katsuki, *Ttetrahedron Assymetry*,**2**, 1991, 481;

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INFLUENCE OF INDUCTION EFFECT OF SUBSTITUENTS IN IRON PORPHYRINS ON THEIR CATALYTIC ACTIVITY IN THE OXIDATION OF CYCLOOCTANE

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Metalloporphyrins play an important role in both biocatalytic and catalytic processes. Their ability to activate dioxygen and oxidize unreactive organic substrates is a subject of great interest and intensive investigations. The use of molecular oxygen as oxygen donor in the oxidation processes is beneficial not only from economic but also ecological point of view, because dioxygen is inexpensive, eco-friendly and easily available oxidant. Catalytic properties of metalloporphyrins depend on the type of metal center, structure of macrocycle rings, the type of substituents and the type of axial ligand. By changing these elements it is possible to tune the catalytic properties to the requirements of different reactions.

In our study, we investigated the catalytic activity of iron porphyrins and their μ-oxo analogues in high pressure oxidation of cyclooctane with dioxygen. Furthermore, various substituents were introduced into the macrocyclic ring to modify the catalytic activity and stabilize the porphyrin ring against oxidation.

We prepared and characterized the following iron porphyrins with electron donating substituents: $Fe(T(p\text{-}OCH_3)PP)Cl$, Fe(TTP)Cl, FeTMPCl, Fe(TPP)Cl and electron withdrawing substituents: Fe(T(p-Cl))PP)Cl, $FeT(p\text{-}CF_3)PP)Cl$, Fe(TPFPP) and their μ-oxo iron complexes. The catalytic oxidation of cyclooctane has been carried out in a stainless steel batch reactor system at the optimum temperature of 120 °C and under the air pressure of 10 atm, with the molar ratio of cyclooctane to oxygen set at 6.5. The main products of this reaction are cyclooctanone and cyclooctanol.

All synthesized iron porphyrins and iron μ-oxo porphyrins with electron-withdrawing and electron-donating substituents are active in investigated reaction. The activity of such catalysts appears to be dependent on the character and number of substituents in the macrocyclic ligand. All simple iron porphyrins show higher catalytic activity than their iron μ-oxo porphyrin analogues. The reason for the lower efficiency in oxidation of cycloalkanes by μ-oxo iron porphyrins in comparison to simple iron porphyrins is probably connected with blocking of axial coordination positions.

The authors thank the Ministry of Science and Higher Education (grant No: 3 T09A 167 29) and Polish Catalytic Network ”Nanomaterials as catalysts for new Environmentally Friendly Processes” for financial support.

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THE USE OF OXIDATION AND SULPHURISATION OF METHANOL AS COMPLEMENTARY TEST REACTIONS

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Methanol oxidation is a reaction well adapted to characterize the redox and acidic active species on the catalyst surface [e.g. 1,2]. The most accurate characterization could be obtained for the catalysts possessing a single kind of active sites. If the supports contain species which can also play a role of catalytic active centres it is useful to apply an another additionally test reaction. A good choice for the second test reaction seems to be methanol sulphurisation, i.e. the process in which alcohol interacts with the reducing agent (H_2S), contrary to the previously described process in which methanol is in the oxidizing atmosphere. To see how this two reactions give complementary information the well characterized catalysts, iron containing mesoporous sieves, in which Fe was introduced by various methods (impregnation and chemical vapour deposition), were applied in this study.

In both catalytic reactions studied within this work methoxy species are intermediates in the formation of final products. Moreover, both reactions involve the presence of Lewis acid-base pairs. A significant role in the process plays a second reagent, i.e. oxygen or hydrogen sulfide. The first one can be a source of Lewis basic sites, when the oxygen chemisorb on the catalyst surface (on both iron and the support). As a consequence of such a phenomenon it is not possible to differentiate the role of iron centres and those originating from the matrix in oxidation process. The situation differs when one applies hydrogen sulfide as the second reagent. It is not a source of Lewis basic sites if associatively chemisorbed. Therefore, it is getting possible to observe the role of iron species playing on their own or together with those from the matrix. For this reason we could see various product distributions on iron-modified NbMCM-41 and AlMCM-41 catalysts, which are determined by the participation of active centres of the support and the nature of iron active species. The latter is conditional upon the modification procedure. In contrary to oxidation of methanol in which all catalyst used show high activity, in the sulphurisation process the wetness impregnation of NbMCM-41 and AlMCM-41 with Fe salt leads to the most effective catalysts for the formation of sulphur organic products.

References

[1] J-M. Jehng, A.M. Turek, and I.E. Wachs, Appl. Catal. A 83 (1992) 179.
[2] J.M. Tatibouet, Appl. Catal. A: General 148 (1997) 213.

P-95

NOVEL NICKEL CATALYSTS FOR NORBORNENE POLYMERIZATION

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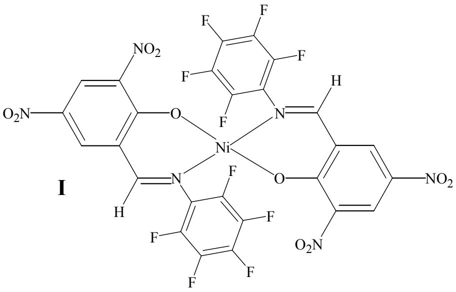
Amorphous vinyl-poly(norbornene) (PNB) is a polymer with very interesting characteristics for microelectronics application like good mechanical strength, heat resistivity and optical transparency. In the last years, different nickel catalysts have been proposed for the vinyl polymerization of norbornene (NB)[1], but a real rationalisation is still far, in fact the results have been obtained under very different reaction conditions. In this respect novel Ni(II) bis(salicylaldiminate) complexes (**I-V**), having nitro- and/or fluoro- substituents on the phenol and on the N-aryl ring were tested in the polymerization of NB to give PNB.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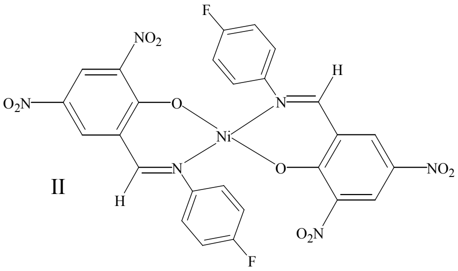
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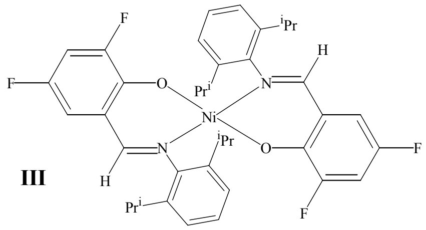
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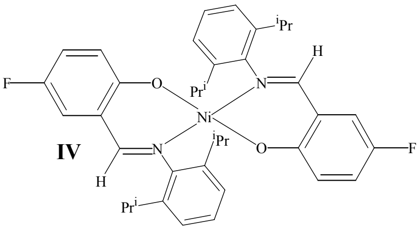
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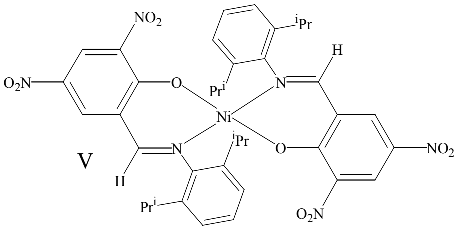
V

To attain the best catalytic results high MAO/Ni molar ratio (1000-2500) and chlorobenzene as solvent were necessary. The polymers showed high molecular weights, with a quite narrow dispersion. They were characterized by ^{1}H- and ^{13}C-NMR in order to confirm vinyl-polymerization of NB and to evidence the absence of stereoregularity. The presence of electron withdrawing nitro groups on the phenol moiety of the chelate ligand and the alkyl substituents on the N-aryl ring appeared to be necessary to maximize the catalytic activity. The system **V**/MAO was the most active (productivity up to 35,000 Kg of PNB/mol of Ni x h). On the contrary, the presence of fluoro substituents both on the phenol moiety and on the N-aryl ring appears detrimental.

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[1] Sun, W.-H.; Yang, H.; Li, Z.; Li, Y. Organometallics, 22, 3678 (2003)

HYDROTALCITES FOR A CLEAN OBTENTION OF 2-PHENYLETHANOL. EFFECT OF USING MICROWAVES DURING HYDROTALCITES PREPARATION ON THE CATALYTIC ACTIVITY

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2-phenylethanol (2-PEA), the main component of rose oil, is widely used in the perfume industry. Catalytic hydrogenation of styrene oxide to obtain selectively 2-phenylethanol is a cleaner alternative to the economical, environmental and purification problems shown by the classical industrial methods. In a previous work, high activity and high selectivity to 2-PEA were obtained when using basic Ni-MgO catalysts [1]. Hydrotalcite-like materials are lamellar hydroxy-compounds having the general formula $[M(II)_{1-x}M(III)_x(OH)_2]\ [A_{x/n}^{n-}]\cdot mH_2O$, where M(II) and M(III) are divalent and trivalent cations and A is the interlayer anion. Hydrotalcites together with the high-area mixed oxides obtained from their calcination have surface and basic properties which can be interesting for this reaction and basically depend on their composition and preparation method. The use of microwaves decreases considerably the preparation times and modifies the properties of hydrotalcites [2].

In this work, we prepared Ni/Mg/Al hydrotalcites with molar ratios 7/1/2 and 3/3/4 by the coprecipitation method. The gels were aged by conventional refluxing at 70 °C for 18 h or by microwaves at 180 °C for 2 h. Afterwards, the hydrotalcites were calcined at 350 °C and then reduced at 350 °C. All samples were characterized by common techniques. Hydrotalcites aged by microwaves showed higher cristallinity, higher surface area and higher basicity than those aged by the conventional method. The catalysts were tested in the hydrogenation of styrene oxide using 1.5 g of catalyst, 4 mmol of styrene oxide and ethanol as a solvent. All the catalysts gave high conversion (90-100%), high selectivity to 2-PEA (90-100%) and high stability with the reaction time. The most important differences were observed during catalytic lifetime studies which can be associated to the differences in basicity observed for these samples from CO_2-TPD studies.

Acknowledgements

The authors are grateful for the financial support of the Ministerio de Educación y Ciencia and FEDER funds (CTQ2005-02384/PPQ).

[1] O. Bergadà, P. Salagre, Y. Cesteros, F. Medina, J.E. Sueiras, *Applied Catalysis A: General*. **2004**, 227 125-132.
[2] G. Fetter, F. Hernández, A. M. Maubert, V. H. Lara, P. Bosch, *Porous Materials*. **1997**, *4*, 27-30.

