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1992-1993

BORESKOV INSTITUTE OF CATALYSIS
SIBERIAN BRANCH OF RUSSIAN ACADEMY OF SCIENCES

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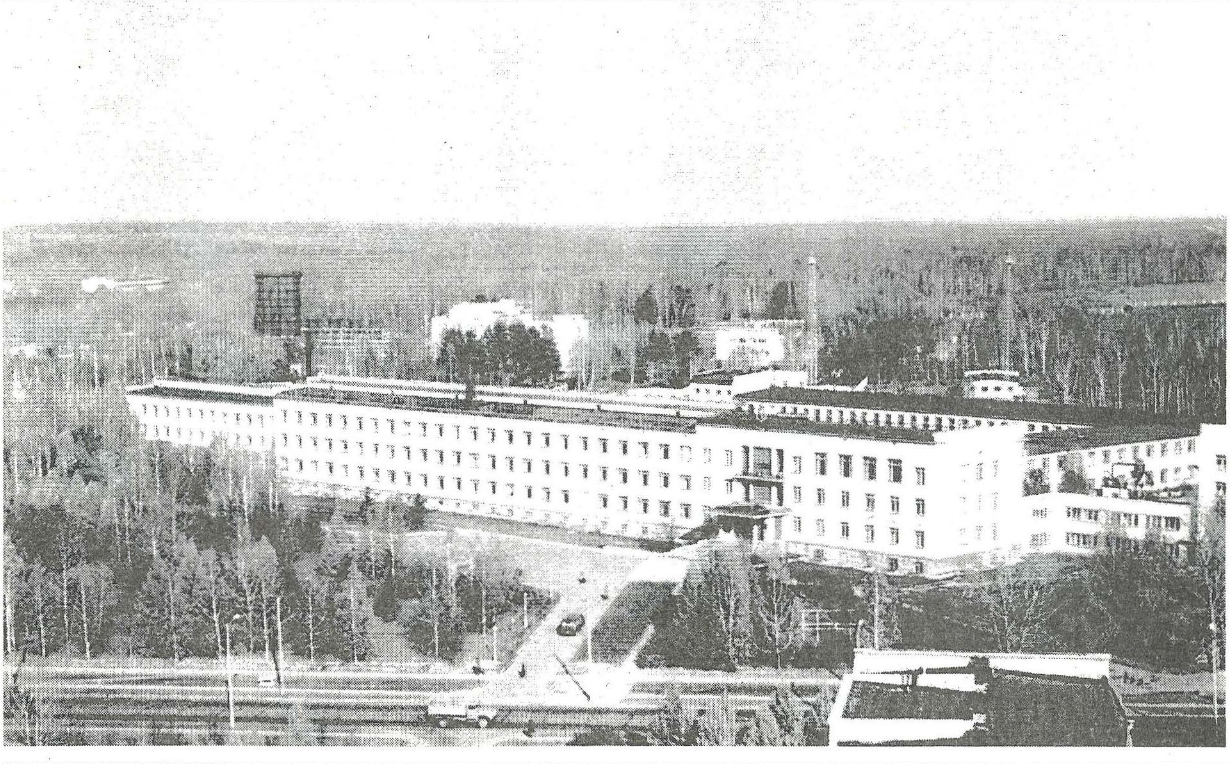

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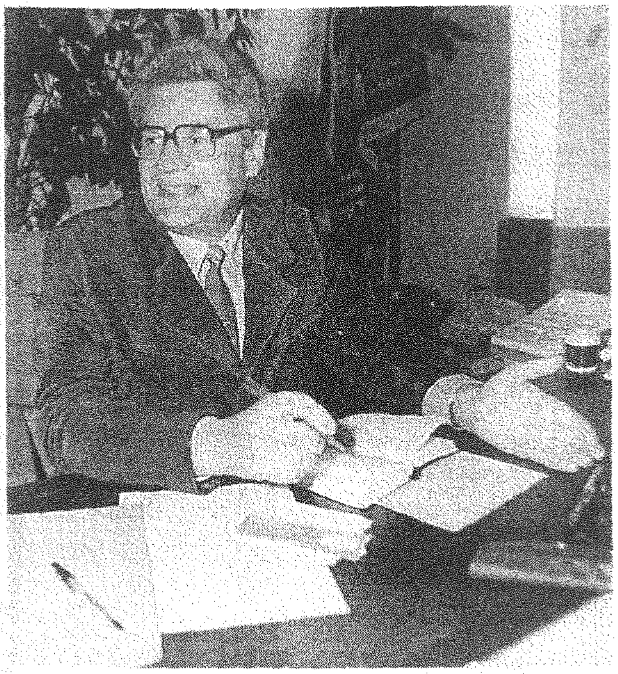
BORESKOV INSTITUTE OF CATALYSIS IN 1992-93



1992-93 were important years for the Boreskov Institute of Catalysis in Novosibirsk. Economic changes in Russia resulted in a noticeable decrease of financing from the Russian Academy of Sciences. However, the Institute was able to find enough funding from other sources to keep all its departments intact. In some important areas, such as studies of catalysis with new instrumentation techniques and quantum chemical methods, as well as commercialization of its new catalysts and technologies abroad, the Institute was even able to increase its activity. Young researchers joined us as new members of the staff in 1992-93. A contract system of employment was introduced at the Institute in 1992. "Isvestiya", a Russian newspaper of international renown has written an article about the Institute "The Institute that Knows How to Live in the Market Economy" (Izvestiya, June 6, 1992).

The International Centre for Catalysts Characterization and Testing (ICCCT) established at the Institute in 1991, continued its successful work. Distinguished scientists and engineers from all over the world has joined its International Advisory Board. Several important international projects have been accomplished by the Institute through the ICCCT in 1992-93.

On April 20, 1993 the Institute has celebrated the 85th anniversary of Prof. G.K. Boreskov, the founder of the Institute and its director until 1984. A special meeting of the Scientific Council and the one day Memorial Symposium took place at the Institute on this date. On the occasion of Prof. G.K. Boreskov's 85th anniversary, the Presidium of the Russian Academy of Sciences has given his name to the Institute. We are proud that now it is called the Boreskov Institute of Catalysis (BIC).

A short memorial article dedicated to Prof. G.K. Boreskov, opens this volume.

Prof. Kirill I. Zamaraev

Director

G.K. BORESKOV: CREATION AND MANAGEMENT IN SCIENCE

April 20, 1992 was a memorial date for the international community of scientists and chemical engineers working in the field of catalysis. This day was the 85th anniversary of Georgii Konstantinovich Boreskov - a famous scientist, an outstanding chemical engineer and a great science manager.

In 1929 at the age of 22 G.K.Boreskov graduated from the Odessa Chemical Institute. From the very beginning of his scientific career he was equally interested in both fundamentals and applications of catalysis and chemical engineering. Soon after graduation he became the head of industrial laboratory of catalysis. Under his guidance the first catalysts for the sulfuric acid production were prepared in the USSR and appropriate methods for design of large scale catalytic reactors were developed.

Prof. G.K.Boreskov was always convinced that catalysis is a chemical phenomenon. In the 50s, during the period of debates in the USSR on the origin of catalytic action he formulated his well known rule of the approximate constancy of specific catalytic activity (the Boreskov rule). He consistently asserted a viewpoint about the necessity to consider the effect of reaction medium on catalyst structure and properties, in particular, when the kinetics of heterogeneous catalytic reaction is concerned. Prof. G.K.Boreskov has made a key contribution to the theory of oxidative catalysis. In particular, he demonstrated the rate of complete oxidation reactions to correlate with the strength of oxygen binding with the surface. He suggested a mechanistic approach to catalysis based on the combination of the concepts of energy compensation and catalytic mechanisms of the stepwise and concerted (associative) types.

Actually, Prof. G.K.Boreskov contributed significantly to all fields of catalysis. He was one of the founders of modern approach to mathematical simulation of chemical reactors. Of great importance are the results of his research in catalysis on metals, in the application of isotopic methods to experimental and fundamental catalysis, catalytic reaction kinetics and in design of novel methods for catalyst preparation.

Prof. G.K.Boreskov was always ready for pioneer ideas in both fundamental and applied catalysis. He suggested and developed such novel trends in the applied catalysis as, e.g., unsteady state performance of catalytic processes, design of catalytic heat generators (catalytic fluidized bed combustion reactors) in chemical technology.

Prof. G.K.Boreskov was the Organizer and the Director of the Institute of Catalysis in Novosibirsk since 1958 until 1984. He has posited the main trends of the Institute research activity. His idea was to combine at the Institute the fundamental research in the theory of catalysis and design of new methods for catalyst preparation with the mathematical simulation of catalytic processes accompanied by the solution of applied problems suggested by the demands of industry.

His outstanding contribution to science and engineering is well recognized. In 1959 he was elected a corresponding member and in 1966 a full member of the USSR Academy of Sciences. He was awarded with the State prize. Prof. G.K.Boreskov is famous also as the untiring organizer of international cooperation in catalysis research. He participated permanently in organization of International Congresses on Catalysis and in 1972-76 was the President of ICC.

Prof. G.K.Boreskov created his school in catalysis and left the unique Institute after him. The studies reported in this annual report reflect the work of his school in catalysis. His outstanding contribution to science, brilliant managing abilities and prominent personal features made him famous among his contemporaries and successors.

BRIEF REVIEW OF BORESKOV INSTITUTE OF CATALYSIS

The Boreskov Institute of Catalysis of the Siberian Branch of Russian Academy of Sciences (SB RAS) is the largest in the world specialized institute working in this field. The Institute carries out fundamental and applied studies practically in all fields of catalysis: structural and mechanistic characterization at the molecular level of various catalysts and catalytic reactions, chemistry of catalyst preparation, kinetic studies of catalytic processes, mathematical modeling and engineering of catalytic reactors and processes, development and commercialization of new industrial catalysts and processes. Sophisticated instrumentation for *in situ* analytical control of catalyst state and reaction mixture composition, including instrumentation for adsorption, kinetic, structural and spectral studies are available at the Institute. All this allows to obtain within short time intervals unique combination of data about the structure of active centers, detailed reaction kinetics and mechanism, and to use these data for purposeful design of new catalysts and catalytic technologies.

The list of personnel of the Institute inscribes 1000 people, among them 434 researchers including 1 full member and 2 corresponding members of the Russian Academy of Sciences, about 40 doctors of sciences and 200 candidates of sciences. The Omsk Branch of the Institute guided by Prof. V.K. Duplyakin unites about 50 researchers. Here, the pilot plant of the Institute for manufacturing adsorbents and catalysts is situated as well. The scientists of the Institute work in 34 research laboratories and 17 research groups in Novosibirsk and 4 research laboratories and 7 research groups in Omsk. Service, Managing and Engineering Departments of the Institute support and promote its research activity.

Institute of Catalysis of Siberian Branch of Academy of Sciences was founded in 1958 and now it is one of major research institutions in catalytic chemistry over the world. Initiator of the Institute and its permanent director up to 1984 was academician Georgii K. Boreskov (1907-1984), an outstanding specialist in chemistry and catalysis with international recognition, a significant manager of research. In 1992 his name was assigned to the Institute. G.Boreskov contributed remarkably to generation of scientific traditions and style, research trends and activities. Over several last decades fundamental and applied catalysis became a separate trend in chemistry and chemical engineering encompassing various fields of physics, mathematics, biology and engineering. Boreskov Institute of Catalysis has played a key role in this breakthrough.

Scientific Council of the Institute is its brain center. Besides the heads of Laboratories and Departments, leading researchers are the members of the Council as well.

MAIN DIRECTIONS OF THE INSTITUTE RESEARCH ACTIVITY

Catalysis is a backbone of the technical progress in chemistry, oil refinery and oil chemistry. About 90% of modern chemical technologies appear to be based on catalytic processes. Current commercial production of sulfuric and nitric acids, fertilizers, motor fuels, monomeric and polymeric materials can not exist without catalysts. Catalytic methods are rapidly penetrating into the food industry, energetics, metallurgy and transportation. Currently, catalysts are used more frequently to solve important environmental problems.

At the same time catalysis itself is a complex and multiform phenomenon. Among the problems of paramount importance is the prediction of catalytic action. To solve this problem it is necessary to know the nature of interaction between reactants and catalysts, the composition and structure of intermediates, the combination of consecutive steps of processes and the main properties of substances that determine the catalytic activity. The other problems of primary concern are: development of methods for catalyst preparation and investigation of their structure and also elaboration of procedures for commercial process performance, optimization and simulation of catalytic reactors and reactions on the basis of detailed analysis of catalytic reaction kinetics.

At present, the study of the nature of catalytic action and catalyst structure, development of both fundamental and practical approaches to catalyst preparation and performance are, in effect, not possible without various chemical, physical and combined methods.

The quantum-chemical research is mainly directed torwards calculation of electronic structures of the models of activated complexes, intermediates and catalysts.

Methods for determining the chemical and phase composition of catalysts and those of catalytic reaction products are in progress now for all the elements of Periodic System and for their various combinations and ratios. Atomic absorption spectroscopy, various analytical physico-chemical and chemical methods serve for catalyst analysis. Chromatography is employed mainly to examine the composition of catalyst reaction products.

Adsorption methods, porosimetry, calorimetry are extensively used to study geometry and chemistry of catalyst surface, specific area, pore structure, adsorption heats, etc.

Design of industrial catalytic processes is based on the detailed study of reaction kinetics.

The Institute possesses various highly potential and precise physical research methods. The structure and properties of catalysts and reaction products are studied by means of X-ray electron diffraction, high resolution transmission electron microscopy, vibrational and UV-VIS spectroscopies. IR spectra can be registered within the range of 10-1500 cm^{-1} at the temperatures ranging from 196 to 700 °C, UV and VIS spectra - within 200-2500 nm, diffuse scattering spectra - 220-1000 nm. Laser Raman spectra are recorded upon excitation at wavelengths within 440-630 nm, the exciting radiation being tuned continuously. For fast processes pulse radiolysis and pulse photolysis as well as ion cyclotron resonance are employed.

Electron spin resonance (ESR) and nuclear magnetic resonance (NMR) are the powerful tools for investigating the phase composition, electronic structure of catalysts and processes, proceeding between reaction components and active sites of catalysts. Radioisotopes and ionizing radiation are used to study kinetics and mechanisms of heterogeneous reactions.

Photoelectron and Auger spectroscopy provides information about the surface chemical composition of heterogeneous catalysts and electronic structure of adsorbed atoms and molecules. Usually these methods are complemented with thermodesorption and low energy electron diffraction (LEED) technique.

Synchrotron radiation opens new possibilities to study catalytic properties (charge of active component, radii of coordination spheres, coordination numbers of atoms, surface composition). The complementary methods of small angular scattering (evaluation of size and size distributions of microparticles and micropores with computer data processing), X-ray, photoelectron spectroscopies and EXAFS (extended X-ray analysis of structure) are commonly used. Various modifications of EXAFS method are in progress: fluorescence EXAFS for studying the bulk and supported catalysts containing small concentrations of active component and Auger-EXAFS for determining the composition and structure of catalyst surface and adsorption events.

DIRECTIONS OF RESEARCH

Fundamentals of Homogeneous, Heterogeneous Catalysis and Catalysis with Enzymes

Fundamentals of Catalysts Preparation

Development of New and Improvement of Existing Catalysts and Catalytic Processes

Mathematical Modeling and Chemical Engineering of Catalytic Processes

Automation of Catalytic Research

A fruitful combination of fundamental and applied research is a basis principle of the Institute activity. All applied investigations use novel results of fundamental science, bring them into practice promoting and enriching the academic science with practical knowledge and experience. The Institute is a leader of R&D company named MNTK "KATALIZATOR" arranged to solve key problems in design and implementation of new generations of highly efficient catalysts and catalytic processes. MNTK "Katalizator" was founded in 1985 due to the vital necessity to concentrate scientific forces and means in industrial catalysis providing 10-15% of the overall national produce.

The International Center for Catalysts' Characterization and Testing was established in 1991 on the basis of Boreskov Institute of Catalysis and MNTK "KATALIZATOR". The center performs complex research in fundamental and applied catalysis. Highly educated specialists trained in various trends of science contribute to the Center activities. Within a short time it is possible to obtain a unique combination of data on the structure of active sites, detailed reaction kinetics and mechanisms and to apply these data for design of new catalysts and processes desired. The Center arranges and brings to practice projects required by various organizations from Russia and foreign countries, as well as bilateral and multilateral projects.

INSTITUTE OF CATALYSIS DEALS WITH THE CATALYTIC PROCESSES:

- Chemistry and processing of gas and oil: catalytic conversion of various hydrocarbons including methane, hydropurification and hydrodemetallation.
- Synthesis of organic and inorganic chemicals: oxidation of SO_2 to SO_3; synthesis of methanol, partial oxidation of alkanes, alkenes, alcohols, aromatics; polymerization of olefins; synthesis of organic sulfides and amines; etc.
- Fine organic synthesis: synthesis of biologically active substances, vitamins, herbicides, aminoacids, etc.
- Synthesis of new materials: carbon-carbon, carbon-mineral and mineral-mineral composites.
- Processes of energy conversion: catalytic combustion and heat generation systems, solar energy conversion, high temperature fuel cells, etc.
- Processes for environmental protection: catalytic detoxication of industrial wastes including those containing organics, carbon monooxide, compounds of sulfur and nitrogen, purification of automotive exhaust gases and wastes from thermal power plants.

THE SOURCE OF RESEARCHERS

Education of research personnel plays a great role in the Institute activities. It is a part and parcel of teaching students at High School and University and their direct participation in research activities of the Institute. This brings a possibility to attract talented young people and to train them for independent creative work. Many leading researchers of the Institute work as instructors at the Novosibirsk State University providing a high level of teaching and continuous improvement of education programs with respect to the progress of the world science attracting young highly skilled students to participate in the Institute activities.