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NANOSTRUCTURED CATALYSTS BY PLASMA TECHNOLOGY

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Investigations and author̕s considerations about plasma-chemical preparation, regeneration and activation of nanostructured catalysts in low-temperature plasma conditions (electric-arc torch, high frequency and other discharges) have been summarized in this author's review. The four main trends in the plasma-chemical preparation, regeneration and activation of catalysts are described [1,2]:

1. Plasma-chemical synthesis and activation of nanodispersed catalysts in the condensed phase;
2. Plasma-assisted deposition of catalytically active compounds and composites on various carriers;
3. Plasma-chemical regeneration of spent catalysts, and
4. Activation of catalytic processes in the plasma conditions.

The theoretical basis and advantages of plasma-chemical synthesis and regeneration of spent catalysts are discussed. And finally the investigations on plasma modification of catalysts have been reviewed as a new direction in this area.

It is pointed out that the high catalytic activity and thermal stability of plasma-chemical prepared, modified and regenerated nanostructured catalysts make them a potential competitor to their industrial analogies.

References

1. Vissokov, G.P., Plasma nanotechnologies – nanopowders – preparation, properties and applications, Sofia, UMG "St. Iv. Rilski" Press, 2005, p. 303.
2. Vissokov, G.P., P.S. Pirgov, Nanodispersed powders – plasma-chemical synthesis, properties and applications, Sofia, Poliprint, 1998, p. 395.

ACTIVE AND STABLE $Cu_xCe_{0.7-x}Zr_{0.1}Y_{0.2}$ SYSTEMS PROMOTED BY Cr AND Al PREPARED VIA UREA-NITRATE COMBUSTION METHOD FOR STEAM REFORMING OF METHANOL

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Steam reforming of methanol (SRM) is a promising route to produce hydrogen for small solid polymer fuel cells (SPFS) which can be an attractive power source for on-board or portable devices. Present-day reforming technologies require a CO clean-up step to the level not exceeding a few ppm prior to the fuel cell, since CO poisons a Pt electrode in SPFS [1].

Widely used catalysts for generating hydrogen from methanol are copper-based, such as Cu-ZnO-(Al_2O_3). Recently, the catalysts based on Cu-CeO_2 were found to be more active for SRM than various Cu-Zn-Al-oxide catalysts whose major shortcomings are the low thermal and long-term stability especially at temperatures up to 300°C [2].

The objective of the present work is to design active and selective catalysts for SRM based on $Cu_xCe_{0.7-x}Zr_{0.1}Y_{0.2}$ (CCZY) promoted by Al_2O_3 (CCZYA) and Cr (CCZYA+Cr). To synthesize catalysts the urea-nitrate combustion method was used [3]. Urea $CO(NH_2)_2$ was added to a mixed solution of Cu, Ce, Zr, Y and Cr nirtates in the appropriate molar ratios. Al_2O_3 powder (10-40 w.%) was added to the mixed solution with urea and then it was steamed until a gel formation followed by calcination in air at 400°C. Catalysts characteristics were studied by XRD, IR spectroscopy, Differential Dissolution (DD) and H_2-TPR.

According to XRD for CCZY samples the solid solutions of fluorite structure are already formed after calcination at 400°C. CuO phase presents in all CCZY samples. According to XRD, IR and DD the phase composition of CCZYA and CCZYA+Cr samples is presented as a solid solution of fluorite type, highly dispersed $YCuO_x$, Al_2O_3 and Cr_2O_3.

The specific surface area (SSA) of CCZY samples are in range of 6-33 m^2/g. For CCZYA and CCZYA+Cr samples SSA significantly increases (up to 170 m^2/g).

The methanol conversion over CCZY increases with the copper content for all temperatures and reach 82% for $x_{Cu}=0.2$ at 350°C. For all samples CO_2 selectivity is 100% at 250-300°C and decreases to 98-99% at 350°C. For CCZYA and CCZYA+Cr catalysts methanol conversion attains 98-100% at 350ºC, but CO_2 selectivities are 68-95%. Investigation of the stability of the catalysts revealed that CCZYA and CCZYA+Cr are much more stable than CCZY in SRM at 350°C.

This work is supported by INTAS № 05-1000005-7663 project.

1. D. L. Trimm and Z. I. Onsan, Cat. Rev., 43 (2001) 31.
2. Y. Liu, T. Hayakawa, K. Suzuki, S. Hamakawa, et.al, Appl. Cat. A 223 (2002) 137.
3. J. Papavasiliou, G. Avgouropoulos, T. Ionnides, Cat. Commun. 5(2004) 231.

P-99

CO OXIDATION ON CARBON SUPPORTED COBALT CATALYSTS IN HYDROGEN-RICH MIXTURES

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The ability to oxidize CO at low temperatures is important in many applications. The use of a low temperature active catalyst can lower the emissions during a cold-start of a car, and VOC in exhaust gases from stationary sources might be treated without the need of preheating the gas. Proton-exchange membrane (PEM) cells are particularly attractive for small-scale and automotive applications, but they suffer from one major disadvantage: CO contamination in the hydrogen feed poisons the metal electrodes, and concentrations below 10 ppm are required for steady-state operation. In this work cobalt oxide supported on carbon surface was chosen as a model catalyst for a highly active CO oxidation catalyst even in the presence of a lot of hydrogen.

In our investigation carbon-supported cobalt oxide catalysts were tested in low temperature CO oxidation and CO oxidation in excess of hydrogen.

The samples were prepared by wet impregnation of activated carbon KAU with $Co(NO_3)_2$ aqueous solution or $Co(acac)_3$ in acetonitrile medium, then dried at 110 °C and calcinated in Ar at 450 °C. After that samples were reduced in H_2 at 350-600 °C or oxidized in air at 250 °C. Nominal Co loading was 1-5 wt%.

The specific surface area of samples were determined by thermal desorption of argon. The prepared catalysts were characterized also by XPS and AFM methods. The catalysts were tested for the CO oxidation using the following feed mixtures: 1%CO, 2%O, and balance He and 1% CO, 2% O, 50% H_2, and balance He, respectively. In both cases the total flow rate was 30 mL/min.

Investigation of a cobalt nanoclusters structure on the carbon surface show that for samples synthesized from $Co(acac)_3$ the formation of nanodispersed oxide particles with the primary sizes of 60-120 nm is characteristic, while for the samples synthesized from $Co(NO_3)_2$ they are much larger. Introduction of cobalt oxide on activated carbon less influences on its porous structure.

The total CO conversion is decreased significantly by decreasing cobalt amount on the active carbon surface. It was determined the strong influence of activation catalysts conditions on their activity in CO oxidation: both pretreatments (reduction and oxidation) lead to increasing of catalytic activity. The temperature of complete CO oxidation on non-treated samples is 120-170 °C higher in comparison with pretreated catalysts.

Introduction in reaction mixture of hydrogen (up to 50%) less influences on CO conversion and selectivity of its oxidation. Oxidation of carbon support is suppressed in reducing atmosphere and stable work of the best catalyst (5%Co/C) over the 10 h without loss its activity was observed.

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NICKEL-CATALYZED ARYLTHIOLS ADDITION TO ALKYNES: THE MECHANISM OF C–S AND C–C BOND FORMATION

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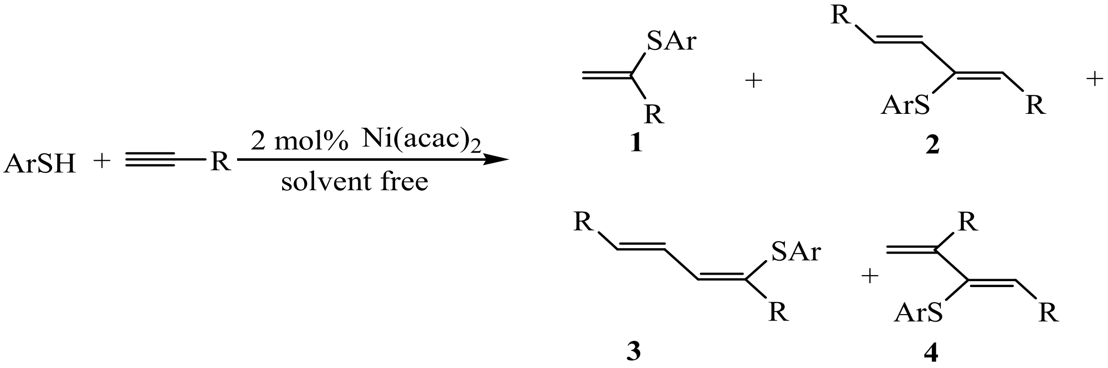
Recently we have shown that nickel complexes are selective and efficient catalysts for addition of arylthiols to alkynes [1, 2]. Under optimized conditions vinylsulfides (**1**) were formed with good yields 50-79% [2].



Scheme 1

The yields of **1** and **2-4** appeared to depend on ArSH:alkyne ratio. With 2:1 ratio of PhSH and alkyne vinylsulphide (**1**) and dienes (**2-4**) were formed in 50-67% and 33-50% yields, respectively. Using equimolar ratio of ArSH and alkyne lead to the formation of dienes (**2-4**) as major products (60%). The structures of **2-4** were determined with 2D NMR COSY and NOESY experiments. We have found that slow addition of alkyne to the reaction mixture allows to suppress the dienes formation, thus increasing the yield of **1**. The scope of the reaction and results of mechanistic investigations will be presented and discussed.

Acknowledgements: The work was supported by the Russian Foundation for Basic Research (Grants № 06-03-32762 and 04-03-32501).

References

1. V.P. Ananikov, D.A. Malyshev, I.P. Beletskaya, G.G. Aleksandrov, I.L. Eremenko, *Adv. Synth. Catal.*, **2005**, 347, 1993.
2. V.P. Ananikov, N.V. Orlov, I.P. Beletskaya, *Organometallics*, **2006**, *25*, 1970

P-101

MRI STUDY OF INTERACTION BETWEEN CHEMICAL WAVES AND REAGENTS TRANSPORT

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Propagating reaction fronts nowadays are well-known phenomena of non-linear dynamics, which arises from complex interaction of an autocatalytic reaction with diffusive instabilities. It is interesting, that chemotaxis, morphologies of growing bacteria colonies, heart beats, excitation nerve impulses and many other instances in living nature are also examples of chemical waves. On the other hand, interface motion and front propagation in fluids occur in many different areas of interest to science and technology.

The main goal of the present work is to investigate the simplest chemical systems, which demonstrate wave activity in respect of advection influence on a chemical wave in the packed-bed reactor. As conventional optical imaging techniques are unable to penetrate the interior of the packed bed, NMR imaging techniques were used.

In our investigations, two wave active chemical systems were examined. Namely, one is Co^{2+} to Co^{3+} hydrogen peroxide oxidation reaction [1], and another is Fe^{2+} to Fe^{3+} nitric acid oxidation reaction [2]. For the Co-system, because of oxygen gassing during the reaction, only qualitative data were acquired. For the Fe-system quantitative representation was obtained, that is dimensionless front velocity dependence vs dimensionless fluid velocity. Also, it was shown that, contrary to BZ [3] no stationary concentration patterns evolve in Fe-system.

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References:

[1] X. Xe, K. Kustin, I. Nagypal, G. Paintler. – Inorg. Chem., 33, 2077–2078 (1994).
[2] J. A. Pojman, I. P. Nagy, I. Nagypal, I. R. Epstein. – J. Phys. Chem., 95, 1306–1311 (1991).
[3] M. Kaern, M. Menzinger. – J. Phys. Chem. B, 106, 3751-3758 (2002).

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PHYSICAL-CHEMICAL STUDIES OF $Ce_{0.8}Zr_{0.2}O_2$ MIXED OXIDE AND $Pt/Ce_{0.8}Zr_{0.2}O_2$ AND $Pd/Ce_{0.8}Zr_{0.2}O_2$ CATALYSTS FOR AUTOMOTIVE EXHAUST PURIFICATION

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Mixed cerium-zirconium oxides have found a wide use as oxygen storage materials in preparation of three-way catalysts for purification of harmful automotive exhaust gases. In this work, we have studied the effect of a high-temperature treatment on physical-chemical characteristics of $Ce_{0.8}Zr_{0.2}O_2$ mixed oxide and $Pt/Ce_{0.8}Zr_{0.2}O_2$ and $Pd/Ce_{0.8}Zr_{0.2}O_2$ catalysts using X-ray Photoelectron Spectroscopy (XPS), X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and other methods.

Based on XRD and TEM data, two types of particles in $Ce_{0.8}Zr_{0.2}O_2$ oxide differing in morphology and chemical composition are identified. Well-crystallized particles of the first type are 20 nm in average size; they are characterized by relatively low content of Zr. Particles of the second type are highly dispersed (~ 4 nm) and contain much of Zr. The two-phase composition of the mixed oxide is responsible for a significant enrichment of its surface with Zr that is revealed by XPS. Calcination of mixed oxide in air at 1000 °C results in formation of a cubic fluorite-like phase of a CeO_2-ZrO_2 solid solution with more or less homogeneous Zr distribution and a monoclinic ZrO_2 phase.

In $Pt/Ce_{0.2}Zr_{0.8}O_2$ catalyst, particles of supported metallic platinum are very small in size (~ 1.5 nm). Platinum has been found to be predominantly located on the surface of highly dispersed support particles enriched with Zr. Under calcination in air, platinum particles grow in size up to ~ 2.5 nm. $Pd/Ce_{0.8}Zr_{0.2}O_2$ catalyst contains palladium in an oxidized form, both in the initial state and after calcination in air.

The obtained physical-chemical characteristics are used for interpretation of results of temperature-programmed reduction of $Ce_{0.8}Zr_{0.2}O_2$ and supported Pt and Pd catalysts in hydrogen. The properties of the materials studied are discussed in the light of their practical application for formulation of catalysts for automotive exhaust purification.

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SURFACE CHARACTERIZATIONS OF Co-Pb DOPED SBA-15 MESOPOROUS CATALYSTS

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Mesoporous materials with ordered arrays of uniform nanochannels are special type of nanomaterials which have important applications in a wide range of fields such as catalysis, adsorption and separation. Pore size distribution, high surface area and pore volume makes periodic mesoporous silicas to be promising supports for metal and oxide catalysts. Highly ordered hexagonal mesochannels, larger pores, thicker walls and higher thermal stability when compared with other mesoporous silicas make SBA-15 a promising catalyst support.

In the present study, SBA-15 samples are evolved by the incorporation of Co and/or Pb at different weight loadings via using direct synthesis method. The characterization of the synthesized samples was executed by powder X-ray diffraction, N_2 adsorption isotherms and TEM images. The surface area of pure SBA-15 mesoporous structure is observed to be slowly diminishing by doping metal oxides into the structure. In the large angle XRD pattern, no characteristic peaks of metal oxide are observed by the loading of 5, 10, 15 wt %Pb into SBA-15 structure, which indicates that metal particles are well dispersed in the SiO_2 structure. However, 20 wt% Pb loaded SBA-15 showed more appreciable characteristic peaks, indicating small quantity of crystallites of metal oxide exist on the surface of silica. The incorporation of high amount of cobalt and lead oxides to SBA-15 resulted in the long range order according to the low angle XRD patterns. TEM images confirmed the hexagonal structure of pure SBA-15 and 1-D channel structure in hexagonal type was observed. Besides, when SBA-15 structures were overloaded with Co, Co was observed to be extending outside the structure. Studies regarding the performance tests of the materials as methane partial oxidation catalyst for hydrogen generation are still in research. Furthermore, characterizations of the samples regarding ^1H NMR and oxygen adsorption/desorption will be carried out.

MECHANICAL-CHEMICAL ACTIVATION OF Ni(Co)-Mo/γ-Al_2O_3 CATALYSTS FOR HYDRODESULFURIZATION

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The continuous deterioration of the quality of the extracted oil and the high environment requirements for reduction of the SO_x emissions impose the development of more efficient catalysts for hydrodesulfurization (HDS). The mechanical-chemical activation (MCA) is a comparatively new method for modification of the catalysts structure, the goal of which is to increase the catalytic activity and selectivity. In our recent investigation [1], it was established that the MCA of Ni(Co)-Mo/γ-Al_2O_3 catalysts for HDS for 7 hours promoted considerably the catalytic activity.

The aim of the present study is to carry out a detail research of the changes in the structure, phase composition, catalytic activity and selectivity of Ni(Co)-Mo/γ-Al_2O_3 catalysts after different MCA times, as well as to establish relationship between catalytic properties and the duration of the activation.

MCA of the catalysts has been carried out for intervals of 15, 30, 45 and 60 min in a "Fritish-Pulverizate-7" high-energy planet-ball-mill. As a model reaction for the determination of the activity and selectivity of the initial and activated samples is used the reaction of HDS of thiophene at atmospheric pressure. The initial and treated samples have been characterized by means of X-ray diffraction, X-ray photoelectron spectroscopy and Temperature-programmed reduction. The specific surface area has been determined by using BET method.

It is established that samples prepared with MCA for 15 min. exhibit higher HDS activity than non-treated catalysts. With the increase of the MCA time, the activity of the catalysts increases, as samples prepared by MCA treatment for 30 min exhibit maximum HDS activity for the entire investigated temperature interval. The MCA treatment of the samples caused partial amorphization of the active catalyst components deposited on the support, decrease of the average particle size and destruction of the crystal structure of MoO_3 and $Al_2(MoO_4)_3$ phases. The increase of the time of MCA treatment enhances these effects. The higher HDS activity of the mechano-chemically activated catalysts most probably is related to the increase of the number of active sites of the high-dispersed molybdate structures.

References: [1] S.Andonova, Ch. Vladov, B. Kunev, I. Mitov, G. Tyuliev, J.L.G. Fierro, S. Damyanova and L. Petrov, *Applied Catalysis A: General*, 298 (2006) 94-102.

P-105

BONDING CONFIGURATIONS OF ADSORBED 1,3-CYCLOHEXADIENE ON Si(100)-(2x1)

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The adsorption and the thermal-induced dissociation of 1,3-cyclohexadiene on a Si(100)-(2×1) reconstructed surface was studied experimentally by means of high-resolution electron energy loss spectroscopy and theoretically using density functional theory. At low temperature of 90 K the hydrocarbon was found to adsorb molecularly. Between 400 K and 700 K a significant desorption of C_6H_6 species was observed. As a result of the cyclohexadiene decomposition a well-ordered monohydride layer on Si(100)-(2×1) can be prepared. Theoretically, the surface reconstruction was described by means of periodic slab-model, whereas 1,3-cyclohexadiene adsorption was studied using cluster approach, cutting appropriate cluster structures from the optimized Si(001)-(2×1) slab. The vibrational frequencies of several possible bonding geometries of the adsorbate were calculated and compared with the experimental results. This comparison between theoretical and experimental vibrational spectra allowed to distinguish the most probable adsorption structures of 1,3-cyclohexadiene on Si(100)-(2×1).

COPPER IONS STABILIZED IN INORGANIC MATRICES FOR CYCLOHEXANE OXIDATION BY HYDROGEN PEROXIDE

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Copper oxidation chemistry is well known to be a base of numerous biological processes. Activation of oxygen on Cu protein complexes produces the active intermediates with $Cu^{II}–O_2^-$, $Cu^{II}–O/Cu^{III}=O$, $Cu^{II}–OOH$ fragments. The biological processes have been simulated by means of a number of homogeneous and zeolite incorporated Cu complexes catalyzing hydrocarbon oxidations by H_2O_2. The necessary components of the catalytic systems are organic ligands which play an important role in oxygen and electron transfer, but unfortunately, are subjected to oxidative degeneration under reaction conditions. To gain oxidative resistance, the Cu systems should not contain any organic components.

In the present study inorganic zirconium phosphate (ZF) and glass fiber (GF) matrices were applied to create the effect of ligand surrounding for cooper ions. Catalysts were differing by following parameters: (1) the value of copper content varied from 0,07 wt.% for GF to 3-9 wt.% for ZF; (2) difference between surface area also varied in two orders – 1,2 m^2/g for GF and ~ 200 m^2/g for ZF; (3) active form of copper ions in ZF were oxidized state of metal Cu(II), but in the case of GF active form comprised Cu(I)–Cu(0) species or small copper oxygen aggregates, state of copper ions varied from 0 to +1.

We compared catalytic activity of 2 inorganic matrices with incorporated copper ions in cyclohexane oxidation by hydrogen peroxide. Over a Cu-ZF decomposition of H_2O_2 passed mainly by catalytic way. We have got common pattern in the decomposition of H_2O_2 over a Cu/GF; based on these results we supposed the branching-chain mechanism. Decomposition rate of H_2O_2 increased with the rise of the reaction temperature and copper loading. In the presence of organic substrate (cyclohexane) at the same time occurred its oxidation to the main products – cyclohexanol and cyclohexanon. We studied basic factors which affected on oxidation rate of cyhlohexane. Accumulation of products correlated with decomposition of hydrogen peroxide; hydroxyl radicals were the active intermediates. Oxygen along with H_2O_2 takes part in a catalytic cycle of oxidation of cyclohexane, as a result effectiveness of the H_2O_2 using increases by one order. In spite of negligible amount of copper content in Cu/GF, this type of catalyst showed much higher activity in the catalytic oxidation of cyclohexane.