INTERNATIONAL COOPERATION

Boreskov Institute of Catalysis is in continuous contact with scientific centers over the world. In 1980 the Institute received the international award "Golden Mercury". In 1992 its Program of International Cooperation has encompassed the contacts with the Research Society of Germany: Institute of Inorganic Chemistry in Munich in the field "Preparation and Study of Metal Catalysts Supported on Carbon", Institute of Physical Chemistry of Munich University in the field "Catalytic Chemistry of Carbon", Institute of Inorganic and Analytic Chemistry of Mainz University in the field "Synthesis and Study of Wide Pore Zeolites". The joint research program was started with the Institute of Crystallography and Mineralogy of Frankfurt University: "Investigation of Catalyst Structure with Neutronography and Precise X-Ray Analysis". Together with the London Royal Institution (UK) a theoretic study of diffusion and molecular reagent reactions in the zeolite pores via molecular mechanics and molecular dynamics was performed. The mechanism of oxygen and ammonia interaction with the surface of copper monocrystal with electron spectroscopy was studied in cooperation with Yale University (Cardiff, UK). Within the framework of International Cooperation Program between RAS and National Research Center (CNRS) of France investigations of the problem "Catalysis and Environment" are in progress. Long term joint fundamental research with Science and Technology Department of India and RAS provided interesting results. Collaboration with Lanjow Institute of Chemical Physics (China) concerns photocatalysis. In progress are joint "Theoretical Studies of Zeolites with Quantum, Monte Carlo and Molecular Dynamic Methods" with the University of Milan (Italy).

A fruitful collaboration has been attained with the Institute of Energy Conversion and Storage of Messina (Italy) in the complex program: "Catalysis and Energy Conversion". X-ray diffraction studies of structure and chemical properties of highly dispersed supported metals have been started within the program "Physics and Chemistry of Highly Dispersed Materials". The principles of cooperation in investigating catalysis and catalytic processes with the Center of Molecular Research in Seoul (Korea) were postulated. Numerous contacts with researches from the Netherlands, Sweden, Finland, Mexico, Japan, Austria, Romany, Yugoslavia, etc., were provided. Guest researchers from various countries participated in seminars, meetings, talks, probations, discussions at the Institute of Catalysis, which contributes significantly to international cooperation and tends to expand the spheres of research contacts in fundamental and applied catalysis.

PARTICIPATION IN CONFERENCES AND EXHIBITIONS

In 1992, 43 researchers of the Institute took part in 20 international conferences and symposia abroad, 12 researchers were the participants of the 10th ICC in Budapest (Hungary).

The Institute of Catalysis organized the International Meeting "Zeolite Catalysis for the Solution of Environmental Problems" in Yaroslavl (Russia) with 21 quest foreign researchers. The 2nd Meeting "Monolith supports and catalysts with honeycomb structure" was held in Novosibirsk (Russia) in October 1992. The broadened session of Scientific Council of the Institute devoted to 85 anniversary of academician G.K.Boreskov united the leading scientists of Russia, Byelorussia, Ukraine (Novosibirsk, April 1992). An International Seminar "Instruments of "Micromeritics Co" (USA) for Studying the Texture Catalysts and other Porous Materials" was held at the Institute in April, 1993.

The Institute of Catalysis participated in International Exhibitions: "Chemistry-92" (Moscow, Russia), "Siberia-Chemistry-92" (Novosibirsk, Russia), "Medfarm-92" (Novosibirsk, Russia), "Intersib-92" (Omsk, Russia), Science and Technology Fair (Hannower, Germany), Fair "West-East" (Strasbourg, France), "Russian Fine Technologies" (Vienna, Austria) and exhibitions of Russia: "Oka - Pure River" (Moscow), "Ecology of Novosibirsk" (Novosibirsk)

CAMPUS AND RESIDENCE

Boreskov Institute of Catalysis is situated in Akademgorodok (Siberian Scientific Center) at 30 km from Novosibirsk, the largest city of Siberia. The residence of Akademgorodok is a picturesque place near the Ob Lake. It is surrounded by forest and is pleasant not for the work only but for recreation as well. Silence, beautiful landscape, pure air are the factors promoting scientific activity and creativity.

RESEARCH ACTIVITY

CLUSTER QUANTUM-CHEMICAL STUDY OF ADSORPTION OF METHANE AND CARBON MONOXIDE ON ZINC AND ON MODIFIED MAGNESIUM OXIDE SURFACES

N.U. Zhanpeisov, G.M. Zhidomirov,

M.Baerns(Ruhr Universitat Bochum, Germany)
Surface Sci., to be published

A modified MINDO/3 method is used to study the interactions of methane and carbon monoxide with a zinc oxide and with a modified magnesium oxide surfaces by a supermolecular approach. The latter catalyst corresponds to a lithium promoted magnesium oxide doped by the zinc oxide (Zn/Li/MgO). Zinc oxide was modelled by a $Zn_{16}O_{16}$ four layer molecular cluster and magnesium oxide - by a $Mg_{32}O_{32}$ one; both molecular clusters contain all types of low-coordinated Zn^{2+}_{LC} and O^{2-}_{LC} or Mg^{2+}_{LC} and O^{2-}_{LC} ions of various faces, edges, corners, etc. Molecular clusters of Zn/Li/MgO were calculated via the substitution of one Mg^{2+}_{LC} by Li^{+}_{LC} and proton and another Mg^{2+}_{LC} by Zn^{2+}_{LC}.

The calculated heats of dissociative adsorption of methane on the various pairs of acid-base sites of ZnO surface show the $Zn^{2+}_{2C} - O^{2-}_{3C}$ pair of centers to be responsible for the initial activation of methane. Results obtained for Zn/Li/MgO allows one to explain why the selectivity of oxidative coupling of methane reactions on a NaOH/CaO catalyst increases when the catalyst contains only small amounts of Zn^{2+} ions.

Carbon monoxide adsorbs on a polar (0001) surface of zinc oxide in the on-top position with C atom directed towards Zn^{2+}_{3C}. The heat of CO adsorption and its dependence on CO coverage and the CO bond stretching vibrational frequency ν_{CO} calculated by the harmonic oscillator approach are in good agreement with experimental data available.

CO MOLECULE ADSORPTION ON Zn OXIDE AND Al CONTAINING OXIDE SYSTEMS: CLUSTER QUANTUM-CHEMICAL MINDO/3 STUDY

N.U. Zhanpeisov, G.M. Zhidomirov

Zh. Strukt. Khim., 35 (1994) 12-16

A modified MINDO/3 method is used to study carbon monoxide adsorption on zinc oxide and aluminium containing oxide systems within a supermolecular approach. The former was modelled by a $Zn_{16}O_{16}$ four-layer molecular cluster, the latter - by a six-member octahedra with a composition of $Al_6O_{24}H_{30}$. These molecular clusters allow to consider all types of low-coordnated zinc and oxygen ions belonging to various surface irregularities and the formation of a lone and/or pair Lewis acid sites (LAS) on aluminium containing oxide systems, respectively.

Geometry of both CO molecules and various adsorption complexes was completely optimized to the total energy minimum with regard to structural relaxation at the active sites of oxide surface.

Carbon monoxide adsorbs on a polar (0001) surface of zinc oxide and on the five-coordinated Al^{3+}_{5C} of aluminium-containing oxide systems in the on-top position with C atom directed towards the LAS. The calculated heats of CO adsorption and its dependence on the coverage, calculated by the harmonic oscillator approach, and CO bond stretching vibrational frequency ν_{CO} are in a good agreement with the experiment data available.

CLUSTER QUANTUM-CHEMICAL MINDO/3 STUDY OF DMMP MOLECULE INTERACTION WITH A DEHYDROXYLATED MAGNESIUM OXIDE SURFACE

N.U. Zhanpeisov, G.M. Zhidomirov

J. *Phys. Chem.*, to be published

Magnesium oxide in the form of nanoscale particles with the ultra-high surface area can be used for air purification and as a reagent, immobilizing and destroying hazardous chemicals. Herein we report on the theoretical MINDO/3 studies of dimethyl methyl phosphonate (DMMP) adsorption on a completely dehydroxylated magnesium oxide. The latter was modeled by molecular clusters of Mg_9O_9, $Mg_{12}O_{12}$, $Mg_{24}O_{24}$ and $Mg_{32}O_{32}$, containing all possible types of chemically active low-coordinated magnesium and oxygen ions. Geometry of both DMMP molecule and various chemisorption complexes was optimizaed to the overall energy minimum with regard to structural relaxation at the active centres (AC) on the oxide surface.

According to experimental data available [1,2], the strong adsorption of DMMP occured on magnesium oxide proportionally to the surface area. On the basis of calculations two various mechanisms of DMMP adsorption, a plausible mechanism of DMMP destructive decomposition and some other problems are discussed.

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NON-EMPIRICAL CALCULATIONS FOR THE INTERACTION OF DIHYDROGEN WITH HYDRIDE AND ALKYL COMPLEXES OF BORON, ALUMINIUM AND TITANIUM

I.I. Zakharov, G.M. Zhidomirov, V.A. Zakharov

J. Molec. Catal., 68 (1991) 149-157

Woodward-Hoffman rules of orbital symmetry based on correlation diagrams of molecular orbitals for the transition from reactants to reaction products are known to improve the understanding of organic reaction mechanisms [1]. However, the attempt to generalize these rules for catalytic systems provided no positive recommendations [2].

Since a catalyst is not a reaction product, it is more reasonable to consider the transition state and its energetic stability as a factor reflecting the action of the catalyst. These characteristics determine the height of energy barrier and a more advantageous reaction pathway. Node properties of wave functions are indeed dominating for the principles of the orbital symmetry. The symmetry itself is a factor of these properties. Therefore, the orbital symmetry conservation law may serve as a rule of conserving the node properties of molecular orbitals. Thus, if the interaction of boundary molecular orbitals (MO) of reacting fragments provides the formation of additional nodes in the orbital structure of the transition state (TS), then this TS will be less stable than that formed with no additional nodes. (The orbital with a greater number of nodes corresponds to a higher energy [3]).

For illustration of a rule for conserving the node properties of boundary MO's, reaction X_2MR+H_2 —> X_2M-H+RH (M=B,Al,Ti; R=H,CH_3; X=H,F) was studied by *ab initio* calculation with a double-basis set. The electronic correlation according to the Moller-Plesset perturbation theory at the fourth order was also taken into account.

The structures of transition states were rigorously located and determined via diagonalizing the matrix of force constants. The calculated activation energies are in a good agreement with the conservation rule for the node properties of TS of molecular system.

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NON-EMPIRICAL CLUSTER MODEL CALCULATIONS OF H2O ADSORPTION ON Ni(III)

I.I. Zakharov, V.I. Avdeyev, G.M. Zhidomirov

Surface Sci., 277 (1992) 407-413

The cluster model for Ni(III) surface is simulated by the surface cluster Ni_{10} calculated by *ab initio* method with a modified effective potential. H_2O adsorption is calculated with regard to the four-valence GVB pairs of a water molecule. The calculated structure of the adsorbed H_2O monomer with inclined molecular axis (α=35-60^0) and adsorption energy (E_{ads} ca. 50-70 kJ/mol) is in agreement with experimental results. Earlier this bonding of isolated molecule of H_2O with Al(100) and Cu(100) has been theoretically confirmed by the density functional method, while the calculations by *ab initio* Hartree-Fock method even accounting for the correlation energy have not confirmed the "tilted" geometry.

With our calculations, the critical effect of d orbitals of the oxygen atom on the structure of the adsorbed H_2O monomer is recognized.

The nature of H_2O monomer bonding to the surface depends mostly on characteristics of the H_2O lone pairs. The GBV splitting energy of σ-lone pair is smaller than that of π-lone pair. This characterizes σ-lone pair as the electron pair of a more spatial spreading providing the maximum overlap with the orbitals of surface atoms. On the other hand, the ionization potential of π-lone pair is much less than that of σ-lone pair. This characterizes π-lone pair to be more reactive as the electron donor. Thus, prevailing σ-lone pair in the orbital overlap together with the predominance of π-lone pair in electron donation drives the competition between σ- and π-lone pairs for the maximum bonding to the surface. This results in the "inclined" geometry of the adsorbed H_2O.

THEORETICAL ANALYSIS OF CH4 CONVERSION ON Ni(100) SURFACE

V.I. Avdeev, G.M. Zhidomirov

Kinet. Katal., 2 (1994).

In the framework of the *ab initio* Hartree-Fock cluster model calculations the energy profile of methane dissociative adsorption on Ni(100) surface has been analyzed.

The stationary points of reactive path of CH_4 decomposition to CH_3 and ·H, the corresponding molecular adsorption, transition state (activated complex) and reaction products have been defined.

Data analysis shows, that methane molecular adsorption is regulated by the electron accepting properties of Ni surface. Meanwhile, dissociative adsorption of CH_4 requires electron donating properties of Ni surface.

For $CH_4/Ni_{20}(100)$ system we have calculated molecular adsorption heat (50 kJ/mol), reaction heat (88 kJ/mol) and the barrier (54 kJ/mol) of methane decomposition to CH_3 and H.

QUANTUM-CHEMICAL STUDY OF TITANIUM SILICALITE STRUCTURE

I.V. Yudanov, V.I. Avdeev, G.M. Zhidomirov

Submitted to 10th Intern. Zeol. Conf., Garmisch-Partenkirchen, Germany, 1994

Titanium silicalites of ZSM-5 and ZSM-11 structure are known to be efficient catalysts for selective oxidation of hydrocarbons. Tetracoordinated Ti^{4+} ions responsible for catalytic activity are assumed to be substituted isomorphously by Si^{4+} ions in the crystal framework (Fig. 1) [1]. However, Trong On et al., using the EXAFS and XANES spectra analysis, have suggested a certain defect structure (Fig.2) resulting from the Ti^{4+} incorporation into the crystal [2]. In order to investigate the reliability of these two structures, we have performed *ab initio* quantum chemical calculations of corresponding molecular cluster models.

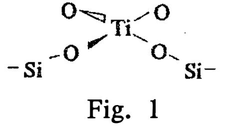

Fig. 1

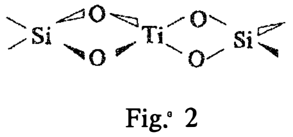

Fig. 2

Structures 1 and 2 were modeled by $Ti(OH)_2(OX)_2$ (X = H, SiH_3, $SiH_2(OH)$, models a,b,c) and $H_2Si\genfrac{}{}{0pt}{}{O}{O}Ti\genfrac{}{}{0pt}{}{O}{O}SiH_2$ (d) molecular clusters, respectively. We performed *ab initio* Hartree-Fock calculations using the effective core potential approximation to describe the inner core electrons of Ti and Si atoms. Gaussian-type basis set for valence electrons was of double-ζ quality.

The optimized geometry of cluster (d) of symmetry D_{2d} is characterized by the following parameters: Ti-O and Si-O bond lengths are 1.79 and 1.72 Å, O-Ti-O, Ti-O-Si and O-Si-O angles are 83^o, 95^o and 87^o, Ti-Si distance is 2.60 Å. This cluster can be obtained from cluster (c) if two H_2O molecules are eliminated. Comparing the energies of these clusters we can estimate the relative stability of structures 1 and 2. The latter appears to be by 107 kcal/mol less stable if we compare it with the completely optimized model (c). From the calculated energy difference we can not, of course, exclude the formation of structure 2 during the initial zeolite synthesis. But we can expect it to be easily and irreversibly destroyed at the further sample treatment. For example, being hydroxylated once, this structure will not be restored in the course of dehydroxylation but likely rearrange to structure 1.

Knowing the structure of Ti^{4+} placed in the framework we can investigate theoretically the models of intermediates [1-3] from the data on titanium silicalite treatment by H_2O_2 involved in the oxidation of hydrocarbons.

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AB INITIO CALCULATIONS FOR THE INTERACTION BETWEEN THE HYDRATED Fe^{2+} ION AND THE MOLECULAR OZONE

I.I. Zakharov, I.V. Yudanov, G.M. Zhidomirov

Zh. Strukt. Khim., 35 (1994) 32-39

Electronical and geometrical structure of different iron aqua complexes Fe^{2+} and Fe^{3+} were calculated by *ab initio* SCF-MO-LCAO method with the minimal basis sets. High-spin and low-spin states of these complexes as well as its interaction with molecular ozone were considered.

The general chemical scheme of intrasphere interaction between the hydrated Fe^{2+} ion and molecular ozone in acidic and basic medium was suggested with regard to calculations and experiment. The intermediate oxo complex of the ferril-ion FeO^{2+} type was shown to play the key role in the mechanism of this interaction.

NDDO/MC: A NEW SEMI-EMPIRICAL SCF MO METHOD FOR TRANSITION METAL COMPLEXES. PARAMETRIZATION FOR H, C, N, O, Si, Al, Fe, Co AND Ni

M.Yu. Filatov, I.L. Zilberberg, G.M. Zhidomirov

Int. J. Quant. Chem., 44 (1992) 563

A new semi-empirical SCF MO procedure available for prediction of transition metal complexes binding energy and molecular geometry has been developed. The peculiarities of this method are: (i) an explicit account of the orthogonality of the basis set; (ii) use of a new formula for the resonance integral; (iii) an effective account of the Coulomb correlation of electrons in the calculation of the two-electron integrals based on the approach of a model Coulomb nole function. The parametrization for H, C, N, O, Si, Al, Fe, Co and Ni was elaborated. The results of NDDO/MC (NDDO for Metal Compounds) calculations of molecular geometries and binding energies for a number of organic compounds and more than 40 ferrum, cobalt and nickel complexes were compared to available experimental and *ab initio* data. The average absolute errors for the binding energies are 5-10 kcal/mol.