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REACTIVITY OF VANADIUM OXIDE-BASED CATALYSTS IN PROPANE OXIDATION: A COMBINATION OF ODH, PARTIAL OXIDATION AND WGS

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The oxidation of propane over V_2O_5 and supported vanadium oxide under conditions which are usually employed for the oxidehydrogenation (ODH) of alkanes (i.e., hydrocarbon-rich conditions), indeed included several reactions which contributed to the hydrocarbon conversion. Besides ODH and oxidative fragmentation to oxygenates, catalytic dehydrogenation and formation of coke precursors became relevant under conditions of total oxygen consumption. Moreover, in the case of unsupported vanadium oxide, the formation of H_2 occurred by combination of propane oxidation to CO_x and H_2O, with the WGS reaction occurring in the anaerobic section of the reactor, to generate CO_2 and H_2. The latter reaction was catalyzed by reduced vanadium oxide, which developed in the fraction of the reactor that operated in the absence of oxygen. When instead vanadium oxide was supported over silica or over alumina, the catalyst was not able to promote the WGS, and the amount of H_2 produced was lower.

USING OF Zr-CONTAINING ZEOLITES AS PERSPECTIVE CATALYST OF THE JOINT METHANOL AND ALKANES C_3-C_4 CONVERSION TO LOWER OLEFINS

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The process of the joint conversion of methanol and low–molecular hydrocarbons is a new perspective method of obtaining olefins and aromatic compounds. When using non-modified HZSM-5 the selectivity to olefins formation did not exceed 20% and to aromatic compounds - 18%. The purpose of this work is to study the possibilities of applying Zr as a promoting additive to the initial zeolite.

Zr - containing zeolites were prepared in two ways: by ion exchange and a mechanical mixing. Zr-modified catalysts reveal high catalytic activity for olefins production. The maximum selectivity to olefins was observed for 5%ZrO_2/ZSM-5 prepared by the mechanical mixing method. The acid features to the surfaces of the examined samples were determined by the IR spectroscopy of absorbed CO.

The modification of H/ZSM-5 leads to the reduction of the concentration of B centers at the expanse of partial exchange of hydrogen in cation sites of zeolite by the modifier ions. The injection of zirconium by both methods promotes change of the Lewis centers nature and increasing of their concentrations. In particular, modification by mechanic mixing leads to formation of rather intensive absorption band connected with zirconium oxide which can be the carrier of Lewis acidity.

Thus, high dehydration ability of 5%ZrO_2/ZSM-5 can be connected with sharp increase in concentration of Lewis acid centers.

P-109

COPPER AND IRON PILLARED CLAYS FOR THE WHPCO OF WASTEWATERS FROM OLIVE OIL MILLING PRODUCTION

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Recently, there is a growing attention to the problem of organic effluents reduction in waste waters using catalytic treatments [1], in particular using hydrogen peroxide as oxidant to achieve a high conversion of pollutants. This method, if compared with the wet air catalytic oxidation, avoids the use of costly reactors, can be selective towards the conversion of specific substrates and is easy manageable. Organic pollutants contained in waste waters, if treated with H_2O_2 in the precence of Cu or Fe salts, are degraded mostly to CO_2 and H_2O with a Fenton mechanism, being the active oxidizing species the OH· radicals, generated on the transition metal cation. Various catalysts based on iron or copper are active as heterogeneous Fenton-type catalysts, but the majority of them show significant leaching of the active metal. We will show that it is possible to insert efficiently not only iron but also copper in the pillars of the clays up to an amount of about 2% wt. The properties of copper-based pillared clays (Cu-PILC) have been studied and compared with those of the analogous iron-based clays (Fe-PILC) in the wet hydrogen peroxide catalytic oxidation (WHPCO) with model phenolic compounds (p-coumaric and p-hydroxybenzoic acids) and real olive oil milling wastewater (OMW). The screening tests of the prepared catalysts are carried out in a lab scale reactor (batch type stirred reactor) in the 60-90°C range and at atmospheric pressure. Results will be presented both in the conversion of (i) model compounds (p-cumaric and p-hydroxybenzoic acid), and (ii) real waste water stream from olive oil milling. Both catalysts show no leaching of the transition metal even if the performances of copper pillared clays are better than those of the analogous Fe-based pillared-clays. In particular, Cu-PILC shows lower formation of oxalic acid (main reaction recalcitrant intermediate) compared to Fe-PILC. The absence of leaching and high catalytic activity in the conversion of model compounds and TOC abatement of real samples show that the iron and copper pillared clays are interesting and promising catalysts for the oxidative degradation of phytotoxic organic compounds present in olive oil mills waste water.

References

1) G. Centi, S. Perathoner, in *Catalysis*, J.Spivey Ed., The Royal Society of Chemistry, 18-(2004) 46
2) J.Barrault, M.Abdellaoui, C.Bouchoule, A.Majeste, J.M. Tatibouet, A. Louloudi, N. Papayannakos, N.H. Gangas, *Applied Catalysis B: Environmental* 27 (2000) L225-L230)

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MICROCALORIMETRIC CHARACTERISATION OF Pt-Sn DIRECT ETHANOL FUEL CELL CATALYSTS

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In this study microcalorimetric measurements of carbon monoxide, hydrogen, oxygen, and ethanol were performed on 5%Pt/γ-Al_2O_3. The catalysts were prepared by incipient wetness impregnation of $PtCl_2(NH_3)\cdot 2H_2O$ and $SnCl_2\cdot 2H_2O$ salts. Microcalorimetric measurements were performed at 323 K by using a Tian-Calvet type heat flow calorimeter (Seteram C-80) connected to a gas handling system and a volumetric adsorption apparatus employing Baratron capacitance manometers in the range of 10^{-4}-10 Torr for precise pressure measurement. The amount of Sn was adjusted to obtain Pt:Sn atomic ratios varying between 1:0 to 15:1. The initial heats of adsorption, saturation coverages and the saturation coverages of the defect like sites are presented in Table 1.

Table 1

The microcalorimetric results of carbon monoxide, hydrogen, oxygen, and ethanol on Al_2O_3 supported Pt-Sn bimetallic catalysts

Catalyst	Initial Heat of Adsorption (kJ/mole)				Saturation Coverage (μmol/g cat.)			Edge and Corner Sites Saturation Coverage (μmol/g cat)			
Pt: Sn atomic ratio	H_2	CO	O_2	EtOH	H_2	CO	O_2	H_2	CO	O_2	EtOH
1:0	101	172	N/A	N/A	276	127	N/A	18	11	N/A	N/A
9:1 (A)	74	142	191	263	27	19	7.44	13	8	7.4	18
9:1 (B)	105	113	136	238	79	22	4.70	23	9	4.7	15
6:1 (A)	107	178	184	172	9	8	2.60	6	8	2.6	13
15:1 (A)	-	-	-	195	-	-	-	-	-		19

(A) sequential impregnated
(B) co-impregnated

Initial heats of adsorption were influenced in the presence of tin as it can be seen from the Table 1. 5% Pt-Sn (9:1) catalysts were prepared using two different impregnation techniques. By the addition of the tin, low and intermediate heats were not observed and there is sharp decrease indicating the blockage of the adsorption sites with low and intermediate heats with Sn. Experiments are in progress with Vulcan supported bimetallic catalysts.

P-111

ACTIVITY AND STRUCTURE PREDICTIONS ON MONO- AND BI-METALLIC CATAYSTS

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The purpose of this study is to simulate Pt–IB (IB=Ag, Au, Cu) and Pt-Pd bimetallic catalysts with Monte Carlo method for 201, 586, 1289, and 2406 atom containing clusters in the temperature range between 298–1000 K. The simulations were based on a coordination-dependent potential model in which binary interaction parameters were used. The binary interaction parameters were determined from the available thermodynamic data and classical thermodynamics mixing rules. The equilibrium structure of the clusters was dictated as a perfect cubo-octohedral shape. In the first part of this study, Pt–IB bimetallics were modelled in order to test the Monte Carlo program against the previously published work. In the second part of the study, the surface composition of Pt-Pd bimetallic catalysts as a function of temperature and cluster size were estimated in order to offer further insight to the catalytic activity for CO oxidation reaction. It was found that at low temperatures Pd segregation took place on the catalyst. The Monte Carlo predictions were in good agreement with the published experimental data on the surface compositions.

P-112

HIGH SELECTIVE METHOD OF VINYLARENES LINEAR DIMERS PREPARING ON ZEOLITES

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The linear dimers of vinylarenes, such as styrene and α-methylstyrene, are known to be practically important oil-producing compounds. Their hydrogenated derivatives are of interest as a base for synthetic oil lubricants, a high-grade plastificators, growth regulators of polymer chains and heat-bearers.

The present paper is devoted to development of a high effective and selective method for preparing vinylarene linear dimers in the presence of active and stable zeolite catalytic systems.

Catalytic properties of different structural type zeolites (X, Y, BEA, ZSM-5, ZSM-12) in dimerization of vinylarenes were studied.

The products obtained in the presence of all investigating zeolites consist of linear and cyclic dimers and trimers.

Large-pore zeolites Y, BEA and ZSM-12 are found to be most effective catalysts of α-methylstyrene dimerization. The α-methylstyrene conversion reach 95–100 wt.% in the presence of BEA at 20°C, and at 60-80°C in the presence of Y and ZSM-12.

A selectivity (97 %) for α-methylstyrene linear dimers - 4-methyl-2,4-diphenylpenten-1 and 4-methyl-2,4-diphenylpenten-2 – is obtained in the presence of ZSM-12.

The yield of linear dimers sufficiently decreases with catalyst concentration and temperature rise.

The styrene linear dimer - 1,3-diphenylbytene-1 – is obtained at relatively high temperature (100 - 130°C) and catalyst concentration (10 – 20 wt.%)

In order to improve the linear dimer's yield it is necessary to carry out reaction in the presence of solvent (methyl-, chlorobenzenes). The styrene dimerization in methylbenzenes solution results in a mixture of styrene dimers and alkylate.

Zeolite BEA appeared to be most active (90 – 100 wt.% styrene conversion) and selective (selectivity for styrene linear dimer - 70 %) catalyst of styrene dimerization.

P-113

INVESTIGATION OF REACTION CONDITIONS IN PROX OF CO BY CoO_x-CuO_x-CeO_2 COMPOSITE CATALYST

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In the last decade, proton exchange membrane fuel cell (PEMFC) have been studied and developed. CO concentration has to be <100 ppm according to poisonous effect on Pt-Ru PEMFC-electrodes and <10 ppm for standard platinum electrode. CO must be removed at low temperature (70-250 °C) by preferential oxidation (PROX) in which CO is catalytically oxidized. Therefore an effective catalyst should be developed to eliminate CO from H_2 rich streams at low temperature. Due to limited availability and high costs of precious metals, transition metal oxide catalysts (Co,Cu,Ce and Zr) attracted attention.