THE NATURE OF SUPERACTIVE CENTERS IN H-ZSM-5 ZEOLITES. QUANTUM-CHEMICAL CALCULATIONS

M.Yu.Filatov, A.G.Pelmenshchikov, G.M.Zhidomirov

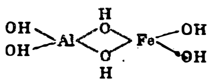
10th Intern. Congr. Catal., Hungary, 1992.
Preprint and Abstract Book, p. 31-33

The results of the experiments [1] point to the existence of unusual Fe-containing catalytic centers in the H-FeZSM-5 zeolites. In the reaction

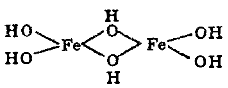
$$N_2O + Z \longrightarrow N_2 + OZ, \qquad (1)$$

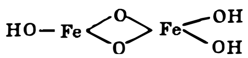
these centers are by 2 orders of magnitude more active than the iron atoms of Fe_2O_3 surface. A form of oxygen produced in reaction (1) exhibits the enormously high activity in selective oxidation of aromatic compounds.

In accordance with the known experimental data, we associate the catalytic properties of this system with the super-fine hydroxide forms like



or



forming during the initial stages of zeolite thermal decomposition. The NDDO/MC calculations showed, that the dehydroxylation of the latter structure results in the formation of  $HO{-}Fe{<}^{O}_{O}{>}Fe{<}^{OH}_{OH}$ cluster which can exhibit extraordinary catalytic properties in of N_2O decomposition and benzene oxidation. At the same time Al-containing structure was not so efficient in this reaction.

AB INITIO CALCULATIONS FOR DISSOCIATIVE CHEMISORPTION OF H_2O ON NICKEL

V.I. Avdeyev, I.I. Zakharov, G.M. Zhidomirov

Many catalytic processes on transition metals are known to involve H_2O either as a reactant or as a product.

In our articles [1-3], we have presented some energetical aspects of relationships between the associative and dissociative adsorption of water on nickel.

Three surface reactions in cluster approximations were studied:

$$H_2O_g \longrightarrow H_2O_s \qquad (1)$$

$$H_2O_s \longrightarrow H_s + OH_s \qquad (2)$$

$$H_2O_s + O_s \longrightarrow 2\ OH_s \qquad (3)$$

The first reaction is a molecular adsorption of water, the second and third - dissociative adsorption on a “clean” (2) and modified by oxygen (3) surfaces. For all cases stationary points have been found on the reaction path. On a “clean” surface of Ni(100) the heat of molecular adsorption of H_2O is $Q = 9$ kcal/mol, the activation energy of dissociation, $E_{diss} = 31$ kcal/mol, the reaction heat, $H = 26$ kcal/mol.

At modification of the surface by oxygen, the activation energy decreases sharply to $E_{diss} = 4$ kcal/mol.

A promoting influence of oxygen on dissociative adsorption relates to localization of a positive charge on the surface in the vicinity of the sites for reaction product adsorption.

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THEORETICAL STUDY OF THE MECHANISM OF RADICAL CATION FORMATION UPON AROMATIC HYDROCARBON ADSORPTION ON ZEOLITES

I.V. Yudanov, I.I. Zakharov, G.M. Zhidomirov

React. Kinet. Catal. Lett., 48 ,2 (1992) 411-417

Ab initio quantum-chemical calculations are carried out for certain lattice structures that are hypothetically essential in the electron transfer from the aromatic compounds. The role of molecular oxygen in the formation of electron accepting centers is studied. The calculated electron affinity of O_2-$Al(OH)_3$ cluster modelling adsorption of oxygen on the Lewis acid site is equal to 2.2 eV. This cluster is suggested to be a center for electron trapping during the hydrocarbon radical cation generation. As a result of electron transfer the structure O_2^--$Al(OH)_3$ is formed. A hypothetical route for further chemical conversion of O_2^- anion via HO_2 radical formation as a result of interaction with terminal or bridging hydroxyl group is suggested. The HO_2 radical possesses a high mobility and can migrate from the system due to recombination and various chemical reactions. The suggested hypothesis permits to explain the failure of experimental attempts to observe the conjugative anion-radical form.

THE DEVELOPMENT OF THE GREEN FUNCTION TECHNIQUE FOR CALCULATIONS OF THE SURFACE ELECTRONIC STRUCTURE FOR SEMI-INFINITE CRYSTALS

V.M. Tapilin

Zh. Strukt. Khim., 35 (1994) 17-24
Zh. Strukt. Khim., 35 (1994) 127-129

We propose an efficient method for constructing the Dyson equations for the Green function of semi-infinite crystals. The technique is applied for self-consistent calculations of Cu, Ag, Au, Ni, Pd, Pt and Ir(III) surface electronic structures in the LMTO-TB approximation.

THE WANNIER FUNCTIONS IN CALCULATIONS OF THE SURFACE ELECTRONIC STRUCTURE OF CRYSTALS WITH COMPLEX UNIT CELLS

V.M. Tapilin

Surface Sci., to be published

The Wannier function representation is shown to simplify drastically the calculations of the surface electronic structure especially for the crystals with a complex unit cell. The representation permits to make simple estimations of what happens with the electronic structure when going from a bulk to the surface. Only the bulk band structure calculated with some method or received experimentally is needed for these estimations. As an example, the local density of states on the surface of the high-T_c superconductor $YBa_2Cu_3O_7$ in the vicinity of the Fermi energy at the center of the surface Brillouin zone has been calculated.

THE LINEAR MUFFIN-TIN ORBITALS (TIGHT-BINDING) DIRECT SCREENING METHOD FOR CALCULATIONS OF THE ELECTRONIC STRUCTURE OF CRYSTALS

E.M. Borovskoy*, A.Ya*. Kraftmaher(Inst. Neorg. Chem. SB RAN, Novosibirsk), V.M. Tapilin

J. Phys.: Condens. Matter, 4 (1992) 1069

A new version of the tight-binding representation of the linear muffin-tin orbital method based on the direct-screening of the muffin-tin orbitals (LMTO-TB-DS) is presented. The equation for the screened basis wave functions, the screened structure matrix and the corresponding Hamiltonian are obtained. Test calculations of chromium and $YBa_2Cu_3O_7$ band structures proved the validity and accuracy of the method.

PROGRAM COMPLEX FOR ELECTRONIC STRUCTURE CALCULATION BY SCF-Xα-SW METHOD

S.F. Ruzankin

The program complex realizes completely the self-consistent field Xα scattered wave method. The complex consists of several programs:

Xα OMEGA is a basic program for calculating SCF potentials and ene-electron spin-orbitals.

Xα CONTINUOUS calculates XANES and EXAFS spectra in energy regions of photoelectrons up to 1000 eV.

Xα PROPERTIES calculates physical parameters of systems (dipole and quadrupole moments, diamagnetic susceptibility tensor, electric field gradient tensor, isotropic diamagnetic shielding, anisotropic hyperfine coupling tensor, etc.).

Xα MAPS builds maps of spin orbitals and electronic density.

Xα DENSITY builds graphics of density of states and XANES and EXAFS spectra.

The complex is notable for minimum input data required, universality and automatism of calculations. Calculation algorithms are strongly optimized. Use of special methods allows to find close or degenerative one-electron states of large systems. Program takes into consideration various forms of boundary conditions (pseudoatoms, Madelung potential, etc.).

The complex is quite convenient for introducing the various forms of exchange-correlation potentials and self-interaction correction into program.

ULTRASOFT X-RAY SPECTROSCOPY OF nd-METAL OXIDES

P.V.Avramov (Inst. of Physics, Krasnoyarsk), S.F. Ruzankin

X-ray absorption spectroscopy ranging from the soft X-ray to the extreme ultraviolet is rather complex and informative. There is a possibility to obtain spectra with a higher resolution, as well. Such specific peculiarities of the spectra as Cooper minima and Giant resonances are theoretically investigated in detail only for atoms. No systematic theoretical investigations of absorption spectra of molecules and solids in the 50-300 eV energy region have been carried out until now.

Ultrasoft X-ray absorption spectra of Ti, Cu, Y, Ba, La and Ce oxides in XANES and EXAFS energy regions have been studied by the SCF-Xα-SW method.

The spectra were shown to depend strongly on the chemical bonding. In all absorption spectra of nα-metal oxides, with initial one-electron subvalent states, Cooper peculiarities can be found from both the change of peak intensity ratio relative to that in the spectra of core level excitations and the form of traditional Cooper minima. In the spectra, where according to the dipole selection rules, two types of state (s- and d- or p- and f) are revealed upon the increase of the main quantum number n of the initial state, the relative intensities of components responsible for transitions into the states with minimum orbital moment l increase sharply due to the Cooper peculiarities observed in the channels of maximal l.

In the ultrasoft energy region the strong effects of spectra superposition are observed. These effects and the presence of Cooper peculiarities can appreciably hamper the traditional Fourier analysis of EXAFS spectra.

ADSORPTION DEPENDENCE OF VACANT ELECTRONIC STATE DENSITIES AS ADATOM ON LANTHANUM-OXIDE SURFACE

P.V. Avramov (Inst. of Physics, Krasnoyarsk), S.F. Ruzankin, G.M. Zhidomirov

Phys. Rev. B, 46 (1992) 6553-6559

The electronic structure of the lanthanum-oxide surface with the adsorbed As atom has been investigated by the $X\alpha$ method. Analysis of electron density of the occupied states and maps of the valence electron charge density for the bulk and adsorbed surface clusters show the pronounced differences related to the As p^- and La s + La sd state hybridization. With the change of As oxidation degree below threshold structures of the As K-, As $M_{4,5}$- and O K - spectra also change due to the As 4p+O 2p band filling. Intensity increase at the threshold of La $N_{4,5}$-spectrum (La f-states) is apparently connected with a monotonous growth of electron charge on As atom.

QUANTUM-CHEMICAL SCF-$X\alpha$-SW INVESTIGATION OF La_2CuO_4 SURFACE VACANT ELECTRON STATES

P.V.Avramov (Inst. Phys., Krasnoyarsk), S.F. Ruzankin, G.M. Zhidomirov

Phys. Rev. B., 46 (1992) 6495-64500

The vacant electronic states of the La_2CuO_4 surface, formed by a cleft between two La-O layers have been studied by the SCF-$X\alpha$-SW method on $Cu_4O_{12}(La_5O_4)_2^{2-}$ and $Cu_4O_{12}(La_5O_5)_2^{6-}$ clusters. It was shown, that the vacant electronic states of La_2CuO_4 surface do not practically differ from those in the bulk. It was explained by the fact that in spite of appreciable changes in the density of one-electron states near the Fermi-level in the thin film modeled, a spatial distribution of the total electron charge remains practically unchanged.

SCF potentials and wave functions of the initial states have been calculated by the modified version program $X\alpha$ OMEGA, the final states and absorption spectra were calculated by program $X\alpha$ CONTINUOUS.

SCF-$X\alpha$-SW CALCULATION FOR THE CORE AND VALENCE LEVEL COORDINATION BEHAVIOR OF LOW-COORDINATED OXYGEN IONS ON THE SURFACE OF MAGNESIUM OXIDE

E.P. Mikheeva, S.F. Ruzankin, G.M. Zhidomirov

Submitted to *Surface Sci.*

The core 01s and valence 02s-, 02p levels for the low-coordinated (2,3,4,5) surface oxygen ions have been calculated by $X\alpha$-scattered wave method. All calculations were performed with the modified program version $X\alpha$ OMEGA including Madelung potential.

It was shown that the binding energy for the 1s, 2s and 2p oxygen states decreases with the lowering coordination. This can be explained by more considerable changes in Madelung potential as compared to that in the electron shell repulsion energy at varying the number of nearest magnesium ions.

EFFECT OF Ni(II) BINDING ON THE GUANINE TAUTOMERISM: QUANTUM-CHEMICAL NDDO INVESTIGATION

I.L. Zilberberg, G.M. Zhidomirov, I.Ya. Skuratovskii (Inst. Molec. Genetics, Moscow).

J. Molec. Struct. (Theochem), 285 (1993) 129-136

Using a new semi-empirical quantum-chemical method, the so-called NDDO/MC, some aqua and amine Ni(II) complexes with guanine nucleic base have been calculated. The results obtained allow to suggest that the most substantial action of transition metal is its influence on the keto-enol tautomerism of the base. The effect on the tautomerism is shown to result from a charge transfer from the guanine to form a coordinative bond with the Ni(II) complex. When the octahedral nickel(II) complex with the guanine is formed, a charge transfer from heterocycle is small and such a complex stabilizes the keto form. The formation of planar complexes facilitating a stronger transfer leads to the enol tautomer stabilization. As a consequence, these cations binding with guanine in nucleic acid can substantially increase the probability of nucleic base misparing.

THE EVALUATION OF THE HYBRID ONE-CENTER INTEGRALS USED IN THE SEMI-EMPIRICAL NDDO-TYPE METHODS FOR d-ELEMENTS FROM SPECTRA

I.L. Zilberberg, M.Yu. Filatov,
G.M. Zhidomirov

Int. J. Quant. Chem., 42 (1992) 439-444

When semi-empirical SCF MO methods based on the NDDO assumption are developed, the so-called one-centre hybrid integrals of (ab/cd) type are required. These integrals are expressed in terms of the Slater-Condon parameters (SCP) R_k(abcd) with different radial functions. We suggest to evaluate the SCP's from atomic spectra by taking into account the configurational interaction (CI). As an example, the R_1(sdpp), R_2(sdpp) and R_2(sddd) SCP's for Ti II and Ti III have been evaluated and values of these parameters are compared with those calculated with the Slater-type orbitals.

HARTREE-FOCK POTENTIAL ENERGY SURFACE FOR HIGHLY-SYMMETRIC STRUCTURES DESCRIBED BY NON-ROOTHAAN WAVE FUNCTIONS

B.N. Plakhutin, L.N. Shchegoleva (Inst. Organ. Chem.), G.M. Zhidomirov

J. Struct. Chem., 33 (1992) 3-11

A critical analysis of methodological problems is presented. These problems arise upon studying the antiaromatic molecules and their reactions within the framework of one-electron approximation.

For isomerization of the cyclobutadiene C_4 (D_{4h}), it was shown that the Hartree-Fock approach leads to serious incorrectness in the physical background (there are discontinuities in the wave function and/or its derivatives in the vicinity of the stationary points, crossing of leaves of the potential surface that correspond to the states with the same symmetry).

By means of the group-theoretical analysis we derived "the selection rules" on the force constants, that can be formally and correctly calculated by the Hartree-Fock method. In the Table we present the results of such analysis for a square molecule X_4 with electronic configuration e^2.

State	$k(a_{1g})$	$k(b_{1g})$	$k(b_{1u})$	$k(b_{2g})$	$k(e_u)$
$^3A_{2g}$	+	+	+	+	+
$^1B_{1g}$	+	-	+	+	+
$^1B_{2g}$	+	+	+	-	-
$^1A_{1g}$	+	-	+	-	-

Sign (+) means here that the force constant may be formally-correct by calculated by the Hartree-Fock method. Sign (-) means that such calculation is not possible. (The correct calculation is possible by more general methods only, such as CI or MC SCF).

EXACT EXPRESSION FOR THE FOCK OPERATOR IN THE GENERALIZED SCF COUPLING OPERATOR METHOD

A.V. Arbuznikov, B.N. Plakhutin

Dokl. Ros. Akad. Nauk, 324, 2 (1992) 349-352

The commonly used expression for the open-shell Fock operator [1]

$$\hat{F}_i = f_i\left[\hat{H} + \sum_j f_j (2a_{ij}\hat{J}_j - b_{ij}\hat{K}_j)\right] \qquad (1)$$

is believed to origin from the energy functional of type

$$E_{RHF} = 2\sum_i f_i H_{ii} + \sum_i\sum_j f_i f_j (2a_{ij}J_{ij} - b_{ij}K_{ij}) \qquad (2)$$

Carrying out the usual variational procedure with the energy functional (2), we derived a new formula for Fock operator

$$\hat{F}_i = f_i\left[\hat{H} + \sum_j f_j (2A_{ij}\hat{J}_j - B_{ij}\hat{K}_j)\right] \qquad (3)$$

differing from the previous one (eq. 1) only by the coefficients
$A_{ij} = (a_{ij} + a_{ji})/2$ and $B_{ij} = (b_{ij} + b_{ji})/2$

The difference between two formulas (eqs. (1) and (3)) is essential when the problem of symmetry of coupling coefficients a_{ij} and b_{ij} entering the energy functional (2) are discussed. Several ("non-Roothaan") states arising from the atomic configuration d^N are known to be correctly described by non-symmetric coupling coefficients only, i.e. $a_{ij} \neq a_{ji}$ and/or $b_{ij} \neq b_{ji}$, [2]. As follows from the present results that these coefficients must be symmetric for any state.

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COUPLING COEFFICIENTS FOR SYSTEMS WITH TWO OPEN ELECTRONIC SHELLS. TRANSITION-METAL IONS WITH p^Md^N CONFIGURATION

B.N. Plakhutin, A.V. Arbuznikov, A.B. Trofimov (State University, Irkutsk)

Int. J. Quant. Chem., 45 (1993) 363-383

We derived the necessary conditions to which the vector coupling coefficients (VCC)

a_{mn} and b_{mn}, describing atomic L, S multiplets of $p^M d^N$ and $d^N s^1$ configurations ($1 \leq N \leq 9$, $1 \leq M \leq 5$), should satisfy. It is shown, that for two-open-shell systems under consideration, the unknown VCC should satisfy not only usual restrictions resulting from the spheric symmetry, but also some additional equation, introduced in the present paper *in the form of a postulate.*

VCC obtained were used for the *ab initio* calculations (by the general SCF coupling operator method) of several transition-metal atoms and ions with electronic configurations $3d^1 4p^1$, $3p^5 3d^3$ and $3p^4 3d^3$. To check the presented theory, we comparied in detail these results with analogous data obtained by the atomic Roothaan-Hartree-Fock method.