In this study, 20wt.% CoO_x – 20wt.% CuO_x – 60wt.% CeO_2 composite catalysts were prepared by coprecipitation method and tested in a micro-reactor flow system for the low temperature preferential oxidation of CO in hydrogen rich streams. The effect of reaction conditions such as temperature (120-160 °C), CO, O_2, CO_2, and H_2O concentrations in the feed mixture, time-on-stream, space velocity (1-2.5 mg.min/ml) were investigated. The catalysts were prepared at the optimum conditions pH 10.0 and 37.5 °C in a semibatch system. Drying time and temperature were 24 hours and 105 °C respectively. Calcination temperature was 650 °C and calcination time was 5 hours, aging was not applied.

It was found that increasing of both temperature and space velocity caused increase in conversion. Existence of H_2O and CO_2 in the feed gas reduced both activity and selectivity. However, negative effect of water vapour was concealed by the presence of CO_2. 100 % conversion was obtained at 150 °C and 1.75 mg.min/ml.

THE INFLUENCE OF IMPREGNATION TIME ON THE ACTIVITY OF DeSONOx CATALYSTS BASED ON MONTMORILLONITE

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The mineral layered nanomaterials based on modified montmorillonites exemplify promising material as the DeSONOx type of catalysts. Main goal of this work is preparation of catalyst. Additionally, the authors studied the influence of different impregnation time on physico-chemical properties of prepared materials. The studied montmorillonite was prepared form bentonite from Jelsovy Potok. Support for catalysts was calcined at the temperature 773 K during 2 hours in air. These supports were at the first step impregnated by EDTA solution at the 373 K by 30 minutes. At the second step the active material was impregnated by $Na_4V_4O_7$ solution during different time: 2, 4, 8, 16, 32 and 64 minutes. The V_2O_5 supported montmorillonite was studied by methods of low temperature argon sorption, X-ray diffraction (XRD), bulk density and concentration of vanadium was determined by X-ray fluorescence (XRF) method.

The catalytic properties were studied in reaction of coal burning in the flow reactor. Hard coal from Silesian mine “Julian” from Poland with or without the catalysts addition were burnt in an atmosphere of air at 1123 K during 4 hours and using an electric furnace. The mass ratio of the DeSONOx catalyst added to the investigated samples of the hard coal was 1:500.

Sulphur concentration in the samples of coal ashes which included DeSONOx catalysts was determined by the XRF method in the Analytical Laboratory of Chemistry Faculty of UMCS. The degree of the sulphur removal ($R_{\%}$) from the coal was calculated according to the sulphur concentration in the coal ashes.

Burning of coal from the Silesian mine "Julian" in the presence only of supports - modified montmorillonite did not show any reduction of SO_2 emission in combustion gases. For the catalysts over montmorillonite support degree of sulphur removal formed a sequence: MontV1 < MontV2 ≈ MontV32 < MontV64 < MontV8 ≈ MontV16.

P-115

ACIDITY OF MODIFIED MONTMORILLONITE DOPED WITH Ni, Cu AND Mn OXIDES

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Pillared clays were studied and used as catalysts for example in Friedel-Crafts reaction, cracking of heavy oil fractions, DeNOx. These materials are very interesting because texture, structure, acidity of surface and physical, chemical and catalytic properties can be modified by different methods. Considering the fact that modification by intercalation of clay with polycations (e.g. Al, Zr or Ti) increases interlayer distance and specific surface area interesting nanomaterials as supports of catalysts may be prepared. On the other hand introduction of active materials as well as Cu^{2+}, Fe^{3+}, Mn^{2+} increases catalytic activity in selective catalytic reduction with ammonia or hydrocarbons. This work presents results of studying of acidity of the ZrO_2-pillared montmorillonite from Jelesovy Potok with introduced Ni, Cu and Mn oxides as active material. Before intercalation a part of clay was activated with HCl. The prepared material was studied by argon and ammonia sorption and photoelectron spectroscopy XPS.

The method of determining acidity of activated supports and catalysts according to the chemisorption of ammonia was used. Ammonia sorption was studied at temperature 273 K (physical and chemical sorption – first isotherm) and after removal of physically sorbed ammonia at 273 K (only physical sorption – second isotherm). The amount of chemisorbed ammonia was determined by the difference in the isotherms I and II patterns. Rectilinear forms of isotherms were fitted into Dubinin-Raduszkiewicz, Langmuir or BET equations.

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COMPARISON OF CATALYTIC ACTIVITY OF ZrO_2-PILLARED MONTMORILLONITE IMPREGNATED WITH V_2O_5 AS DeSONOx TYPE CATALYSTS

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Pillared with ZrO_2 montmorillonites are very interesting materials. Modification of these materials may be made by different methods and results in supports of a lot of catalysts. The subject of this work is comparison of catalytic properties of ZrO_2–pillared montmorillonite used as DeSONOx type catalyst for the coal burn reaction. Series of supports were prepared as follows: bentonite → Na^+-montmorillonite → H^+-montmorillonite. Na^+- and H^+-montmorillonite intercalated with Zr^{4+} oligocations and calcinated. The active material V_2O_5 was impregnated by double impregnation method (DIM)

The activity of catalysts was studied in coal burn reaction in flow reactor. Hard coals from Silesian mine "Julian" from Poland with or without the catalysts addition were burnt in an atmosphere of air at 1123 K during 4 hours using an electric furnace. The mass ratio of the DeSONOx catalyst added to the investigated samples of the hard coal was 1:500. Sulphur concentration in the samples of coal ashes which included DeSONOx catalysts were determined by the XRF method in the Analytical Laboratory of Chemistry Faculty of UMCS. The degree of the sulphur removal ($R_{\%}$) from the coal was calculated according to the sulphur concentration in the coal ashes.

Burning of the coal from the Silesian mine "Julian" in the presence of only supports – modified montmorillonite - did not show any reduction of SO_2 emission in combustion gases. For the catalysts with montmorillonite supports degree of sulphur removal formed a sequence: Mont-Zr-V (57 %) < Mont-H-V (59 %) < Mont-V (67 %).

Obtained supports based on montmorillonite had specific surface area: Mont – 41 m^2/g for Na-montmorillonite, 190 m^2/g for montmorillonite activated with HCl, 300 m^2/g for montmorillonite pillared with ZrO_2. After impregnation with $Na_4V_4O_7$ this parameter drastically decreased as follows: 2 m^2/g, 161 m^2/g, 132 m^2/g, respectively for catalysts. That suggests that the active material accumulates on pores exit and plugs them. As a results radius and size of pores and a specific surface area decrease.

P-117

INVESTIGATION OF CATALYTIC ACTIVITIES OF CERIA BASED COBALT AND COPPER OXIDE CATALYSTS IN PROX REACTION

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INTRODUCTION

Reformed gas contains 0.5-2% CO and it can be ppm level by the selective oxidation of CO [1]. For use in the fuel cells, hydrogen should be removed form CO because it poisons the anode catalysts PEMFC and cause decrease in the cell performance [2]. At present, there is a worldwide interest in development of CO oxidation catalysts [3]. Due to limited availability and high costs of precious metals, non-noble metal catalysts like cobalt oxide, copper oxide has been recently widely used for the selective oxidation of carbon monoxide [4].

EXPERIMENTAL

In this study, for the purpose of observing the effect of CoO_x loading to CuO_x-CeO_2 catalyst, catalysts with different metal contents (0-100 %wt.) were prepared for CO oxidation in hydrogen rich stream. Prepared catalysts were characterized by different physical and chemical methods using AAS, XRD and N_2 adsorption-desorption method, respectively.

RESULTS

The results of activity and selectivity tests of prepared catalysts were correlated with their physical and chemical properties to understand the effect of metal loadings. The results show that the addition of Co as a second metal leads to bimetallic interaction which gives way to enhanced activities at very low temperatures.

REFERENCES

1. A. Martinez-Arias, A. B. Hungaria, M. Fernandez-Garcia, J. C. Conesa, G. Munuera, J. Power Sources, 151 (2005) 32
2. Kim, D.H., Cha, J.E., Catalysis Letters, vol.86, 2003,107
3. P.C. Hulteberg, J.G.M. Brandin, F.A. Silversand, M.Lundberg, Int.J. Hyd.Energy 30 (2005) 1235
4. G. Avgouropoulos, T. Ioannides, H. K. Matralis, J. Batista, S. Hocevar, Cat. Lett., 73 (2001) 33

P-118

DFT SIMULATION OF Al,Zr-COMPLEXES AS KEY INTERMEDIATES OF CATALYTIC OLEFIN HYDROALUMINATION

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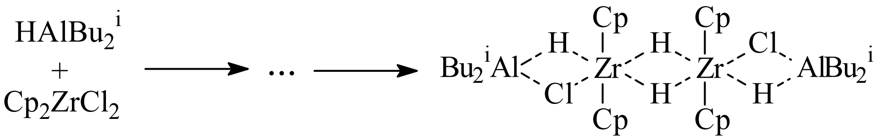
Recently the authors investigated the mechanism of olefin hydroalumination by $HAlBu^i_2$ in presence of Cp_2ZrCl_2 catalyst by means of DNMR spectroscopy and encounter synthesis [1]. It has been shown that complex **1** is the key intermediate for olefin hydroalumination.



1

In order to understand the mechanism of formation of **1** we performed a series of calculation of related structures on the DFT level of theory (PBE/3z, program "Priroda 4.07", Dr Laikov D., Moscow State University). It was found that the formation of **1** occurs *via* the steps **a-d** (T=203,15K).

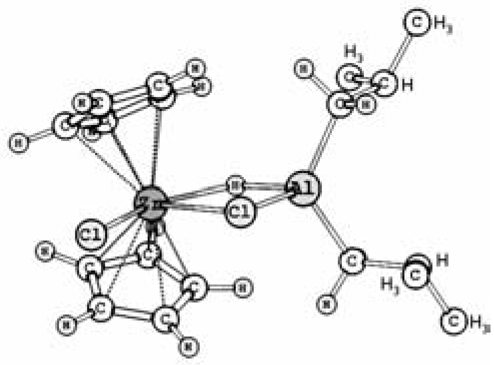
a. $Cp_2ZrCl_2 + HAlBu_2^i \rightarrow Cp_2ZrCl_2 \bullet HAlBu_2^i$ ($\Delta H_r^0 =$-18.8 kcal/mol)

b. $Cp_2ZrCl_2 \bullet HAlBu_2^i \rightarrow Cp_2ZrClH + ClAlBu_2^i$ ($\Delta H_r^0 =$ 15.0 kcal/mol)

c. $2Cp_2ZrHCl \rightarrow (Cp_2ZrHCl)_2$ ($\Delta H_r^0 =$ -8.3 kcal/mol)

d. $(Cp_2ZrHCl)_2 + 2HAlBu_2^i \rightarrow (Cp_2ZrHCl \bullet HAlBu_2^i)_2$ ($\Delta H_r^0 =$-49.3 kcal/mol)

According to step **b** the bridged Al,Zr-complex **2** dissociates through transition state **3** with activation energy of 2.7 kcal/mol.



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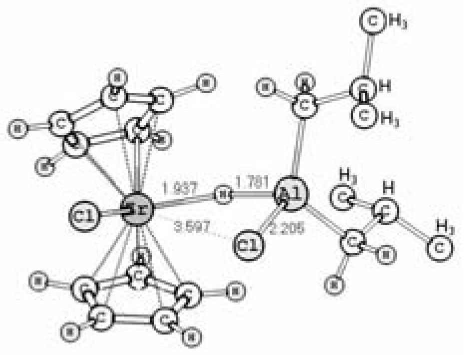

3

Summarised enthalpy of reactions **a-d** is $\Delta H_r^0 =$-65.0 kcal/mol.

Acknowledgements: The authors thank the Russian Science Support Foundation (Grants for Young Ph.D. Scientists, Tyumkina T.V., Parfenova L.V.) and the Foundation of the President of Russian Federation (Program for Support of Leading Scientific Schools, U.M. Dzhemilev, Grant NSh-7470.2006.3).

Reference

[1] Parfenova, L. V.; Pechatkina, S. V.; Khalilov, L. M.; Dzhemilev, U. M. *Russ. Chem. Bull.*, **2005**, *54*, 316.

P-119

ON MECHANISM OF OLEFIN CARBOALUMINATION CATALYZED WITH Cp_2ZrCl_2

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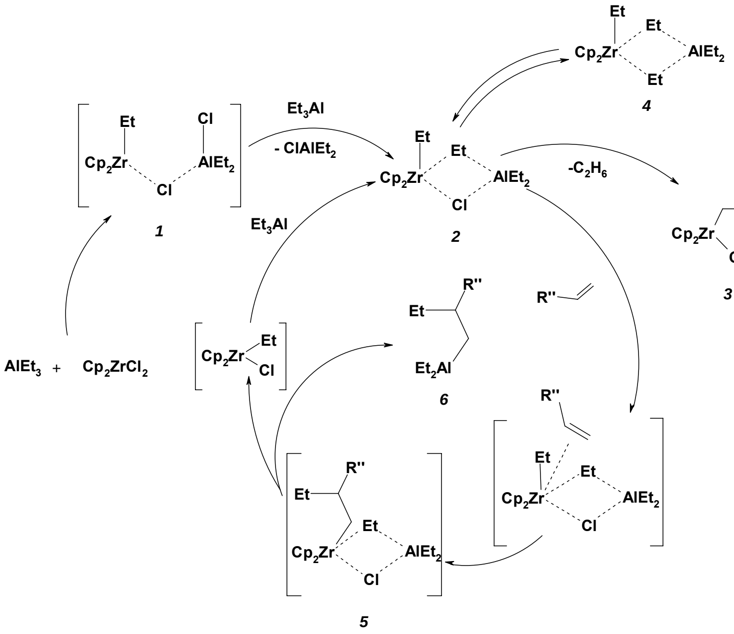
The presented work continues our study of mechanism of organoaluminium compounds (OAC) reactions with olefins, acetylenes and dienes in the presence of Cp_2ZrCl_2 catalyst [1,2]. Despite the fact that the mechanism of olefin carboalumination, which takes place in the catalytic system mentioned above, was frequently discussed in literature (see, for example, Ref. [3]), it remains questionable for now on.

Within the mechanism investigation we have studied the influence of OAC nature, π-ligand environment of Zr atom, solvent type and reagents concentration on the chemoselectivity of OAC-olefin-Cp_2ZrCl_2 system. The structure of the intermediate Zr,Al- complexes that appear in the reaction of olefins carboalumination was identified by the means of dynamic NMR spectroscopy and encounter synthesis; afterwards, the mechanism of the reaction was proposed (Scheme). The Zr,Al-complex ***2*** was suggested as a key intermediate, which coordinates the olefin and gives the carboalumination product ***6***.



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References

[1] Parfenova, L. V.; Pechatkina, S. V.; Khalilov, L. M.; Dzhemilev, U. M. *Russ. Chem. Bull.,* **2005**, *54*, 316.
[2] Khalilov, L. M.; Parfenova, L. V.; Rusakov, S. V.; Ibragimov, A. G.; Dzhemilev, U. M. *Russ. Chem. Bull.,* **2000**, *49*, 2051.
[3] E. Negishi, D.Y. Kondakov, D. Choueiry, K. Kasai, T. Takahashi, *J. Am. Chem. Soc.*, **1996**, *118*, 9577.

P-120

VARIOUS METAL DOPED VANADIUM MAGNESIUM OXIDE CATALYSTS IN DEHYDROGENATION OF ISOBUTANE TO ISOBUTENE WITH CARBON DIOXIDE

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Vanadium magnesium oxide catalysts are known for their activity and selectivity in the oxidative dehydrogenation of various hydrocarbons: ethane [1, 2], propane [1-3], n-butane [1, 2, 4], isobutane [1, 2], pentane [5], cyclohexane [1, 2] and ethylbenzene [6, 7]. Moreover, the catalysts show high activity and selectivity when the dehydrogenation is proceeded in the presence of mild oxidizing agents such as CO_2 [8-11], SO_2 [12] and N_2O [13]. The influence of vanadium content and preparation method on the physicochemical properties of $VMgO_x$ system were widely studied [10, 11, 14-17] while the effect of the metal additives attracted much less attention.

In this investigation, the effect of the addition of twenty-two different elements to $VMgO_x$ catalyst has been studied. The metals were selected from almost all groups of periodic table: alkali and alkaline earth metals (Be, K, Li, Rb), transition elements (Ag, Bi, Co, Cr, Cu, Fe, Ga, Mn, Mo, Ni, Sn, W, Y, Zn and Zr) and rare-earth metals from lanthanide series (La, Nd, Sm). All the catalysts were prepared by citrate method [10, 11] in such manner to yield the samples with metal: vanadium: magnesium molar ratio equal to 1: 9: 90. Changes in the catalytic activity and physicochemical properties of $VMgO_x$ system caused by a metal addition were investigated using catalytic tests and temperature-programmed techniques. The experimental results are discussed in the terms of:

- changing of the conversion and selectivity during the isobutane dehydrogenation with carbon dioxide over modified $VMgO_x$ catalysts
- comparison the results with the data on the isobutane dehydrogenation in the inert gas (helium) atmosphere
- study of reducibility using temperature-programmed analysis (TPR-H_2)
- acid-basic properties of the catalyst surface in the presence of helium and carbon dioxide determined by test reaction (decomposition of 2-propanol)

Obtained results show that addition in small amounts of metal cation to vanadium magnesium oxides significantly changes their catalytic activity and physicochemical properties. For example: presence of alkali metals (Li, K, Rb) and rare-earth elements (Nd, Sm) decreased the isobutane conversion in both reaction atmospheres, however promoting effect of CO_2 was observed. On the other hand, additives such as Cu, Ag, Bi and Co improved the reducibility of $VMgO_x$ system at the low temperatures. Moreover, these catalysts were very active but the isobutene yields in an inert gas atmosphere were much higher in comparison to dehydrogenation with carbon dioxide. Such differences in the catalytic performance can be also explained on the basis of 2-propanol test reaction, as the presence of carbon dioxide in the reaction atmosphere changes the acid-base properties of the catalyst surface.

References:

[1] P.M. Michalakos, M.C. Kung, I. Jahan, H.H. Kung: Journal of Catalysis 140 (1993) 226-242
[2] H.H. Kung, M.C. Kung: Applied Catalysis A: General 157 (1997) 105-116
[3] L. Balderas-Tapia, I. Hernandez-Perez, P. Schacht, I.R. Cordova, G.G. Aguilar-Rios: Catalysis Today 107-108 (2005) 371-376
[4] C. Tellez, M. Abon, J.A. Dalmon, C. Mirodatos, J. Santamaria: Journal of Catalysis 195 (2000) 113-124
[5] S.A. Korili, P. Ruiz, B. Delmon: Catalysis Today 32 (1996) 229-235
[6] W.S. Chang, Y.Z. Chen, B.L. Yang: Applied Catalysis A: General 124 (1995) 221-243
[7] W. Oganowski, J. Hanuza, L. Kepinski: Applied Catalysis A: General 171 (1998) 145-154
[8] S. Ge, Ch. Liu, S. Zhang, Z. Li: Chemical Engineering Journal 94 (2003) 121-126
[9] Y. Sakurai, T. Suzaki, K. Nakagawa, N. Ikenaga, H. Aota, T. Suzuki: Journal of Catalysis 209 (2002) 16-24
[10] J. Ogonowski, E. Skrzynska: Chim. Chim. Techn., 48 (2005) 129-132
[11] J. Ogonowski, E. Skrzynska: React. Kinet. Catal. Lett., 86 (2005) 195-201
[12] Г.В.Исагулянц, И.П.Беломестных: Нефтехимия 39 (1999) 339-342
[13] J.M. Lopez Nieto, A. Dejoz, M.I. Vazquez, W. O’Leary, J. Cunningham: Catalysis Today 40 (1998) 215-228
[14] M.K. Yurdakoc, R. Haffner, D. Honicke: Materials Chemistry and Physics 44 (1996) 273-276
[15] X. Gao, P. Ruiz, Q. Xin, X. Guo, B. Delmon: Catalysis Letters 23 (1994) 321-337
[16] L. Balderas-Tapia, J.A. Wang, I. Hernandez-Perez, G.G. Aguilar-Rios, G. P. Schacht: Materials Letters 58 (2004) 3034–3039
[17] A. Corma, J. M. Lopez-Nieto, N. Paredes: Journal of Catalysis 144 (1993) 425-438

PERFORMANCE OF Cu-Zn-Si OXIDE CATALYSTS IN CO HYDROGENATION

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Methanol is the main product of CO hydrogenation over copper-containing catalysts. Cu-Zn-Si oxide catalysts attract much attention due to their higher thermostability comparing to the industrial Cu-Zn-Al oxide catalysts. Here we report the experimental data on the effect of the composition and structure of the Cu-Zn-Si catalyst precursor on its performance in CO hydrogenation. We also consider the experimental FTIR data on coadsorption of CO and H_2 and conclude about the nature of the most abundant intermediates on the metallic copper surface.