THE NEW ALGORITHM FOR CALCULATION OF FORCE CONSTANTS MATRIX

V.P. Baltakhinov

Studies on force constant simulation using the frequencies of experimental spectra in harmonic approximation are still in progress. The solution of secular equation:

$$T^{-1}UL = L\Lambda \qquad (1)$$

with respect to the matrix of force constants U in the system of dependent internal coordinates (the changes of all valent bonds and angles, etc) is of particular interest. Here T^{-1} is the matrix of kinematic coefficients, Λ is diagonal matrix of square frequencies of normal vibrations, L is the matrix of normal vibration forms.

In [1], equation (1) was presented in the form:

$$U = T^{1/2} \sum \lambda_i H_i T^{1/2} + \Theta_1 V + V\Theta_1 - \Theta_1 V \Theta_1, \qquad (2)$$

where V is the arbitrary symmetric matrix, $\lambda_i = \omega_i^2$, ω_i are experimental frequencies, Θ_1 is spectral projector corresponding to zero eigen values of the matrix T^{-1}, $T^{1/2}$ is generalized inverse matrix, H_i are orthogonal projectors with the following properties:
(1) $\Sigma H_i = I$, where I is unit matrix;
(2) $H_i H_j = 0$, if $i \neq j$; (3) $H_1 = \Theta_1$.

The vibrational equation, rewritten in form (2), enables us to obtain an analytical solution, when the vibrational spectrum of a single molecule is known:

$$\hat{U} = T^{1/2} \sum \lambda_i^{exp} H_i^0 T^{1/2} + \Theta_1 U_0 + U_0 \Theta_1 - \Theta_1 U_0 \Theta_1 \qquad (3)$$

The matrix U reproduces λ_i^{exp} with given assignment on the forms of normal vibrations in the zero approximation of force constants U_0 and has the least deviation from U_0 in the euclidean norm. An *ab initio* or semi-empirical quantum chemical values are recommended to form matrix U_0. The solution obtained (3) is used for designing the general algorithm accounting for different additional information on the structure of matrix to be found. The algorithm developed simplifies the problem of vibrational spectrum simulation [2] if compared to the existing algorithms.

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Perspectives in Catalysis

A "Chemistry for the 21st Century" monograph

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PERSPECTIVES IN CATALYSIS: VIA STUDIES ON MOLECULAR LEVEL TO NEW INDUSTRIAL CATALYSTS AND PROCESSES

K.I. Zamaraev

Within the last three decades we have witnessed a progressive shift of catalysis science from phenomenological approaches to structural and mechanistic studies on the molecular level. Molecular design is already playing an important role in development of new industrial catalysts and catalytic properties. New ideas emerging from basic research in catalysis are promising technological breakthroughs that may change the profile of chemical industry and introduce catalytic processes into many other industries where nowadays they are not widely used. This will make these industries much more safe and ecologically pure, and improve worldwide the quality of life.

DESIGN OF CATALYSTS BASED ON METAL COMPLEXES

V.A. Likholobov

Possible approaches are demonstrated to the prognosis of catalytic properties for metal complexes and to the international design of catalytic systems, which are based on these complexes. The emphasis is made on catalytic reactions, involving olefins, carbon monoxide, hydrogen and oxygen. With reactions of these molecules as examples, it is demonstrated, how the data that are available nowadays about the mechanisms of activation of various molecules upon their coordination to metal atoms (ions), mechanisms of ligand rearrangements and stoichiometric reactions that are typical for certain metal complexes, can be used for the international design of various catalytic systems. When applied to metal complexes that are anchored to solid surfaces these approaches often permit one to prepare structurally organized catalytically active sites that can not be prepared in solutions. Examples of multi-substrate reactions of propylene hydroformylation and hydrocondensation of formaldehyde demonstrate, that such active sites that are structurally organized on solid surface can possess much higher activity and selectivity than catalysts having structurally disorganized active sites but made of the same components. When reaction mechanism is known well enough, it becomes possible to estimate a priori the changes in the catalytic properties of metal complexes upon rather wide variation of central atoms (ions), ligands and solvents. A promising trend in prognosis of catalytic properties of metal complexes can be also the design of special information-oriented or logic-oriented computer programs. Examples, demonstrating the potentialities of such computer programs for the prognosis of catalytic properties, are presented.

KINETIC MODELS OF HETEROGENEOUS CATALYSIS

G.S. Yablonskii (Touvivian Complex Department, Kyzyl, 667000, Russian Federation), V.I.Elokhin

Kinetic models of heterogeneous catalysis are discussed, including both the simplest Langmuir-Hinshelwood and Eley-Rideal models of reactions in ideal adsorbed layer and more complex model that account for reactions in real adsorbed layer. In particular, the models are considered, that take into account such phenomena as graphical and induced nonuniformity of the adsorbed layer; reconstruction of the catalyst surface upon its interaction with the reaction mixture; ordering of the adsorbed layer due to lateral interactions between adsorbed species; phase transitions in the adsorbed layer; critical phenomena such as multiplicity of kinetic hysteresis, self-oscillation of the reaction rates, slow relaxations in the vicinity of bifurcation point, etc. The results of mathematical analysis of the kinetic equations for various models of heterogeneous catalysis are discussed. The importance of kinetic studies for elucidation of detailed reaction mechanisms, as well as design and optimization of catalytic processes and reactors is outlined.

CATALYSIS FOR ENERGY PRODUCTION

V.N.Parmon, Z.R.Ismagilov, M.A.Kerzhentsev

The paper presents an overview of the modern trends in application of catalysis to energy industry. The catalytic are outlined that can provide conversion of one form of energy to another. Discussed are both a more traditional field of catalysis application to obtain heat via a controlled combustion of various fuels and nontraditional fields dealing with the use of catalysis in nuclear, solar and electrochemical energetics.

CATALYSIS AND NEW TECHNOLOGIES FOR SUSTAINABLE DEVELOPMENT

K.I. Zamaraev

Chemistry for Sustainable Development 1 (1993) 133-145

In the first part of the paper it is demonstrated how knowledge that comes from studies of catalysis at the molecular level helps to design new, very efficient catalysts and catalytic processes. In the second part the importance of catalytic technologies for providing sustainable development is discussed. It is demonstrated how catalysis helps:

- to protect the ozone layer,
- to combat the greenhouse effect,
- to create environmentally safer transport,
- to solve environmental problems of energy production,
- to prevent pollution by H_2S in gas and oil mining and by CH_4 in coal mining,
- to purify exhausts of chemical and various other industries,
- to provide the highest possible energy efficiency and minimize consumption of raw materials in the chemical, petroleum and other industries,
- to process renewable raw materials, such as biomass, into valuable chemicals.

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Catalysts and Adsorbents

K.I. Zamaraev and V.L. Kuznetsov

New Materials for catalysts and adsorbents created by molecular design will make industry in the 20th century much more effiicient and safe and improve worldwide the quality of life.

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ION-CYCLOTRON RESONANCE STUDY OF ELEMENTARY STAGES OF THE CATALYTIC OXIDATION OF CO BY N_2O IN THE PRESENCE OF VI A GROUP METAL IONS

A.V. Kikhtenko, V.B. Goncharov, K.I. Zamaraev

Catal. Lett., **21** (1993) 353-360

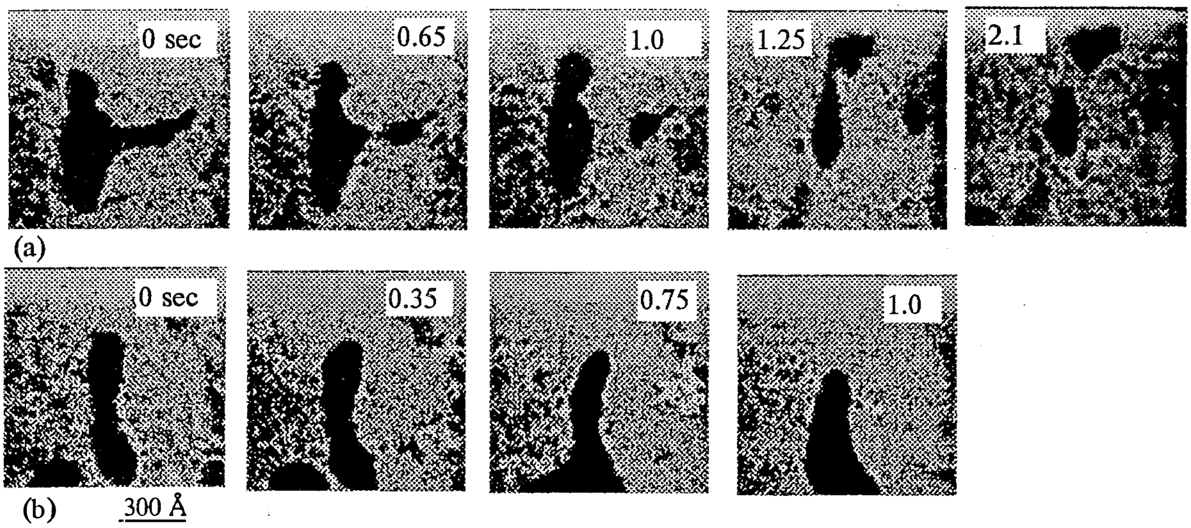
Gas phase reactions of Mo^+ and W^+ ions with the molecules of various oxidants (NO, O_2, N_2O, CH_2O, C_2H_4O) were studied using ion cyclotron resonance. In oxidation with N_2O the mono-, di- and trioxide metal cations are formed consecutively. The trioxide MO_3^+ ions of both metals react with CO to form CO_2 and MO_2^+ ions. In this way, catalytic reaction $N_2O+CO \rightarrow N_2+CO_2$ occurs in the gas phase with MoO_3^+/MoO_2^+ and WO_3^+/WO_2^+ couples as catalysts. The rate constants have been measured for both stages of the catalytic cycle as well as for the stages of the catalyst preparation. Metal-oxygen bond energies were estimated for MoO_x^+ and WO_x^+ species with various x. The mechanism of CO oxidation with MoO_x^+ and WO_x^+ cations as catalysts in the gas phase is discussed in comparison with that for oxidation over classical solid oxide catalysts.

FORMATION OF UNUSUAL LIQUID-LIKE Fe-C PARTICLES AND THEIR DYNAMICS ON THE SURFACE OF AMORPHOUS CARBON AT 920-1170 K

O.P. Krivoruchko, V.I. Zaikovskii and K.I. Zamaraev

Dokl. Akad. Nauk, Fiz. Khim.,
329 (1993) 744-748

An unusual liquid-like state of Fe-C particles supported on amorphous carbon is observed and characterized at 920-1170 K, i.e. at temperatures considerably lower than the melting temperatures of Fe-C eutectics (1420 K), pure Fe (1810 K) and carbide Fe_3C (1920 K). Liquid-like Fe-C particles form upon heating of α-FeO(OH) or α-Fe_2O_3 crystallites supported on amorphous carbon in vacuum. These liquid-like particles serve as catalytic intermediates of the amorphous carbon-to-graphite conversion.



Fragments of video film illustrating the movement of liquid-like Fe-C particles over the surface of amorphous carbon:

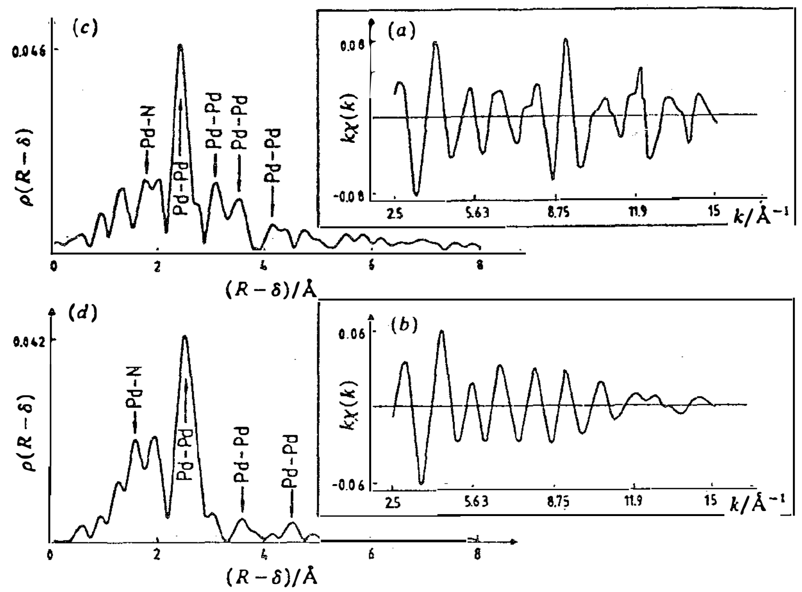
a - movement with a splitting of a bigger liquid-like particle into several smaller;
b - movement with a merging of two smaller liquid-like particles in a bigger one.

GIANT PALLADIUM CLUSTERS: SYNTHESIS AND CHARACTERIZATION

M.N.Vargaftik*, I.I.Moiseev* (Inst.Gener. & Inorg.Chem.,Moscow), D.I. Kochubey, K.I. Zamaraev

Faraday Discuss., **92** (1991) 13-29

A series of palladium clusters containing from four to several hundred Pd atoms in the metal skeleton has been prepared and characterized with respect to structure and chemical properties, including catalytic activity. For smaller clusters good agreement was observed between single-crystal X-ray and EXAFS structural data. Giant clusters approximating to $Pd_{561}L_{60}(OCOCH_3)_{180}$ (L=phen,bipy) and $Pd_{561}phen_{60}O_{60}X_{60}$ (X = PF_6, ClO_4, BF_4, CF_3CO_2) were characterized with TEM, SAXS, EXAFS, NMR and magnetic succeptibility data. These clusters contain a close-packed metal core and ligands L and X that are located at the periphery of a cluster. They are very soluble in water and polar organic solvents and can be considered as a bridge between low molecular clusters and particles of colloidal metals. Giant Pd clusters were found to be active homogeneous catalysts for various organic reactions, e.g., oxidative acetoxylation of alkenes and alkylarenes, oxidation of alkenes, formic acid and alcohols, dehydration of alcohols and formation of acetals. The kinetics and mechanism of the homogeneous oxidation of alkenes and HCO_2H in solutions of giant clusters were elucidated.



(a), (b) Pd K-edge EXAFS spectra and (c), (d) RDA curves for the surroundings of Pd atoms for 6 in the initial [(a),(c)] and relaxed [(b), (d)] forms.

PHOTOINDUCED ELECTRON TUNNELING REACTIONS IN CHEMISTRY AND BIOLOGY

Topics Current Chemistry, vol. 163,

K.I. Zamaraev, R.F. Khairutdinov

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3. Electron Tunneling in PET Reactions Involving Porphyrin Molecules

A comprehensive review is given of the works on electron tunneling at large distances in photoinduced electron transfer reactions. Evidence is presented showing that electron tunneling reactions are rather widely spread in photochemistry and photobiology. The ability to participate in such reactions is inherent in both excited and ground states of various organic and inorganic molecules and radical ions, transition metal complexes and clusters, porphyrins, redox sites of proteins, etc.

The regularities of photoinduced electron tunneling are discussed in detail. The most outstanding feature of electron tunneling is demonstrated to be its ability to provide the occurrence of both primary and secondary reactions of PET between remote electron donor and electron acceptor sites, at distances sometimes as great as several tens of angstroms. It is shown to be responsible also for rather unusual kinetic regularities of certain PET reactions. Electron tunneling can also provide a new type of photoinduced electron transfer reactions, i.e. PET simulated by illumination into the tunnel electron transfer band.

The rate of the tunnel PET reactions increases strongly when mediator centers are placed in the space between the donor and the acceptor. This effect is the more pronounced the smaller gap is between the energy of the tunneling electron and the energy levels of the mediator.

The ability of electron tunneling to provide PET at large distances is shown to open up unique opportunities in organizing photochemical conversions on the molecular level. These opportunities are widely used in photobiology as well as in photochemistry of: (1) specially designed organic molecules containing photochemically active electron donor and acceptor sites which are oriented in a certain fashion and linked together by one or several molecular bridges, and (2) photochemically active organized molecular assemblies such as molecular multilayers, micelles, vesicles, etc.

PHOTOINDUCED ELECTRON TRANSFER ACROSS MEMBRANES

Topics in Current Chemistry, vol. 159,

S.V. Lymar, V.N. Parmon and K.I. Zamaraev

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Vectorial photoinduced electron transfer (PET) across bilayer lipid and surfactant membranes provides a unique opportunity for the spatial separation of photochemically generated oxidants and reductants. In this chapter a review is given of the data on vectorial PET across the membranes of vesicles and planar bilayer membranes. The key steps that determine the efficiency of PET across membranes are discussed., i.e. (i) primary photochemical charge separation processes, (ii) secondary recombination reactions and (iii) electron transfer across membranes that provides stabilization of the charges generated in step (i). Step (iii) can be performed by three mechanisms: (1) via the diffusion of electron (or hole) carrier through the membrane, (2) via reactions of electron exchange between molecules located in different monolayers of a bilayer membrane and (3) via intramolecular electron transfer along bridging molecules, molecular wires and ultrafine semiconductor particles embedded into membranes. The possibility of conjugating PET across membranes with catalytic redox reactions is discussed with the emphasis on the water cleavage.

THEORETICAL AND EXPERIMENTAL STUDIES OF SOLAR CATALYTIC POWER PLANTS BASED ON REVERSIBLE REACTIONS WITH PARTICIPATION OF METHANE AND SYNTHESIS GAS

V.I. Anikeev, V.N. Parmon, V.A. Kirillov, K.I. Zamaraev

Int.J.Hydrogen Energy, **15**, 4 (1990) 275-286

The results of complex theoretical and experimental investigations of applicatibility of the thermochemical cycles based on reversible catalytic reactions of the "Methane reforming-methanation process" for the needs of concentrated solar energy utilization are presented. The data obtained evidence for practical possibility to obtain sufficiently high efficiency for both primary conversion of the concentrated solar light into well-stored energy of chemical bonds and conversion of the latter into high-potential heat. The experimentally registered values of efficiency exceeding 40% for the first process and 23% for the closed-loop system which allow obtaining heat at more than 700°C.

PROCESSES OF ELECTRON TUNNELING DECAY OF RADIATION INDUCED DEFECTS IN DISPERSED DIELECTRIC OXIDES

Yu.I. Aristov, V.N. Parmon, K.I. Zamaraev

Zh. Fiz. Khim., **65**, 6(1991) 1575-1591

The decay of radiation induced defects in MgO, Al_2O_3, CaO, SiO_2, Sc_2O_3 was shown experimentally to proceed by electron tunneling over large distances. At 77 K and within 10^3 s, electron tunnneling usually provides the decay of electron donor and electron acceptor defects, which are located at 15-35 Å from each other.

NEW POSSIBILITIES OF NMR IN MECHANISTIC STUDIES OF HOMOGENEOUS AND HETEROGENEOUS CATALYSIS

K.I. Zamaraev

J.Molec.Catal., **82** (1993) 275-324

Results are presented that demonstrate new possibilities provided by modern Fourier-transform NMR spectrometers in the mechanistic studies of both homogeneous and heterogeneous catalysis. As particular examples, are discussed: (1) *in situ* characterization of the intermediate alkylperoxo complexes of Mo(VI), V(V) and Co(III) in the course of homogeneous epoxidation of cyclohexene and oxidation of cyclohexane from simultaneously recorded ^{95}Mo, ^{51}V or ^{59}Co NMR spectra and ^{1}H, ^{17}O NMR spectra. (2) *In situ* characterization of reaction intermediates from the rates of paramagnetic ^{1}H and ^{13}C nuclear relaxation in the course of homogeneous decomposition of cumyl hydroperoxide in the presence of μ_3-oxotricobalt(II,III,III) acetate and μ_3-oxotriruthenium(III) acetate and propylene oxidation into propylene glycol by $CuCl_2$-I_2 catalytic system. (3) Characterization with ^{51}V NMR of a family of V(V) sites in supported vanadium catalysts. (4) Elucidation from a combination of ^{13}C CP/MAS NMR, ^{13}C 2D/MAS NMR and ^{2}H NMR of butyl silyl ether intermediates in the course of dehydration of butanols on H-ZSM-5 zeolite.

^{51}V SOLID STATE NMR STUDIES OF VANADIA BASED CATALYSTS

O.B. Lapina, V.M. Mastikhin, A.A. Shubin, V.N. Krasilnikov, K.I. Zamaraev

Progress in NMR Spectrsocopy, 24 (1992) 457-525

CONTENTS

COMPOSITION AND STRUCTURE OF PARAMAGNETIC COORDINATION COMPOUNDS IN SOLUTIONS: NUCLEAR SPIN RELAXATION RATES

K.I. Zamaraev, V.M. Nekipelov

Zh. Strukt. Khim., **31**, 4 (1990) 111-136

Theory and application of nuclear spin relaxation method, revealing the composition and structure of labile transition metal complexes in solution, have been considered. Method actual advantages and disadvantages are discussed. Conclusions on the method capacity in characterizing paramagnetic sites in solutions are made and the optimal strategy of such studies is outlined. Examples are given, which illustrate how the measurements of nuclear spin relaxation rates have enabled to elucidate the composition and structure of transition metal complexes in real chemical and biological systems.

ROLE OF ALKYLPEROXO COMPLEXES OF COBALT(III) IN CATALYTIC OXIDATION OF CYCLOHEXANE BY CUMENE HYDROPEROXIDE IN THE PRESENCE OF BIS (ACETYLACETONATO) COBALT(II)

E.P.Talsi, V.D. Chinakov, V.P. Babenko, V.N. Sidelnikov, K.I. Zamaraev

J. Molec.Catal., 81 (1993) 215-233

Alkylperoxo complexes of the Co(acac)$_2$(OOR)B family (acac is acetylacetonato ligand; R = PhMe$_2$C; B = Py, Py-d$_5$ or 3-Br-Py) were isolated and their role in the oxidation of cyclohexane with ROOH was studied.

According to the ^{1}H and ^{59}Co NMR data obtained in benzene solutions containing Co(acac)$_2$+ROOH+B, cobalt exists at 20°C mainly as the Co(acac)$_2$(OOR)B species. In benzene solutions of Co(acac)$_2$+ROOH that contain no B, cobalt exists mainly as three complexes of the Co$_x$(acac)$_y$(OH)$_z$ family.

Similar yields were found for various products of cyclohexane oxidation in benzene: cyclohexane = 1:1 solutions of Co(acac)$_2$+ROOH+B, where the alkylperoxo complexes of Co^{III} prevail, and of Co(acac)$_2$+ROOH, where alkylperoxo complexes were not detected. This suggests that the key intermediates of cyclohexane oxidation with the Co(acac)$_2$+ROOH and Co(acac)$_2$+ROOH+B are the same. Most probably, they are the free radicals RO$_2^\bullet$ and RO$^\bullet$. The role of cobalt catalyst consists in the generation of these radicals. The formation of alkylperoxo complexes in the presence of B inhibits, rather than promotes, the oxidation due to the capture of active radicals RO$_2^\bullet$.

ROLE OF VANADIUM ALKYLPEROXO COMPLEXES IN EPOXIDATION OF CYCLOHEXENE AND OXIDATION OF CYCLOHEXANE BY ORGANIC HYDROPEROXIDES IN THE PRESENCE OF BIS (ACETYLACETONATO)VANADYL

E.P. Talsi, V.D. Chinakov, V.P. Babenko, K.I. Zamaraev

J. Molec. Catal., 81 (1993) 235-254

Vanadium complexes formed from VO(acac)$_2$ as the starting material for the catalysts have been characterized *in situ* with ^{51}V and ^{1}H NMR and EPR in the course of three types of catalytic reactions: (1) decomposition of cumene and tert-butyl hydroperoxides in C$_6$D$_6$, (2) epoxidation of cyclohexene in C$_6$D$_6$: cyclohexene = 1:1 mixture and (3) oxidation of cyclohexane in C$_6$D$_6$: cyclohexane = 1:1 mixture. In the course of all three reactions VO(acac)$_2$ transforms initially into alkkylperoxo complex VO(acac)$_2$OOR and alkoxo complex VO(acac)$_2$OR, which further decompose to produce VO(OR)$_3$ and two other vanadium(V) species: an alkylperoxo complex I and an alkoxo complex II. VO(acac)$_2$OOR reacts with cyclohexene to form VO(acac)$_2$OR and cyclohexene oxide. I reacts with cyclohexene to form II and cyclohexene oxide and with ROH to form II and VO(OR)$_3$. II does not react with cylohexene but reacts with ROOH to form I. No acetylacetonate ligands have been detected in I or II with ^{1}H NMR. I is suggested to be the key species that permits cyclohexene epoxidation with ROOH under steady-state conditions. No complexes of I with cylohexene are observed with ^{51}V NMR. I does not react directly with cylohexane, but through the equilibrium $V^{V}O(OOR) \rightleftarrows V^{IV}O + RO_2^\bullet$ produces free radical RO$_2^\bullet$ that initiates oxidation of cyclohexane.

The latter complex serves as the active particle of epoxidation.

CHARACTERIZATION WITH ^{95}Mo, ^{17}O, ^{1}H NMR AND EPR OF ALKYLPEROXO, ALKOXO, PEROXO AND DIOLO MOLYBDENUM (VII) COMPLEXES FORMED IN THE COURSE OF CATALYTIC EPOXIDATION OF CYCLOHEXENE WITH ORGANIC HYDROPEROXIDES

E.P. Talsi, O.V. Klimov, K.I. Zamaraev

J. *Molec. Catal.*, 83 (1993) 329-346

Using ^{95}Mo, ^{1}H, ^{17}O NMR and EPR, we have characterized molybdenum(VI) complexes, formed in the course of catalytic epoxidation of cyclohexene with tert-butyl and cumene hydroperoxides. Dioxobis (acetylacetonato)molybdenum(VI) and hexacarbonyl molybdenum (O) were used as starting materials for the catalysts. Six new molybdenum (VI) complexes (I-VI) were detected. Complexes **I**, **II** and **III** are formed when ROOH is added to $MoO_2(acac)_2$ solutions in pure benzene. In benzene: cyclohexene:hydroperoxide mixtures complexes I-III are observed only at the initial stage of epoxidation process. Then, they are gradually replaced by complexes **IV-VI** that drive the catalytic cycle of epoxidation. The NMR spectra of complexes **IV-VI** are the same, irrespective of whether $MoO_2(acac)_2$ or $Mo(CO)_6$ have been used as the starting material for the catalysts. On the basis of ^{95}Mo, ^{1}H, ^{17}O NMR, EPR spectra and the reactivity studies, the following compositions for **I-VI** are suggested: **I** is alkylperoxo complex $MoO_2(OOR)_2$, **II** is alkoxo complex $MoO_2(OR)_2$, **III** is monoperoxo complex $MoO(O_2)(acac)_2$, **IV** and **V** are two types of MoO_2(1,2-diolo)$_2$ complexes (where 1,2-diolo is trans-cyclohexane-1,2-diol), and **VI** is alkylperoxo complex MoO_2(1,2-diolo)(OOR).

^{17}O, ^{95}Mo and ^{1}H NMR INVESTIGATION OF THE MECHANISM OF EPOXIDATION OF ALKENES WITH HYDROGEN PEROXIDE IN THE PRESENCE OF MOLYBDENUM COMPLEXES

E.P. Talsi, K.V. Shalyaev, K.I. Zamaraev

J. Molec. Catal., 83 (1993) 347-366

^{17}O, ^{95}Mo and ^{1}H NMR was used to study the composition and reactivity of molybdenum(VI) complexes formed in the course of catalytic epoxidation of cyclohexene and allylic alcohol with hydrogen peroxide in aprotic solvents.

Dioxobis(acetylacetonato)molybdenum(VI) and molybdenum(VI) oxides were used as starting materials for catalysts. Five molybdenum(VI) complexes (I-V) were identified and characterized by NMR. I is a dimeric complex $[MoO_2(acac)]_2O$; II - hexamolybdate anion $Mo_6O_{19}^{2-}$, III - monoperoxo complex $MoO(O_2)(acac)_2$; IV and V - diperoxo complexes $MoO(O_2)_2L$ and $MoO(O_2)_2L\cdot H_2O$, respectively (where L is H_2O or H_2O_2). III and V are inert towards alkenes. IV reacts with cyclohexene yielding cyclohexene oxide and trans-cyclohexane-diol-1,2. In the course of this reaction IV converts mainly to II. Fresh portions of H_2O_2 convert II back to IV and V. Diperoxo molybdenum complex $MoO(O_2)_2L$ is a key intermediate of epoxidation. Cyclohexene attacks directly peroxygen of $MoO(O_2)_2L$ with no preliminary coordination to molybdenum.

WHY DO NOT 7-COORDINATED DIPEROXO MOLYBDENUM COMPLEXES OXIDIZE ALKENES? A THEORETICAL ANALYSIS

M.J. Filatov, K.V. Shalayev, E.P. Talsi

J. Molec. Catal., 87 (1994) L5-L9

The epoxidations of alkenes by 6- and 7-co-ordinated neutral diperoxo molybdenum complexes and those by organic hydroperoxides and peracids were studied on the basis of quantum-chemical calculations. The 6-co-ordinated diperoxo molybdenum complex was found to have similar electrophilic properties to that of the peracid, and the 7-coordinated complex showed electrophilic properties similar to those of alkyl hydroperoxide. It was concluded that the 7-co-ordinated complex was less electrophilic because of additional electron donation to the central ion, destabilizing the anion-radical, which is reflected in their lower reactivity towards the oxidation of olefins than the 6-co-ordinated ones.

^{13}C CP/MAS NMR STUDY OF ISOBUTYL ALCOHOL DEHYDRATION ON H-ZSM-5 ZEOLITE. EVIDENCE FOR THE FORMATION OF STABLE ISOBUTYL SILYL ETHER INTERMEDIATE

A.G. Stepanov, V.N. Romannikov,
K.I. Zamaraev

Catal. Lett., 13 (1992) 395-405

Dehydration of isobutyl alcohol selectively labelled with a ^{13}C nucleus in the CH_2 group (*i*-BuOH[1-^{13}C]) has been studied on H-ZSM-5 zeolite within the temperature range 296-448 K with ^{13}C CP/MAS NMR. The isobutyl silyl ether intermediate (IBSE) has been found to form. It is stable below 398 K. Within the temperature range of 398-423 K IBSE decomposes gradually to produce, first, a butene dimer, probably 2,5-dimethyl-1-hexene and, then, other butene dimers and oligomers. At T>423 K the scrambling of selectively labelled carbon, belonging to initial dimeric product, over various positions in the carbon skeleton of the final dimers (oligomers) is observed. This is explained in terms of carbenium ion formation, which is reaction intermediate.

^{13}C CP/MAS AND ^{2}H NMR STUDY OF *tert*-BUTYL ALCOHOL DEHYDRATION ON H-ZSM-5 ZEOLITE. EVIDENCE FOR THE FORMATION OF *tert*-BUTYL CATION AND *tert*-BUTYL SILYL ETHER INTERMEDIATES

A.G. Stepanov, K.I. Zamaraev, J.M. Thomas (Davy Farad. Res. Lab.,The Royal Inst., London, UK)

Catal. Lett., 13 (1992) 407-422

Dehydration of *tert*-butyl alcohol, selectively labelled with ^{13}C in CH_3 or C-O groups (*t*-BuOH[2-$^{13}C_1$] and *t*-BuOH[1-^{13}C]), as well as selectively deuterated in methyl groups (*t*-BuOH[2-$^{2}H_9$]), was studied on H-ZSM-5 zeolite with ^{13}C CP/MAS and ^{2}H solid state NMR simultaneously. When adsorbed and dehydrated in zeolite at 296 K, *t*-BuOH[2-$^{13}C_1$] and *t*-BuOH[1-^{13}C] give rise to identical ^{13}C CP/MAS NMR spectra of oligomeric aliphatic products. This is explained in terms of the fast isomerization of the *tert*-butyl hydrocarbon skeleton via the formation of *tert*-butyl cation as the key reaction intermediate. An alkoxide species, most probably *tert*-butyl silyl ether (*t*-BuSE), was also detected as the "side" reaction intermediate. This intermediate was stable within the temperature range of 296-373 K and decomposed at 448 K to produce additional amounts of final reaction products, i.e. butene oligomers. The NMR data obtained tell for the existence of equilibria between initial *tert*-butyl alcohol, *tert*-butyl cation and butene, which is formed from the intermediate carbocation.

DEUTERIUM SOLID STATE NMR STUDY OF THE MOLECULAR MOBIILITY AND CATALYTIC DEHYDRATION OF *tert*-BUTYL ALCOHOL ON H-ZSM-5 ZEOLITE

A.G. Stepanov, A.G. Maryasov, V.N. Romannikov, K.I. Zamaraev

Proc. 10th Intern.Congr.Catal., Budapest, Hungary,1992, part A, p.621-634

Using deuterium solid state NMR, we have studied the molecular mobility of initial alcohol and reaction products as well as chemical conversion at the dehydration of *tert*-butyl alcohol, selectively deuterated in methyl groups, in H-ZSM-5 zeolite.

^{13}C SOLID STATE NMR EVIDENCE FOR THE EXISTENCE OF ISOBUTYL CARBENIUM ION IN THE REACTION OF ISOBUTYL ALCOHOL DEHYDRATION IN H-ZSM-5 ZEOLITE

A.G. Stepanov, K.I. Zamaraev

Catal. Lett., **19** (1993) 153-158

Using two-dimensional J-resolved and CP/MAS ^{13}C NMR, the pathway for the transfer of the ^{13}C label from the CH_2 group of isobutyl alcohol into the hydrocarbon skeleton of butene oligomers has been elucidated in the course of isobutyl alcohol dehydration inside H-ZSM-5 zeolite. First, the label is transferred selectively into the CH_2 group of the isobutyl silyl ether reaction intermediate (IBSE), and then into the CH and CH_3 groups of the isobutyl fragment ($-CH_2CH(CH_3)_2$) of IBSE and/or butene oligomers. Finally, it is scrambled over the carbon skeleton of the oligomers. The obtained data suggest that isobutyl carbenium ion is formed as a reaction intermediate or transition state during the transformation of isobutyl silyl ether into butene oligomers.

DEUTERIUM SOLID-STATE NMR STUDY OF THE MOLECULAR MOBILITY AND DEHYDRATION OF *tert*-BUTYL ALCOHOL ON ZEOLITE H-ZSM-5

A.G. Stepanov, A.G. Maryasov, V.N. Romannikov, K.I. Zamaraev

Magn. Res. Chem., **32** (1994)

The molecular mobility and dehydration of *tert*-butyl alcohol, selectively deuterated in the methyl groups (t-BuOH[2-$^2H_9$], dTBA), absorbed on H-ZSM-5 zeolite was studied using ^{2}H NMR spectroscopy. At 173-298 K two modes of fast anisotropic motion were observed for the adsorbed alcohol: rotation of CD_3 groups around the C-C bonds and rotation of the entire $(CD_3)_3C$ fragment around the C-O bond. The influence of the walls of the H-ZSM-5 channels on the geometry of adsorbed dTBA is small, the increase in the CD_3-C-O angle not exceeding $2.7\pm1.2^{\circ}$ compared with the same angle in solid dTBA. This is explained by the location of alcohol molecules at the channel intersections of zeolite, whose dimension exceed those of dTBA molecule. The lifetime of dTBA molecule at these adsorption sites exceeds 1×10^{-5} s. The observed reaction products are: deuteriated water with an unusual ^{2}H NMR lineshape and two types of butene oligomers: less mobile species with the lineshape typical of solid-state ^{2}H NMR and more mobile species with a liquid-like lineshape. The number of more mobile species increases with increase in temperature. In addition, ^{2}H NMR indicates the presence of *tert*-butyl groups in the reaction products. For oligomers with a liquid-like lineshape, the diffusion coefficient D is 3×10^{-13} m^2s^{-1} at 373 K, whereas for oligomers with a solid-like lineshape $D<<5\times10^{-14}$ m^2s^{-1} at 173-373K. The diffusion coefficient for the *t*-BuOH molecule was estimated as $D<< 2\times10^{-14}$ m^2 s^{-1} within the temperature range 173-296 K.