The Cu-Zn-Si catalysts under the study contain 15 % at. of Cu and were prepared by deposition-precipitation method. The precursor of Cu-Si (with no Zn) catalyst is amorphous copper hydroxo-silicate of chrisocolla type structure. Introduction of Zn leads to the formation of Zn phyllosilicate $Zn_3[Si_4O_{10}](OH)_2 \cdot nH_2O$ (zincsilite), which dissolve copper cations.

Increasing Zn content leads to near proportional increase in specific CO hydrogenation activity (Fig. 1), which correlate to amount of copper cations dissolved in zincsilite phase of precursor.

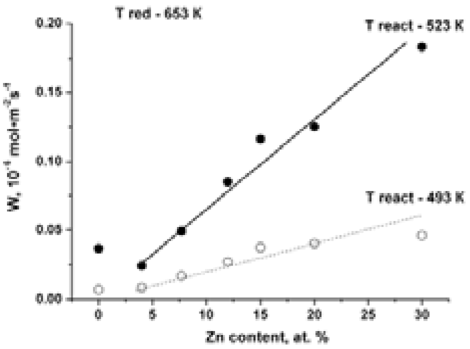

Fig. 1 The influence of Zn content of Cu-Zn-Si (15 % Cu) catalysts on initial specific activity in methanol synthesis (P = 20 bar, $CO:H_2:CO_2$ = 21:77:2)

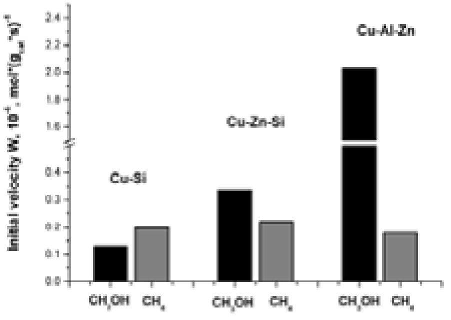

Fig. 2 Comparison of methanol and methane yield for different Cu-containing catalysts: $Cu_{0.14}Si_{0.86}$, $Cu_{0.15}\,Zn_{0.15}Si_{0.7}$, $Cu_{0.3}\,Zn_{0.58}Al_{0.12}$ (P = 20 bar, T_{react} = 533 K, $CO:H_2:CO_2:N_2$ = 31:64:2:3)

Comparing to the industrial Cu-Zn-Al catalyst, the activity of Cu-Zn-Si catalysts and their selectivity to methanol is much lower. Cu-Si catalyst is the least selective. It is noteworthy, that the specific rate of methane formation is similar for all the studied catalysts.

FTIR of CO and H_2 coadsorption evidence that formate and methoxy groups are the most abundant species at the copper surface of Cu-Zn catalyst, while methyls prevail at the surface of Cu-(Zn)-Si catalysts. Thus, the presence of oxygenated species is crucial for methanol synthesis over metallic copper.

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OXIDATIVE COUPLING OF METHANE IN THE PRESENCE OF CO_2 ON LANTHANUM OXIDE CATALYSTS DEPOSITED ON Al_2O_3, SiO_2, TiO_2 AND MgO

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Quest for new proecological solutions for the existing technologies becomes nowadays one of the major research problems. Carbon dioxide is attempted to be used in the reaction of oxidative coupling of methane into hydrocarbons C_2.

Investigations [1] of a series of lanthanum - magnesium oxide catalysts showed that the highest activity has the catalytic system with the composition of 10% La_2O_3/MgO.

On the basis of physico-chemical studies of the catalysts tested, their phase composition, surface area and thermal decomposition characteristics were described. XRD diffraction pattern indicated the presence of La_2O_3, MgO, La_2MgO_x or/and $La(OH)_3$ structures. The TGA- DTA analysis proved the presence of absorbed water on the surface of the 10%La_2O_3/MgO catalyst, which confirmed the presence of $La(OH)_3$ in the tested samples at room temperature. However, lanthanum hydroxide does not occur in the process conditions (600-850°C), because it is decomposed at the temperatures above 400°C. It can be stated that there were no noticeable changes in the composition of the prepared catalysts within the temperatures range where the catalytic tests were carried out.

Further research concerned the influence of the kind of carrier and the preparation techniques of the carrier and the catalysts on the activity of lanthanum system in the process studied. Comparative tests of 10%La_2O_3/MgO catalysts indicated the highest activity exhibited by the catalyst obtained by the method of co-precipitation than by impregnation.

The next step of our research was the determination of changes of catalytic activity of lanthanum oxide catalysts deposited on magnesium oxide from POCH or the magnesium oxide obtained by the precipitation and citrate methods. Moreover the following commercial products were tested as the supports for lanthanum oxide catalysts: silica gel, aluminum oxide (POCH) and titanium dioxide (BDH Chemicals Ltd). According to literature data, these carriers react at high temperature with the active phase of catalyst [2,3].

References:

1. Materiały XXXVIII Ogólnopolskiego Kolokwium Katalitycznego, Kraków 2005
2. L. Kępiński, W. Miśta, „Solid State Sci.", 7, (2005), 1300,
3. W. Zheng, W. Pang, Materiale Letters 33, (1997), 231.

STRUCTURE SENSITIVITY AND COMPENSATION EFFECT OF NH_3 DECOMPOSITION

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NH_3 decomposition to provide CO_x–free H_2 for fuel cells has attracted renewed interests recently due to its unique advantages over conventional routes based on the carbonaceous materials [1–2]. Although significant research efforts have been made, the influence of physicochemical properties on reaction rates has not been well studied [3].

Kinetic studies on NH_3 decomposition over supported Ni and Ru nanoparticles reveal a pronounced particle size effect [3–4]. The forward turnover frequency increases firstly with decreasing average particle size of Ni^0, passes through a maximum at around 2.2 nm and then decreases (Fig. 1). This reaction obeys the Temkin–Pyzhev mechanism, in which the recombinative desorption step of surface N* is rate-determining. A compensation effect between the pre–exponential factor (k_0) and activation energy (E_a) is well detailed (Fig. 2). Highly dispersed Ru nanoparticles with mean size of 2.3 nm, which were synthesized by a novel polyol reduction method, show an outstanding activity for NH_3 decomposition [5].

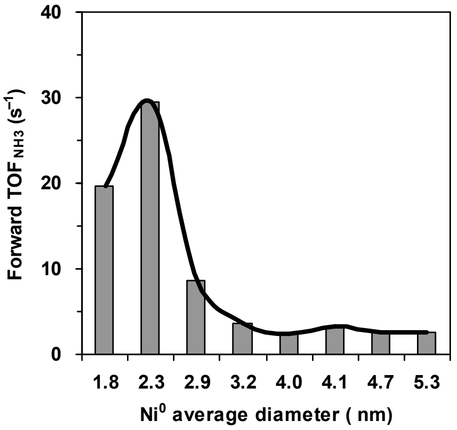

Fig 1. Particle size effect on the forward turnover rate for NH_3 decomposition.

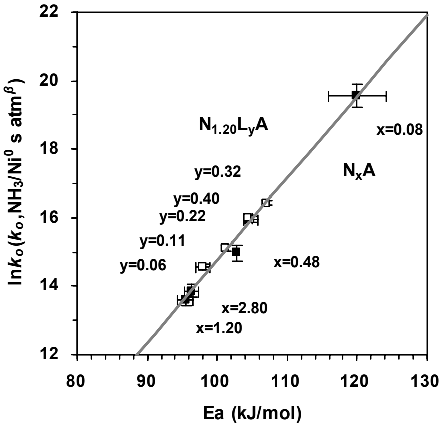

Fig 2. Compensation effect over Ni catalysts. (Data from the Temkin-Pyzhev fitting[3]).

Reference

1. A. T-Rassi, proceeding of the 2002 U.S. DOE hydrogen program review, NREL/CP-610-32405, 2002.
2. Jian Zhang, Hengyong Xu, Xianglan Jin, Qingjie Ge, Wenzhao Li. *Appl. Catal. A: Gen.* 290 (2005) 87.
3. Jian Zhang, Hengyong Xu, Wenzhao Li. *Appl. Catal. A: Gen.* 296 (2005) 257.
4. Jian Zhang, Hengyong Xu, Wenzhao Li. *Ind. Eng. & Chem. Res.*, in revised.
5. Jian Zhang, Hengyong Xu, Qingjie Ge, Wenzhao Li. *Catal. Comm.* 7 (2006) 148.

P-124

SYNTHESIS OF 2-ALKYLIDENMAGNESACYCLOPENT-4-ENES BY CATALYTIC CYCLOMAGNESIATION OF 1,2-DIENES AND ACETYLENES

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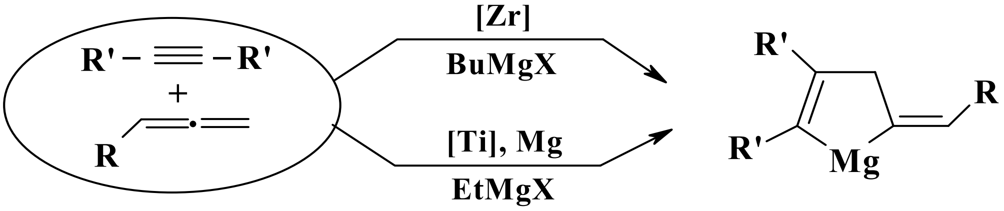
In the report the new procedure for the synthesis of 2-alkylidenmagnesacyclopent-4-enes based on intermolecular cyclomagnesiation of allenes and acetylenes assisted by Ti- and Zr catalysts is represented.

Intermolecular cyclomagnesiation of equimolecular amounts of acetylenes and allenes with BuMgX (Et_2O, 20 °C, 3 h) affected by 10 mol % Cp_2ZrCl_2 catalyst was shown to afford 2-alkylidenmagnesacyclopent-4-enes with high regioselectivity in ~45-50% yield. Simultaneously 2,3,4,5-tetraalkylmagnesacyclopenta-2,4-dienes as the minor product (3-8%) were established to form in the reaction mixture.

Cyclomagnesiation of equimolar mixture acetylenes and allenes with EtMgX in the presence of magnesium (acceptor of halogenide ions) and Cp_2TiCl_2 catalyst led to the mixture of 2-alkylidenemagnesacyclopent-4-enes and related 2,5-dialkylidenemagnesacyclopentanes[1] at 2:1 ratio in a total yield of ~60%.



[Zr] = Cp_2ZrCl_2, [Ti] = Cp_2TiCl_2; X = Cl, Br; R = alkyl, Bn; R' = alkyl

The probable mechanism of 2-alkylidenemagnesacyclopent-4-enes via cyclomagnesiation of allenes and acetylenes using Grignard reagents in the presence of Ti and Zr catalysts is discussed.