CARBENIUM ION PROPERTIES OF OCTENE-1 ADSORBED ON ZEOLITE H-ZSM-5

A.G. Stepanov, M.V. Luzgin, V.N. Romannikov, K.I. Zamaraev

Catal. Lett., 24 (1994) 271-284

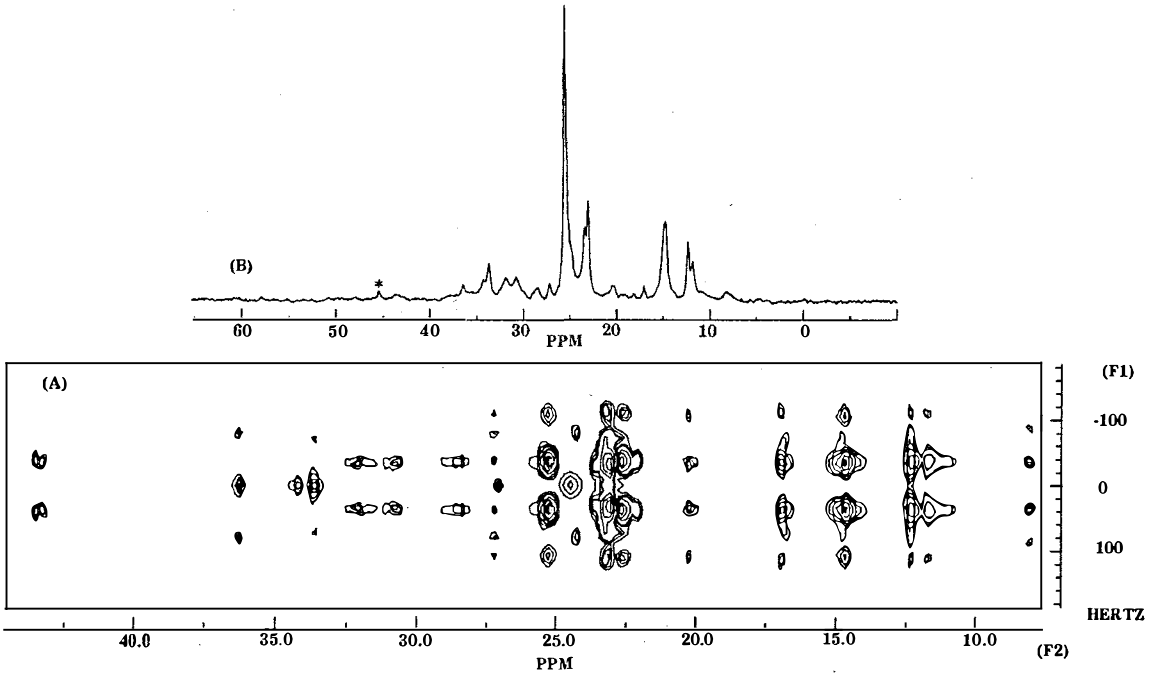
It is shown, that octene-1 adsorbed on zeolite H-ZSM-5 at ambient temperature exhibits carbenium ion properties. Namely: (1) according to ^{2}H NMR, the proton of zeolite acidic ≡Al-OH-Si≡ group is transferred into the CH_2 group of octene-1 molecule; (2) according to ^{13}C NMR the ^{13}C label, inserted into the terminal CH_2 group of octene-1 molecule, is scrambled over its hydrocarbon skeleton. Thermodynamic and kinetic parameters for carbon scrambling are measured within the temperature range of 290-343 K. The zeolite framework is shown to favor the formation of linear rather than branched carbenium ion.

TWO-DIMENSIONAL J-RESOLVED ^{13}C SOLID STATE NMR ANALYSIS OF THE PRODUCTS OF ETHYLENE CONVERSION ON ZEOLITE H-ZSM-5

A.G. Stepanov, V.N. Zudin, K.I. Zamaraev

Solid State Nucl. Magn. Reson., 2 (1993) 89-93

Two dimensional (2D) J-resolved ^{13}C NMR spectroscopy has been used to analyze *in situ* the products of ethylene conversion at 373 K in the channels of H-ZSM-5 zeolite. Using 2D ^{13}C NMR, we reliably attributed the observed ^{13}C signals of aliphatic hydrocarbon fragments to the certain CH_n (n=1-3) groups (see Fig.). Four signals



(A) Contour plot of 2D J-resolved ^{13}C MAS solid state NMR spectrum of products of ethylene conversion at 373 K. The observed value of scalar ^{13}C-^{1}H coupling (J_{CH}) is equal to a half of a real J_{CH}, because of proton high power decoupling during the second half of the evolution time, t_i. (B) One-dimensional ^{13}C MAS NMR spin echo spectrum of the products of ethylene conversion at 373 K. Asterisk denotes the spinning side band.

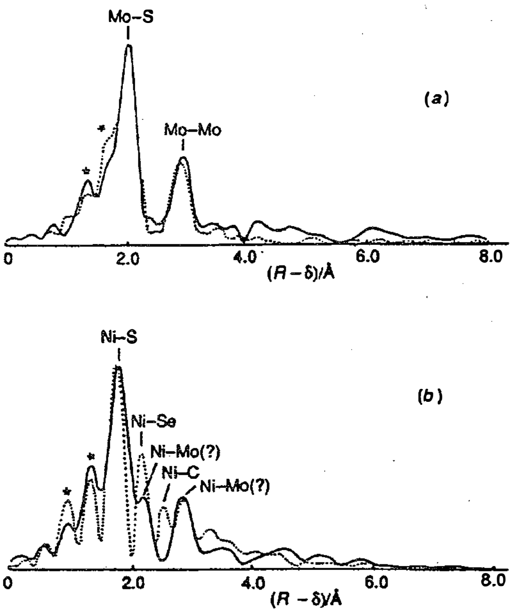
(quartes) in F1 dimension represent CH_3 groups, triplets are the signals of CH_2 groups and doublets should be attributed to CH groups. Further, basing on the position and multiplicity of the ^{13}C signals we concluded that a mixture of linear and branched ethylene oligomers is formed inside zeolite H-ZSM-5 at 373 K.

DIRECT OBSERVATION BY EXAFS OF SELENOPHENE CHEMISORPTION BY SULPHIDE HYDRODESULPHURIZATION CATALYSTS

A.N.Startsev, S.A.Shkuropat, V.V.Kriventsov, D.I.Kochubey, K.I.Zamaraev

Mendeleev Commun., 1 (1991) 6-7.

After adsorption of C_4H_4Se at ambient temperature, two intense peaks appeared in the radial atomic distribution curves obtained from the Ni K-edge EXAFS spectra of the sulphide catalysts Ni-Mo/Al_2O_3, which have been attributed to the coordination of selenophene to Ni with Ni-Se distance R 2.5 Å and Ni-C distance R 3.0 Å; no evidence for the coordination of selenophene to Mo was obtained from Mo K-edge EXAFS.



Radial atomic distribution curves obtained from the Mo K-edge (a) and Ni K-edge (b) EXAFS spectra of sulphide catalyst 1% Ni - 8% Mo/Al_2O_3 before (solid line) and after (dotted line) adsorption of selenophene at room temperature. The asterisks indicate 'false' peaks arising at small distances from the incomplete subtraction of the smooth part of the experimental EXAFS spectra.

NMR STUDY OF STABLE RADICALS IN THE GAS PHASE

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Chem. Phys. 172 (1993) 295-301

The temperature dependence of the NMR spectrum of methyl-substituted nitroxyl radical of imidazoline series has been studied. The NMR signal induced by radicals in the gas phase has been observed. A shift of the NMR spectrum lines in the gas phase according to the Curie law allows to determine the value of the hfi constant of protons of different radical groups directly. The hfi constants for methyl-substituted radical within experimental accuracy coincide with those measured by other methods in the liquid phase. In the absorbed phase of the samples under study, a substantial contribution to NMR line shift is made by volumetric susceptibility of a liquid film. The diamagnetic contribution to the magnetic susceptibility of the radical in the liquid state has been measured ($2x10^{-6}$ in a film). When the thickness of adsorbed film is small, the molecule exchange between the liquid and gas phases becomes noticeable, resulting in the corresponding additional shift of the lines. The gas-kinetic cross-section for the radical (120 Å) has been estimated from the temperature dependence of line width in the gas phase.

DIPOLE BROADENING OF ESR LINES OF PARAMAGNETIC CENTERS OF ARBITRARY SYMMETRY IN MAGNETICALLY DILUTED SOLIDS

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J. Magnet. Reson., to be published

Dipole-dipole interactions of paramagnetic centers (PCs) contain information on spatial distribution of particles. ESE technique is widely used to study this interaction since dipole broadening is usually masked by inhomogeneous broadening of ESR lines due to some other reasons.

The majority of studies in this field concern PCs with practically isotropic g-factors. For PCs identically random-distributed over the crystal with axially symmetric g-tensor the dipole broadening was calculated in [1].

The present study generalizes the results of [1] for the arbitrary symmetry of PC. Dipole broadening of lines in glasses is also considered. With rhomboic symmetry, the dipole interaction depends on the quantity of

$$\tilde{g}(\Theta,\varphi) = \left(\frac{g_{xx}^4\sin^2\Theta\cos^2\varphi + g_{yy}^4\sin^2\Theta\sin^2\varphi + g_{zz}^4\cos^2\Theta}{g_{xx}^2\sin_2\Theta\cos^2\varphi + g_{yy}^2\sin^2\Theta\cos^2\varphi + g_{zz}^2\cos^2\Theta}\right)^{1/2}$$

here g_{aa} are the principal values of g-tensor, Θ and φ determine the orientation of external magnetic field in the principal axes coordinate system.

Approximate formula

$$\Delta\omega=(4\pi^2/9\sqrt{3})\,\beta^2\,h^{-1}C_B\tilde{g}(A)\,(g_{B\parallel}^2 + 2g_{B\perp}^2)/(g_{B\parallel} + 2g_{B\perp})$$

(here C_B stands for B-type concentration of PC, β - Bohr magneton) is suggested for explanation of A-type PC dipole line broadening $\Delta\omega$ in glasses due to interaction with B particles.

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ESR *IN SITU* STUDIES OF PHOTOSTIMULATED FORMATION OF BENZENE CATION RADICALS OVER ZSM-5 ZEOLITES

V.A. Bolshov, Volodin

React. Kinet. Catal. Lett., 46, 2(1992) 337-343

The photoinduced formation of benzene cation radicals adsorbed on ZSM-5 zeolites was studied. The process was shown to be initiated by the absorption of one photon. The process red edge (2.8 eV) was in the field of energies which were significantly lower than ionization potential of benzene molecules in the gas-phase (9.25 eV). The photon was assumed to be absorbed by the electron donor-acceptor complex ([A...B]) of adsorbed benzene molecules (B) with the accepting sites on the zeolite surface (A).

The process includes the intermediate paramagnetic particle formation. They are radical pairs (RP), providing EPR spectra at the decreased temperatures (T = 93 K). When the temperature increases to 173 K, the destruction of radical pairs produces isolated cation radicals of benzene and counter ions.

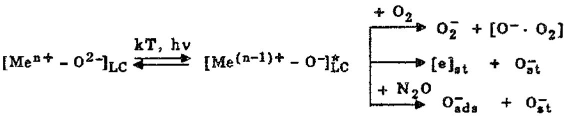
The process of photo-stimulated formation of benzene cation radicals (B^+) adsorbed on ZSM-5 follows the scheme:

$$A+B \rightleftarrows [A\cdots B] \xrightarrow{h\nu} [A\cdots B]^* \dashrightarrow RP \xrightarrow{kT} A^- + B^+$$

FORMATION AND REACTIVITY OF ANION RADICALS O^-_{3C} AND O^-_{4C} OVER MgO AND CaO SURFACES

A.M. Volodin

We have shown [1,2] the possibility to stabilize anion radicals O^- on MgO and CaO surfaces in different coordinations (O^-_{3C} and O^-_{4C}) provided by the electron transfer from the surface of coordinatively-unsaturated anions O^{2-}_{LC} (O^{2-}_{3C} and O^{2-}_{4C}) according to the scheme:



$$[Me^{n+} - O^{2-}]_{LC} \underset{}{\overset{kT,\ hv}{\rightleftarrows}} [Me^{(n-1)+} - O^-]^*_{LC} \begin{cases} \xrightarrow{+O_2} O_2^- + [O^- \cdot O_2] \\ \longrightarrow [e]_{st} + O^-_{st} \\ \xrightarrow{+N_2O} O^-_{ads} + O^-_{st} \end{cases}$$

The coordination of O^- anion radicals is shown to influence significanly the nature of radical products formed upon their interaction with ethylene.

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PHOTOINDUCED FORMATION OF RADICALS FROM m-DINITROBENZENE ADSORBED ON γ-Al_2O_3: EVIDENCES FOR THE FORMATION OF SURFACE ELECTRON-DONOR-ACCEPTOR COMPLEXES INVOLVING SOLVENT MOLECULES

T.A. Konovalova, A.M. Volodin

React. Kinet. Catal. Lett., 52, 1(1993)227-232

Here we present the study on spectral characteristics of photostimulated radical generation from m-dinitrobenzene (NB) adsorbed on γ-Al_2O_3 from the solvents with various donor properties: o-xylene (I_p = 8.56 eV), benzene (I_p = 9.25 eV) and heptane (I_p = 10.1 eV).

The red-edge of the photoprocesses appears to depend on the donor properties of solvent and equals 2.3 eV for o-xylene; 2.8 eV for benzene and 3.4 eV for heptane.

Thus, a solvent molecule D seems to be involved in the electron-donor-acceptor (EDA) complex generated on the surface, the energy characteristics of the latter depend significantly on the donor properties of solvents.

We propose the following scheme of R_{st} radicals formation on γ-Al_2O_3 surface:

$$NB + D_s \leftrightarrow [NB \cdot D_s] \overset{+D}{\rightleftarrows} [D \cdot NB \cdot D_s] \overset{kT,h\nu}{\rightleftarrows} [D \cdot NB \cdot D_s]^* \rightarrow \dot{R}_{st}$$

By analogy with the homogeneous system, we propose the observed R_{st} radical to be a nitroxide species stabilized on the surface.

^{129}Xe NUCLEAR MAGNETIC RESONANCE STUDIES OF SUPPORTED PLATINUM-ALUMINA CATALYSTS

S.V. Filimonova, V.M. Mastikhin, M.D. Smolikov*, S.S. Belyi*, V.K. Duplyakin* (Omsk Dpt. Boreskov Inst.Catal.)

React. Kinet. Catal. Lett., 48 (1992) 209-216

^{129}Xe nuclear magnetic resonance spectra of xenon adsorbed on supported platinum-alumina catalysts have been examined. The state of metallic platinum particles was shown to differ for Pt/Al_2O_3 and $Pt/Al_2O_3(Cl)$ samples. Some assumptions about the mutual arrangement of supported metal particles have been made.

^{109}Ag NMR SPECTRA OF SUPPORTED SILVER CATALYSTS

V.M. Mastikhin, I.L. Mudrakovsky, S.N. Goncharova, B.S. Balzhinimayev, S.P. Noskova, V.I. Zaikovskii

React.Kinet.Catal.Lett., 48 (1992) 425-436

The pioneer recording of ^{109}Ag NMR spectra from the Ag metal particles dispersed over alumina and silica, at Ag contents sometimes as low as 0.1 wt.% has been performed. The Knight shifts and relaxation times appear to be typical for the Ag bulk metal. The distortions of Ag metal crystal lattice contribute to the ^{109}Ag NMR line width. The estimate of Ag crystal size, at which the metal-to-nonmetal transition takes place, was made when the samples with the different size distribution of supported Ag particles were studied.

^{51}V NMR STUDY OF STRONGLY BOUND VANADIA IN V_2O_5/Al_2O_3 CATALYSTS

Z. Sobalik*, M.Markvart*, P. Stopka* (Inst.Inorg.Chem.,Prague,Czechoslovakia), O.B. Lapina, V.M. Mastikhin

J. Molec.Catal., 71 (1992) 69-79

With ^{51}V NMR a partial dissolving of V_2O_5 belonging to vanadia-alumina catalysts in 0.3 N NH_4OH has been studied. The samples, prepared by impregnation and partial dissolving are compared. The relative participation of three vanadia species, identified in both types of samples with low and medium vanadium concentration (NMR lines at -350, -550 and -750 ppm), and the catalyst activity at NO-NH_3 reaction were found to be controlled mainly by vanadium concentration as well as by preparation procedure.

$AlVO_4$ formation at high V concentrations and a complex behavior of the species during subsequent calcination and catalytic testing show a fundamental rearrangement of catalyst surface structure and precluded any viable comparison of samples with higher concentrations, prepared by both procedures.

VO^{2+} content in the oxidized samples was found to be 4-5 times higher in the catalysts prepared by partial dissolving than by impregnation.

CHARACTERIZATION OF SILICA-SUPPORTED VANADIA-PROMOTED RHODIUM CATALYSTS BY ^{51}V NMR SPECTROSCOPY

O.B. Lapina, V.M. Mastikhin, A.V. Nosov, T. Beutel*, H. Knozinger* (Inst. Phys. Chem., Munchen,Germany)

Catal. Lett., 13 (1992) 203-212

Vanadium oxide promoted Rh/SiO_2 catalyst precursors, which were calcined at 573, 773, 973 and 1173 K, were characterized by ^{51}V NMR. V_2O_5 is present in all materials and $RhVO_4$ forms at 1173 K. An additional species containing vanadium in distorted tetrahedral oxygen environment is registered after calcination at 973 K. These phases might have relevance for the catalytic promotion of reduced Rh metal catalysts by VO_x. In addition, distorted tetrahedral VO_4 species, capable to interact with water molecules and distorted octahedral species, having water molecules in their coordination sphere, have been detected.

STUDY OF V_2O_5-Al_2O_3 INTERACTION AT ULTRA-HIGH INTENSITY GRINDING

Z. Sobalik*, P. Stopka* (Inst. Inorg. Chem., Prague,Chechoslovakia), O.B Lapina

Catal. Lett., 13 (1992) 261-266

The ultrahigh intensity grinding of mechanical mixtures of V_2O_5 with γ-Al_2O_3 at ambient temperature was found to create vanadyl complexes with ESR spectral parameters identical to those of vanadia-alumina samples prepared by impregnation.

No interaction was detected after the intensive grinding of γ-Al_2O_3 with V_2O_4.

ROLE OF IRON IMPURITIES IN FORMATION OF ELECTRON-ACCEPTING SITES ON H-ZSM-5 ZEOLITES: ^{15}N NUCLEAR MAGNETIC RESONANCE AND ^{15}N NUCLEAR MAGNETIC RELAXATION OF ADSORBED N_2 AND N_2O

V.M. Mastikhin, S.V. Filimonova, I.L. Mudrakovsky, V.N. Romannikov

J. Chem. Soc. Faraday Trans., 87 (1991) 2247-2252

^{15}N NMR chemical shifts of N_2 and N_2O molecules as well as ^{15}N relaxation rates of N_2O adsorbed on a series of H-ZSM-5 zeolites, H-Y zeolite, SiO_2 and γ-Al_2O_3 containing controlled quantities of iron impurities have been studied. Unlike the SiO_2, γ-Al_2O_3 and H-Y samples, the H-ZSM-5 zeolites have strong electron-accepting sites formed by Fe^{3+} and probably Al^{3+} cations. The possible structure of acidic sites and the geometry of complexes formed during N_2O adsorption are discussed.

^{15}N NUCLEAR MAGNETIC RESONANCE STUDIES OF NO-O_2-NH_3 REACTION OVER ZSM-5 ZEOLITES

V.M. Mastikhin, S.V. Filimonova

J. Chem. Soc. Faraday Trans., 88 (1992) 1473-1476

^{15}N nuclear magnetic resonance spectra produced by NO or NO mixed with O_2 or NH_3 adsorption on ZSM-5 zeolites have been examined. N_2 and N_2O as products of NO disproportionation were identified by ^{15}N NMR. Cation and acidic centers were suggested to be responsible for the zeolite catalytic activity in this reaction. The ^{14}N-^{15}N isotopic exchange shows formation of the intermediate complexes between NH_3 and $N_xO_y \cdot M^+$ adsorbed species.

^{129}Xe NUCLEAR MAGNETIC RESONANCE STUDIES OF SILICA GEL POROUS STRUCTURE

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J. Chem. Soc. Faraday Trans., 89 (1993) 4239-4243

The porous structure of several silica gels is characterized by ^{129}Xe NMR of adsorbed xenon. With regard to experimental data obtained for the samples with a well defined structure, an empirical correlation between the ^{129}Xe NMR chemical shift and porous structure parameters is suggested. The energy parameters of xenon adsorption have been obtained from the temperature dependence of chemical shifts. The possibilities and limitations of ^{129}Xe NMR spectroscopy of adsorbed xenon for studying the porous structure of silica gel are discussed.

CHARACTERIZATION OF SURFACE ACTIVE SITES OF CATALYSTS WITH HIGH-RESOLUTION SOLID-STATE NMR$^{\alpha}$

V.M. Mastikhin

Colloids and Surfaces A: Physicochemical and Engineering Aspects 78 (1993) 143-166

The data on the surface active sites of heterogeneous catalysts were obtained with a high-resolution solid-state NMR. The ^1H NMR MAS (magic angle spinning) data on the chemical shifts of surface OH groups and their interaction with the supported catalytically active complexes are discussed. Relationship between the ^1H chemical shifts of OH groups, on one hand, and their acid strength parameters, such as the proton affinity PA_{OH} of acid residue formed at the heterolytic dissociation of OH groups, on the other hand, is presented. The intensity of ^1H NMR lines from the OH groups of commonly used supports (Al_2O_3, TiO_2, SiO_2 etc.) changes at their interaction with supported oxides. The surface OH groups interact selectively with supported complexes.

For the solid heteropolyacid $H_3PW_{12}O_{40}$ (HPA) supported on SiO_2, HPA molecule binding with the SiO_2 surface is most probably multicentered and produces supported species of different proton structures. The ^1H NMR MAS spectra of zirconium hydrides supported on SiO_2 have proved four types of zirconium hydride complex to form.

The solid-state high-resolution ^1H NMR spectra of H_2S adsorbed on Al_2O_3 modified with KOH, K_2CO_3 and HF and on zeolites NaX, NaY and H-ZSM show dissociative adsorption of H_2S to occur on the coordinatively unsaturated aluminium sites and Na^+ cations in zeolite cavities. The ^1H and ^{13}C NMR spectra indicate, that adsorbed CH_3OH reacts more readily with SH^- species than with H_2S adsorbed in molecular form.

The data on the Lewis acid sites in Al_2O_3, and zeolites Y and ZSM-5 studied with ^1H, ^{13}C and ^{15}N NMR were obtained with regard to a weak adsorption of some bases. The formation of Lewis acid sites in HY zeolites during their hydrothermal treatment has been studied by the ^{15}N NMR of adsorbed N_2O. The strongest Lewis sites are the isolated or weakly associated extralattice Al atoms. The ^1H, ^{13}C and ^{15}N NMR chemical shifts of CH_4, N_2 and N_2O molecules, as well as ^1H and ^{15}N relaxation rates of CH_4 and N_2O adsorbed on a set of HY and H-ZSM zeolites, SiO_2 and Al_2O_3, containing controlled amounts of iron impurities, show that unlike SiO_2, γ-Al_2O_3 and HY zeolites, the H-ZSM-5 zeolites possess the strong electron-accepting sites, formed by Fe^{3+} and, probably, Al^{3+} cations. The possible structure of these sites and the geometry of complexes formed during N_2O and CH_4 adsorption are discussed.

The ^{109}Ag NMR spectra of supported silver catalysts are presented. The potential of ^{109}Ag NMR for the catalysts of this type study is discussed.

NUCLEAR MAGNETIC RESONANCE FOR HETEROGENEOUS CATALYSIS

V.M. Mastikhin, O.B. Lapina, I.L. Mudrakovsky

Monograph, Nauka, Novosbirsk, 1992 (in Russian)

The monograph presents important results concerning heterogeneous catalysis, obtained with advanced high-resolution solid state NMR spectroscopy. The majority of results presented was obtained at the laboratory of Mechanisms of Catalytic Reactions of Boreskov Institute of Catalysis (Novosibirsk). Data, obtained by other scientists, are also discussed.

Besides the fundamentals of the high-resolution solid-state NMR, the data on the surface active sites, adsorbed molecules and surface reactions (^{1}H, ^{13}C, ^{15}N, ^{31}P NMR) as well as on the local environment of atoms in catalysts (^{27}Al, ^{29}Si, ^{71}Ga, ^{9}Be, ^{11}B, ^{17}C, ^{51}V, ^{95}Mo) are presented. The potential and limitations of NMR application in catalysis are discussed.

SURFACE COMPLEXES FORMED IN V_2O_5-TiO_2-SiO_2 CATALYSTS: ^{51}V AND ^{1}H HIGH-RESOLUTION SOLID STATE NMR DATA

O.B. Lapina, A.V. Nosov, V.M. Mastikhin, K.A. Dubkov, V.V. Mokrinskii

J. Molec. Catal., 87, 1(1994)

^{51}V and ^{1}H solid-state NMR data show the formation of several surface tetrahedral and octahedral V complexes in V_2O_5-TiO_2-SiO_2 catalysts. The type of V complexes depends on the sequence of Ti deposition. Triple complexes, containing simultaneously V, Ti and Si, have been observed.

ISOTROPIC PARAMAGNETIC NMR SHIFTS OF ^{14}N AND ^{13}C NUCLEI IN NICKEL AND COBALT COMPLEXES

A.V. Kessenikh*, A. Atayev* (Inst.High.Purity Chemicals), B.N. Plakhutin, M.A. Fedotov

Khim. Fiz., 12 (1993) 1687-1696

^{14}N and ^{13}C isotropic paramagnetic shifts in the dihalogenido trialkylpyrazole nickel(II) and cobalt(II) complexes have been measured and calculated. The Fermi-contact term calculated with the INDO approximation of spin-unlimited Hartree-Fock method agrees well with experimental paramagnetic shifts only for ligand nitrogen atoms.

ON TRIETHANOL AMINE ROLE IN ZEOLITE SYNTHESIS BY THE CHARNELL TECHNIQUE

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Zh. Strukt. Khim., 34, 4 (1993) 67-70

Sodium aluminate specific interaction with triethanolamine has been proved to occur in the starting solutions for zeolite synthesis by multinuclear NMR methods. This interaction determines the synthesis performance on NaX-type zeolites.

Mo/Al_2O_3 CATALYST PREPARED VIA METAL COMPLEX PRECURSORS. SORPTION OF METAL COMPLEXES BY THE SUPPORT SURFACE

O.V. Klimov, M.A. Fedotov, A.N. Startsev

J. Catal., 139, 1(1993) 142-152

The interaction of metal complexes $MoO_2(C_5H_7O_2)_2$, $(N_2H_5)_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]$ and $(NH_4)_2[Mo_3O_4(C_2O_4)(H_2O)_3]$ with the surface of γ-Al_2O_3 was studied by the ^{95}Mo, ^{27}Al, ^{17}O, ^{14}N and ^{13}C NMR, while the composition of surface species formed was studied by IR spectroscopy. Molybdenum acetylacetonate interacts with the support surface via the mechanism of ligand substitution, whereas Mo oxalate complexes appear to adsorb via both ion exchange and ligand substitution mechanisms. In all cases aluminium complexes were requistered in mother solution.

FORMATION OF Fe(III) COMPLEXES WITH $PW_{11}O_{39}^{7-}$ HETEROPOLY ANION IN WATER SOLUTIONS: ^{13}P, ^{17}O and ^{183}W NMR, UV-VIS SPECTROSCOPY AND MAGNETIC SUSCEPTIBILITY STUDIES

M.A. Fedotov, L.G. Detusheva, L.I. Kuznetsova, V.A. Likholobov

Zh. Neorg. Khim., 38, 3(1993) 515-525

The formation of Fe(III) complexes with $PW_{11}O_{39}^{7-}$ HPA has been studied in water solutions at pH=1-7 and Fe/P=0.5-10. Three types of inert complexes were found to form. Two of them contain the polynuclear ferric fragments. The redox properties of complexes were investigated. Spectroscopy and NMR parameters of complexes studied are reported.

REVERSIBLE NITRO-NITROZO CONVERSION IN Ru(II) COMPLEXES: ^{15}N, ^{17}O AND ^{99}Ru NMR STUDY

V.A. Emelyanov*, V.A. Fedotov* (Inst.Inorg.Chem.,Novosibirsk), A.V. Belyaev

Zh. Neorg. Khim., 38, 11(1993) 1842-1848

Conversions of $[RuNO(NO_2)_4OH]^{2-}$ and $[Ru(NO_2)_6]^{4-}$ complexes have been studied in the alkali water solution of $NaNO_3$. The dominating species and its NMR characteristics were determined and the mechanism of $Ru(NO)_2^{4-}$ formation was suggested.

THE KINETICS OF NITROZO-PENTACHLORO RUTHENATE(II) ION NITRATION

V.A. Emelyanov*, M.A. Fedotov, A.V. Belyaev* (Inst.Inorg.Chem.,Novosibirsk)

Zh. Neorg. Khim., 37, 12(1992) 2717-2726

The kinetics of $[RuNOCl_5]^{2-} + 4\ NO_2^- + H_2O \rightarrow [RuNO(NO_2)_4OH]^{2-} + 5\ Cl + H^+$ reaction has been studied by UV-VIS and NMR spectroscopies. Reaction rate constant K_H^{343K} and activation parameters (E_a=110 ± 4 kJ/mol, LgA_0 = 13.3 ± 0.6) have been determined. The substitution of the first chloro ligand was found to be the limiting stage.

MULTINUCLEAR NMR STUDY OF HYDROLYTIC POLYCONDENSATION OF AQUA IONS IN SOLUTIONS OF Al(III) AND Cr(III) NITRATES

M.A. Fedotov, E.A. Taraban, R.A. Buyanov

Zh. Neorg. Khim., 38, 11(1993) 1849-1854

The hydrolytic polycondensation in Al(III) and Cr(III) solutions has been studied by the ^{1}H, ^{2}D, ^{14}N and ^{27}Al NMR and static magnetic susceptibility methods. The polycondensation processes were found to be independent of Al/Cr ratio, to involve simultaneously Al^{3+} and Cr^{3+} ions and to differ from those in other binary solutions with Al^{3+} ions [Al(III)-Fe(III), Al(III)-Co(II), Al(III)-Ni(II)]. Cr^{3+} ions inhibit the formation of $[Al_{13}(OH)_{32}(H_2O)_8]^{7+}$ complex.

SYNTHESIS OF ALUMINIUM HYDROXIDE AND ALUMINA FROM ALUMINIUM HYDROCHLORIDE LIQUID WASTES OF ADAMANTANE PRODUCTION

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Technology Today, 3 (1992) 133-136

The composition of adamantane production liquid wastes has been studied. The wastes contain dissolved aluminium hydrochloride and 50 g/l of Al_2O_3. Three types of Al^{3+} species are present in solutions: $Al(H_2O)_6^{3+}$, $[AlOH(H_2O)_5]^{2+}$ and $[Al_2(OH)_2(H_2O)_8]^{4+}$ (80 atom.% of Al are combined in these species). Residual 20 atom.% of Al are fixed in the polynuclear hydroxo complexes of Al_p. Precipitation of Al hydroxides from the liquid waste solutions as well as from the pure aluminium chloride was performed at constant pH, temperature and ageing time. The Al hydroxide (pseudoboehmite) formation from these solutions and its further conversion to Al_2O_3 at calcination has been demonstrated.

SYNTHESIS AND PROPERTIES OF POTASSIUM-SODIUM HEXANITRO RUTHENATE(II)

V.A. Emelyanov*, A.V. Belyaev* (Inst. Inorg. Chem., Novosibirsk), M.A. Fedotov

Zh. Neorg. Khim., 37, 11(1992) 2515-2523

Complexes of $K_xNa_{4-x}[Ru(NO_2)_6]\ H_2O$ (x = 3.5; 0.15 or 1) have been synthesized and studied by IR spectroscopy, multinuclear NMR and X-Ray analysis. Reversible reaction $[RuNO(NO_2)_4]^{4-}+H_2O \rightarrow [RuNO(NO_2)_4OH]^{2-} + NO_2 + OH^-$ has been studied. The crystal structure and ^{15}N, ^{99}Ru NMR data are been presented.

ESR SPECTRA OF ^{47}Ti-ENRICHED TITANIUM CATALYSTS FOR POLYMERIZATION

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React. Kinet. Catal. Lett., 43, 1(1991) 75-79

For the first time ESR spectra of ^{47}Ti-enriched Ziegler system Ti-TIBA in toluene have been studied. For the ratio Ti/Al ~ 1, more accurate h.f.s. constants have been found. For Ti/Al ~ 1/15 no h.f.s. have been observed, which is ascribed to ordering due to the cooperative Jahn-Teller effect.

INTERACTION OF TRIBENZYLTITANIUM WITH BUTADIENE

V.F. Anufrienko, L.V. Smirnova, E.N. Kropacheva (Inst. Synth. Rubber., St.Petersb.)

React. Kinet. Catal. Lett., 48, 1 (1992) 73-76

It has been established that the interaction of $(C_6H_5CH_2)_3Ti$ with butadiene does not change the parameters of ESR spectra. Only the hydrodynamic radius of this complex increases.

ESR STUDY OF THE INTERACTION OF TRIBENZYLTITANIUM WITH DIISOBUTYLALUMINIUM CHLORIDE

L.V. Smirnova*, V.F. Anufrienko, E.N. Kropacheva*, S.L. Panasyuk* (Inst. Synth. Rubber, St.Petersb.)

React, Kinet. Catal. Lett., 48, 1(1992) 85-91

ESR studies of the interaction between ^{47}Ti enriched tribenzyltitanium and diisobutylaluminium chloride suggest that the observed spectral peculiarities show the formation of the alkylhalide complex of Ti_2^{7+}.

STATE OF COPPER IN MASSIVE Cu-V-Mo OXIDE SYSTEMS

V.F. Anufrienko, A.A. Altynnikov

React. Kinet. Catal. Lett., 48, 2 (1992) 583-588

ESR data for $X(CuO)\ V_2O_5 \cdot 8.3\ MoO_3$ system heated at 400-550°C indicate the occurrence of a copper state with d_{z^2}-ground state. Copper ions are orbitally ordered apparently in $-Cu^{2+}-O-Cu^{1+}-O-Cu^{2+}$-chains.

IDENTIFICATION OF EXCHANGE-COUPLED V^{4+} AND Cu^{2+} IONS IN Cu-V-Mo OXIDE SYSTEMS

V.F. Anufrienko, A.A. Altynnikov, N.N. Chumachenko

React. Kinet. Catal. Lett., 48, 2 (1992) 589-592

ESR studies of $X(CuO) \cdot V_2O_5 \cdot 8.3MoO_3$ (X=1-2) calcined in flowing nitrogen at 250-350°C have revealed the exchange interaction of Cu^{2+} and V^{4+} ions that form a paramagnetic system.