The research work was financially supported by Russian Foundation Basic for Research (The project No 05-03-32367) and grant of the RF President Sci.Sh. (No 7470.2006.3)

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[1] U.M.Dzhemilev, V.A.Dyakonov, L.O.Khafizova, A.G.Ibragimov. Tetrahedron, **60** (2004) 1287.

THE FIRST EXAMPLE OF CATALYTIC PREPARATION OF TETRAALKYLMAGNEZACYCLOPENTA-2,4-DIENES

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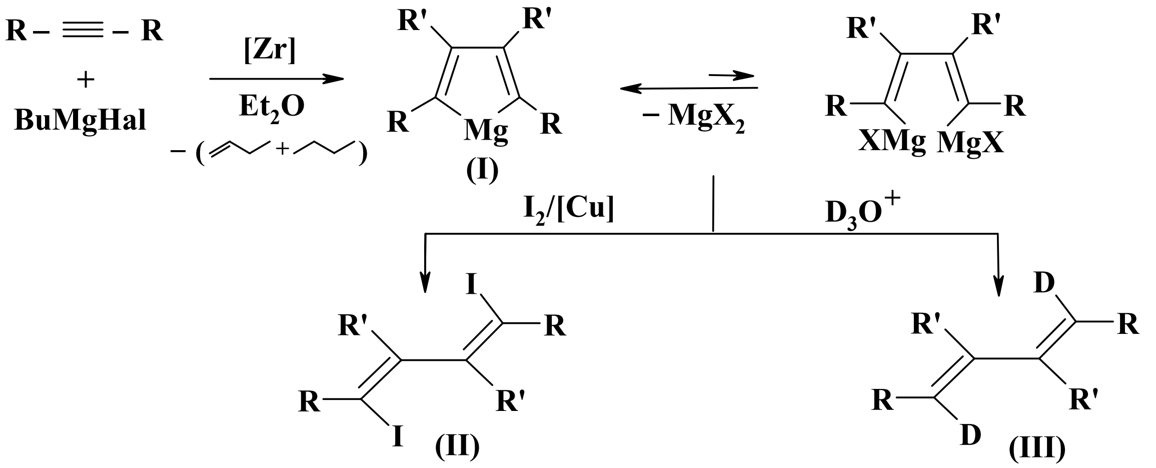
The paper discusses the results on a synthesis of magnezacyclopentadienes by cyclomagnesiation reaction of 1,2-disubstituted alkynes with BuMgHlg (Hlg = Cl, Br) affected by Zr catalysts.

The interaction between aforesaid alkynes and BuMgHlg (two-fold excess) in the presence of Cp_2ZrCl_2 catalyst (10 mole %) under reaction conditions (20 °C, 2 h) in ethereal solvents was found to afford 2,3,4,5-tetraalkylmagnezacyclopenta-2,4-dienes in 50-55 % yield. Structures of magnezacyclopentadienes obtained was determined by spectral methods and subsequent chemical transformations.



[Zr] = Cp_2ZrCl_2; [Cu] = CuCl; X = Cl, Br; R = R' = Et, Pr, Bu; R = Me_3Si, R' = Bu.

The probable mechanism for the formation of unsaturated organomagnesium compounds under the effect of Cp_2ZrCl_2 catalysts is discussed.

The research work was financially supported by Russian Foundation Basic for Research (The project No 05-03-32367) and grant of the RF President Sci.Sh.-(7470.2006.3)

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METHANE DECOMPOSITION ON Ni/METAL SUPPORTED CATALYSTS

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The preparation of pure hydrogen from hydrocarbons is an important task of hydrogen energetics. It is known [1], that Ni and Fe based catalysts are active in the methane decomposition to molecular hydrogen and carbon. The goal of this work is development of active and stable catalyst of methane decomposition on the basis of Fe-Cr-Al alloy.

The samples preparation includes several stages. Nickel was supported on preliminary heat-treated Fe-Cr-Al wire. Then the sample was reduced by hydrogen. The activity tests were conducted at temperature 750-800 °C and residence time 0.5 s. The initial reaction mixture was natural gas with methane content ~ 96.0%. The test duration for one sample was 10-12 h. After testing the sample was weighed and the amount of deposited carbon was determined as the weight difference of sample before and after testing. The reaction rate was determined by using flow-circular setup with chromatographic analysis of methane and hydrogen. The most active samples were regenerated in the flow of nitrogen containing water, and then were retested.

The catalysts before and after testing were investigated by the atomic force microscopy and X-ray analysis. The content of nickel in the samples was determined by atomic-absorption spectroscopy.

It was established, that the preliminary treatment of the metal support leads to essential increasing (in times) of the specific surface and activity of the prepared catalysts.

Literature

1. Buyanov R. A., Zakoksovyvanie Katalizatorov – Novosibirsk, Nauka, 1983, 208 p.

EFFECT OF THE DISPERSION OF $Ca(NO_3)_2$ AND $LiNO_3$ TO THE NANOSIZED SCALE ON THE HYDRATION TEMPERATURE

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It is known that the dispersion of a substance to a small size r increases the contribution of the surface energy $\mu_{sur} = \sigma \cdot \frac{2 \cdot \overline{V}}{r}$ to the total Gibbs energy of the system $\Delta\mu^o = \Delta H^o - T\Delta S^o$ (σ is the surface tension, $\overline{V}$ is the molar volume). It can result in the change of its properties such as the temperature of phase transitions, specific heat, sorption equilibrium, etc.

In this work we have found the increase in the temperature of the hydration T^* of calcium and lithium nitrates, confined to silica pores (3.5 - 15 nm in size), in the course of the reactions:

(1) $Ca(NO_3)_2 + 2H_2O \rightarrow Ca(NO_3)_2{\cdot}2H_2O$ (2) $LiNO_3 + 3H_2O \rightarrow LiNO_3{\cdot}3H_2O$.

This increase can be attributed to the above mentioned contribution of the surface energy.

In equilibrium the chemical potential $\mu^o(T)$ of products is equal to that of reagents, that allows the calculation of the hydration temperature (see Fig.1) $T^* = \Delta H^o(T^*)/\Delta S^o(T^*)$. If the surface energy of the confined salt is superior to the surface energy of the confined hydrate (as it is demonstrated on Fig. 1) by the value $\Delta\mu_{sur}$, the increase in the hydration temperature is $\Delta T^* = [d(T^*)/d(\Delta H^o)]\Delta\mu_{sur} = \Delta\mu_{sur}/\Delta S^o(T^*)$. Assuming the difference in the chemical potentials of the confined $Ca(NO_3)_2$ and $Ca(NO_3)_2{\cdot}2H_2O$ $\Delta\mu_{sur} =$ 0.7 kJ/mol, we found that the hydration temperature should increase from 51.7°C for reaction (1) in bulk to 53.7°C – in the confined state (Fig.1). For the difference of 1.7 kJ/mol it reaches 56.4°C, that is close to the hydration temperatures observed experimentally in silica pores of 15 nm size (54-58°C).

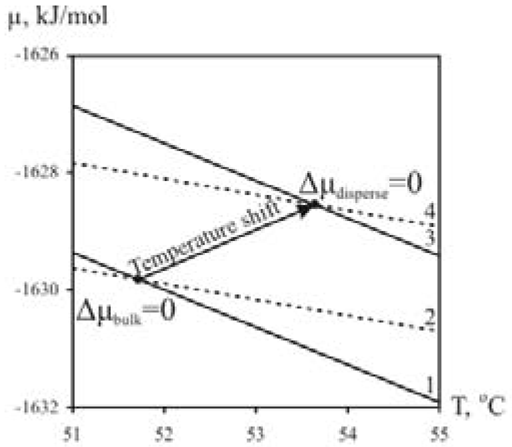

Fig.1. Change of the chemical potentials of bulk (1, and disperse (3) reagents $Ca(NO_3)_2 + 2H_2O_{gas}$ and bulk (2) and disperse (4) product $Ca(NO_3)_2{\cdot}2H_2O$

Thus, the dispersion of inorganic salts in nanoporous matrices is an effective tool for the modifying their physicochemical properties, for instance, the hydration temperature, that could be of practical importance for chemical heat pumps and seasonal storage of heat.

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QUANTUM-CHEMICAL STUDIES OF HYDROGEN AND OXYGEN ATOMS ADSORBED ON Pt(100) AND Pt(111) BY DFT

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It's known that hydrogen oxidation by platinum metals is one of the classical model reaction of heterogeneous catalysis. The reaction is described by Langmuir-Hinshelwood stage mechanism, including dissociative hydrogen and oxygen adsorption. Nowadays we can see many studies of nature of H and O atoms, adsorbed on Pt(100) and Pt(111) surfaces, due to modern theoretical and experimental surface science techniques.

The aim of this work is to calculate adsorption energies, equilibrium heights above the surface, vibration frequencies of adsorbed H- and O- atoms on Pt(100) and Pt(111) based on density functional theory (DFT).

Adsorption of atomic hydrogen and oxygen at coverage of 1 ML has been studied by DFT within the local density approximation (LDA). The simulations were conducted using ADF2003-BAND and ESPRESSO-3.1 programs. We have employed a three layer slab for simulation of Pt(100) and Pt(111) surfaces.

Adsorbing hydrogen and oxygen atoms can occupy following states: two threefold hollow sites, namely the fcc and hcp, twofold bridge site and on-top. Computed frequency of symmetrical valence vibrations occurring perpendicular to the surface heavily depends on the number of metal atoms coordinating with the atom. Vibration frequency dramatically increases with decreasing of number of bonds in adsorption center.

Table 1. Computed adsorption energies (zero point energy effects have been included), equilibrium heights above the surface, vibration frequencies of adsorbed H and O atoms ($\theta = 1$ ML) for following adsorption sites on Pt(100) and Pt(111).

	Site	E_{ads}, ev/atom	r_0, Å	ν, cm^{-1}
H/Pt(111)	on-top	-0.99	1.6	2022
	bridge	-1.36	1.15	1318
	hcp	-1.48	1.0	1290
	fcc	-1.54	1.0	1281
	fcc*	-0.99	-1.1	752
	hcp*	-0.50	-0.6	1102
H/Pt(100)	on-top	-0.88	1.6	2027
	bridge	-1.42	1.1	1359
	hollow	-1.62	0.5	710
O/Pt(111)	on-top	-1.41	1.8	772
	bridge	-1.47	1.4	642
	fcc	-1.73	1.2	564
	hcp	-1.22	1.25	611

Threefold hollow sites (fcc and hcp) for adsorption of H and O atoms are preferred compared to weakly-bond energy sites (on-top or bridge). It is shown that hydrogen atoms can occupy subsurface sites (fcc*and hcp*).

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