RESEARCH IN MEMBRANOLOGY FOR CATALYSIS

O.M. Ilinich

Research in membranology for catalysis, initiated at late eighties with the aim of perfectioning of catalytic technologies, currently covers two main areas - gas separation and reverse osmosis.

In gas separation, an intense testing of polymers was carried out aimed to find those capable to separate methane, ethane and ethylene [1,2], the key components of the reaction mixture for catalytic oxidative coupling of methane. The homologous polyphenyleneoxides (PPOs) - homopolymers of poly-2,6-dimethyl-1,4-phenyleneoxide (p-DMePO) and poly-2,6-diphenyl-1,4-phenyleneoxide (p-DPhPO), as well as copolymers of p-DMePO and p-DPhPO - were found to possess reasonably high steady-state permeabilities towards light olefins and paraffins ($\Pi_{C_2H_4} \equiv$ 2-20 Barrer and $\Pi_{C_2H_6} \equiv 0.7$-7 Barrer for PPOs of different composition at ambient temperatures) and the highest selectivities in separation of ethylene-ethane mixtures ($\alpha_{C_2H_4/C_2H_6} \equiv$ 3-4) in comparison to the other polymers tested.

Permeabilities of polyphenyleneoxides were further analyzed in terms of solubility and diffusivity of the hydrocarbons. Solubilities of the hydrocarbons in PPO and the copolymers were found to change in the sequence $CH_4 < C_2H_4 \equiv C_2H_6$, while for the diffusivities the sequence was different: $CH_4 > C_2H_4 > C_2H_6$. Thus, higher diffusivity of ethylene compared to ethane were shown to be responsible for the higher permeability of the former. On the basis of such relationship between these fundamental components of permeability, transient increase of the separation selectivity upon the rapid increase of ethylene-ethane mixture pressure was predicted and experimentally observed. Separation factors $\alpha_{C_2H_4/C_2H_6}$ as big as 20-50 were achieved, while their steady-state values were typically close to 3 [3, 4].

In addition, marked increase of α_{CH_4/C_2H_6} and α_{CH_4/C_2H_4} (up to 20-fold) over the steady-state values was observed as well upon transient separations of the three-component mixtures containing methane, ethane and ethylene.

Molecular mechanism of gas permeability in polyphenyleneoxides membranes in relation to the supramolecular structure of the polymers was studied by sorptometry technique [5]. Microporosity of polyphenyleneoxides, characterized by the effective diameter of microchannels ca. 4 Å, was revealed. The conclusion was made that the separation of light olefins and paraffins by the polyphenyleneoxides membranes is governed by the geometry of the microporous supramolecular lattice and the interactions gas-polymer.

Potentials of reverse osmosis (RO) in solving the problem of a soluble catalyst separation from the products of the homogeneous catalytic reactions were investigated [6, 7]. Two environmentally important liquid phase processes, occurring in aqueous solutions at ambient temperatures and moderate pH, were considered:

(A) detoxication of NO and H_2S pollutants catalyzed by iron-containing heteropolyanion (HPA):

$$2\,NO + 2O_2 + H_2S \xrightarrow{HPA} 2\,HNO_3 + S \quad (A)$$

(B) detoxication of the water soluble sulfides catalyzed by the sodium salt of tetra(sulfophthalocyanine)-cobalt(II), or briefly (Na-TSPC):

$$(S^{2-} + O_2 \xrightarrow{Na-TSPS}$$

$$(S, SO_3^{2-}, SO_4^{2-}, S_2O_3^{2-}) + H_2O$$

The regularities of both the catalytic reactions and RO separation of the reaction solutions were studied. In the RO experiments, high retention of the catalysts was obtained while that of the reaction products turned out to be markedly lower; moreover, the latter was found to depend strongly upon concentrations of the catalyst and/or other ions present in the reaction solutions, decreasing down to negative values as these concentrations increase. It is largely due to this phenomenon that an efficient RO separation of the catalysts from the reaction solutions was obtained. The structure and activity of the catalysts were not affected by the RO separation, enabling their multifold re-use in the reactions.

These results demonstrate that reverse osmosis is a promising method for the recovery of catalysts from the reaction solutions in homogeneous catalysis. The catalysts recovered by the reverse osmosis retain their catalytic properties, and hence can be re-used, which is important from both the economic and the environmental points of view.

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ANGLE RESOLVED PHOTOEMISSION STUDY AND CALCULATION OF ELECTRONIC STRUCTURE OF Pt(III) SURFACE

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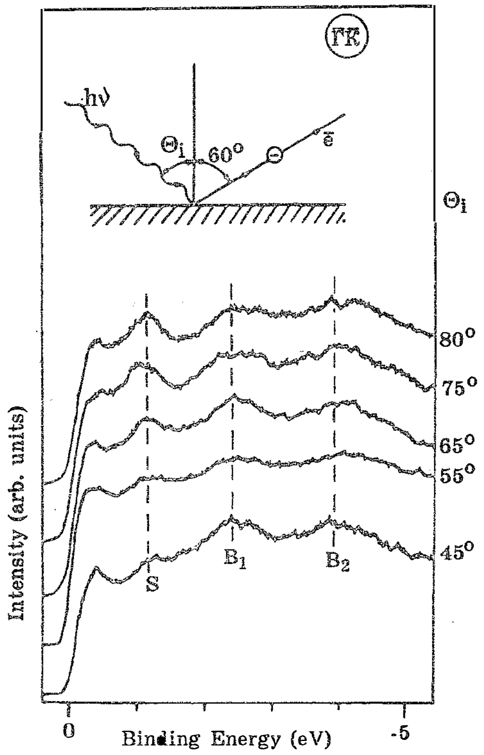
M.Yu. Smirnov, V.V. Gorodetskii

Surf. Sci., 310 (1994) 155-162

Angle-resolved photoemission spectra of Pt(III) surface were measured along $\overline{\Gamma K}$ and $\overline{\Gamma M}$ directions of the surface Brillouine zone using He-I radiation, at $h\nu = 21.2$ eV. For their interpretation, the electronic structure of semi-infinite Pt(III) crystal was calculated in the LMTO-TB approximation.

For the normal emission ($\overline{\Gamma}$-point) the calculation predicts three peaks at 2.0, 4.2 and 8.5 eV below the Fermi level. The first and the second correspond to experimental peaks at 1.7 and 4.2 eV. The density of states, hence the third peak must arise, is very small. Thus, it is difficult to observe it in photoemission experiments. The photoemission spectra taken for the polar angles corresponding to variations of parallel component of the electron wave vector along $\overline{\Gamma K}$ and $\overline{\Gamma M}$ are also described satisfactorily by calculations.

The calculation predicts some surface states and resonances. One of the surface states near the Fermi level in the neighbourhood of $\overline{K}$ point is registered experimentally. A set of spectra obtained along $\overline{\Gamma K}$ and $\Theta_d = 60^o$ (Fig.) shows the growth of electron emission (S peak) at 1.2 eV when the angle of the incident radiation becomes grazing, indicating the surface origin of emitted electrons. CO adsorption causes this peak to remove, whereas the spectral features



attributed to the bulk states, B_1 and B_2, persist without sufficient change.

NO(ad) REDUCTION BY HYDROGEN ON Pt(100) SURFACE

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Catal. Lett., to be published

The titration of nitric oxide adsorption layer on the reconstructed Pt(100)-(5x20) surface by hydrogen was studied by TDS, HREELS and LEED. The room temperature NO adsorption proceeds molecularly and produces islands with a high local concentration of adsorbed particles. The transition into the unreconstructed Pt(100)-(1x1) surface state occurs in the neighbourhood of islands.

The course of nitric oxide titration by hydrogen is found to depend on the initial state of NO(ad) layer. The layer saturated near the room temperature reveals no appreciable reactivity. When the surface is annealed at 375 K before the titration, the desorption of the minor part of nitric oxide without the island dissolving is observed, and the NO(ad) layer acquires activity towards hydrogen. The kinetics of the $NO(ad)+H_2$ reaction exhibits an autocatalytic behaviour. Preliminary adlayer annealing at $T > 430$ K provides dissociation of some NO(ad) molecules causing reaction to proceed without appreciable induction time. When reaction is completed, the platinum surface is in the unreconstructed (1x1) state, covered with hydrogen. Titration by NO of thus produced H(ad) layer reveals the autocatalytic kinetics again.

The autocatalytic behaviour of $NO+H_2$ reaction on Pt(100) surface seems to result from the rate-determined step, NO(ad) dissociation, which requires the vacant adsites whose concentration grows during the reaction. This is mostly pronounced in the case of the NO(ad) islands formation providing the high initial local concentration of adsorbed molecules.

HREELS STUDY: LOW-TEMPERATURE REACTION OF NO WITH ISOLATED CARBON ATOMS ADSORBED ON Pt(111) SURFACE

M.Yu. Smirnov, V.V. Gorodetski

Catal. Lett., 19 (1993) 233

The reaction between isolated carbon atoms and nitrogen oxide molecules in the adlayer on Pt(111) surface has been studied. Carbon atoms were deposited on the surface from the special source. The reaction was found to proceed at T = 100 K and to provide at least two intermediate surface species, which were assigned to the adsorbed isocyanate NCO(ad) and fulminate CNO(ad) particles. Both intermediates dissociated to the on-top state of CO(ad) and N(ad) under heating to T < 300 K.

OSCILLATIONS IN THE CARBON MONOXIDE OXIDATION ON PLATINUM SURFACES OBSERVED BY FIELD-ELECTRON MICROSCOPY

V.V. Gorodetski, J.H. Block*, W. Drachsel*, M. Ehsasi* (Fritz-Haber Inst. der Max Planck Gesellschaft., Berlin,Germany)

Appl. Surf. Sci., 67 (1993) 198

Platinum field emitter tips ((111)-, (001)- and (012)- oriented) were used to investigate local surface properties during the oscillation regime of CO-oxidation at T = 430-480 K and partial pressures of $P_{O2} \simeq 5 \cdot 10^{-4}$ mbar and $P_{CO} \simeq 5 \cdot 10^{-5}$ mbar. Changes in surface coverage and catalytic activity were indicated by the change of local work functions and field emission current. Self-sustaining isothermal oscillations could be observed on different crystal planes:

(i) A fast "starting" of emission currents is initially noticed when the oxygen adsorption layer is transferred into a CO layer. After a certain induction period the oxygen side is quickly switched from region (001) to the CO side which slowly returns back to the catalytically active oxygen side.

(ii) Reactive wave front forms in the (011)-region and propagates along directions (111) and (100). The CO- and O-wavefronts move alternately in the opposite directions and display different propagation velocities which can be measured.

The frequences and amplitudes of oscillations depend critically on temperatures and partial pressures. Compared to single crystal planes, a broadening and shift of oscillatory regimes with regard to parameter space is noticed. In certain cases period doubling can be registered.

OSCILLATING CO-OXIDATION ON Pt-SURFACES OBSERVED WITH FIELD ION MICROSCOPY

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Catal. Lett., 19 (1993) 223.

The oxidation of carbon monoxide on platiinum surfaces is investigated by field ion microscopy (FIM) and compared to earlier studies by field electron microscopy (FEM). The reaction gas is used as the field ion imaging gas at the pressures of < 10^{-4} mbar and catalytic reaction temperatures. With FIM the surface is imaged by O_2^+ ions which are favorably ionized over the oxygen-covered surface areas. Temperature variations produced the regions of bistability detected by FEM and FIM.

Finally, self-sustained isothermal oscillations of catalytic CO-oxidation could be measured from the periodic fluctuations of O_2^+-field ion current. Atomic resolution shows that Pt-(331) planes are the oscillation pace makers.

THE SURFACE SPECIFICITY OF OSCILLATING CO-OXIDATION INVESTIGATED WITH A Pt-FIELD-ION-EMITTER

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Appl. Surf. Sci., submitted for publication

The *in situ* observation of CO-oxidation with the field ion microscope is possible due to the favorable field ionization of molecular oxygen, which acts as imaging gas and displays O(ad)-sites with atomic resolution. A dynamic bistability of oxidation reaction is caused by the catalytically inactive CO(ad)-covered Pt-surfaces and active O(ad)-covered ones. Self-sustained long-lasted oscillations of $CO + 1/2\ O_2 \longrightarrow CO_2$ reaction are investigated at $P_{CO} = 10^{-6}$-10^{-5} mbar, $P_{O_2} = 1 \cdot 10^{-4} - 5 \cdot 10^{-4}$ mbar and 330-550 K. Oscillation frequences increase from 10^{-3} s^{-1} at 330 K to 1 s^{-1} at 550 K. A pronounced surface selectivity is observed. The surface regions near the (110) planes, i.e. (331)- terraces, act as pacemakers. The Pt(111). planes are always CO(ad)-covered and do not participate in the oscillations. Some general conclusions can be made about the surface peculiarity of catalytic surface reactions and about the mechanisms of oscillating surface reactions, which remain unclear yet.

FIELD-ION-MICROSCOPIC STUDIES OF CO-OXIDATION ON PLATINUM: BISTABILITY AND OSCILLATIONS

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J. Chem. Phys., submited for publication

The oscillating CO oxidation is investigated on a Pt field emitter tip with the field ion mode of surface imaging of O(ad)-sites with O2 and imaging gas. According to the data on titration reactions [1], the external control parameters for the bistability and self-sustained isothermal oscillation regions can be found. On the field emitter tip oscillations with varios parameters can be generated. The anti-clockwise hysteresis of O_2^+ ion current in the temperature cycles agrees with results obtained on single crystal planes. Unexpected regular oscillation sequences can be occasionally obtained on the small surface areas of field emitter tip and measured versus CO partial pressure and temperature. Different stages within oscillating cycles are identified by the field ion images. In the manifold of single crystal planes of a field emitter (331) planes around the (011) regions are the starting points for oscillations which mainly proceed along [100] vicinals. This excludes the (111) regions from the autonomous oscillations. With a slightly increased CO partial pressure the fast local oscillations at a few hundred surface sites of the Pt(001) plane display the short-living CO islands 40-50 Å in diameter. The temporal oscillations of total O_2^+ ion current are mainly caused by the specific spatial oscillations of surface. Synchronization is achieved by means of diffusion reaction fronts rather than of gas phase synchronization.

IMAGING WITH REACTIVE GASES IN THE FIELD ION MICROSCOPE

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Surf. Sci., submitted for publication

Catalytically active metal surfaces are observed *in situ* by using reacting gases for imaging in the field ion microscope. In order to identify THE imaging gas ions in the reaction mixture, a mini-mass spectrometer has been designed allowing a mass separation of m/m = 0.1 from the small surface areas covering only 100 surface sites. The imaging processes in the field ion microscope for inert (He, Ne, Xe) and catalytically reacting gases (O_2, H_2, H_2O, CO, CO_2) are compared.

It is shown, how CO oxidation and H_2/O_2 reaction on Pt field emitter surfaces can be studied in their reaction dynamics at the atomic scale.

ISOTHERMAL OSCILLATIONS OF HYDROGEN- OXIDATON ON PLATINUM. INVESTIGATION IN THE FIELD ELECTRON AND FIELD ION MICROSCOPE

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Appl. Surf. Sci., submitted for publication

During reaction $H_2 + 1/2\ O_2 \rightarrow H_2O$ on a platinum field emitter at 300 K <T< 400 K, $P_{H_2} = 5\cdot10^{-7}$ - $5\cdot10^{-4}$ mbar, $P_{O_2} = 3\cdot10^{-5}$-$6\cdot10^{-4}$ mbar, three different adsorption phases can be distinguished with *in situ* FEM and FIM. With FEM the different work functions lead to the bright areas of H(ad) layer and black oxygen structures. In FIM oxygen acts as an imaging gas (O_2^+ ions) of O(ad)-covered surface areas; even brighter images are formed by product-water, characterizing reaction active sites. At steady-state hydrogen adsorbs in islands 30-50 Å in diameter observed as black areas in FIM. The oscillating reaction follows the Langmuir-Hinshelwood mechanism. The O(ad)-covered surface starts at the (111) planes ((331) terraces) in the anisotropic reaction sequence of planes until finally the (001) plane is covered by hydrogen. This H(ad)-layer at the Pt(001) surface is transferred to the O(ad)-layer by a reaction front in reverse direction, starting at the central Pt(001) and propagating to the peripheral (111) planes. Details of this oscillating surface reaction are documented by video.

FIELD-ION-MICROSCOPIC STUDIES OF CO-OXIDATION ON PLATINUM: FIELD ION IMAGING AND TITRATION REACTIONS

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J. Phys. Chem., submitted for publication

The elementary steps of CO-oxidation, which are important for understanding the oscillation behavior of this catalytic reaction, are investigated simultaneously on different Pt-single crystal surfaces by the Field Ion Microscopy. Due to the favorable ionization probabilities of oxygen as imaging gas on the surface sites for oxygen adosrption, these sites can be imaged in a lateral resolution at the atomic scale. In the titration reaction a CO(ad) precovered field emitter surface reacts with gaseous oxygen adsorbed from the gas phase or, vice versa, the O(ad) precovered surfface reacts with carbon monoxide adsorbed from the gas phase. The competition of numerous single crystal planes exposed to the titration on the field emitter tip is studied. The surface specificity can be documented in the specific reaction delay times of different planes and in the propagation rates of reaction-diffusion wave front measured on these individual planes during titration with a time resolution of 40 ms. At 300 K, the CO(ad) precovered surfaces display the (011) regions, precisely the (331) planes as the most active, followed by (012),(122),(001) and finally by (111). Reaction wave front moves with a velocity of 8 Å/s at (012), 0.8 Å/s at (111) and has a very fast "starting" at the (001) plane with 500 Å/s. At higher temperature, T = 350 K, reaction acceleration is combined with shorter delay times.

The titration of precovered O(ad) surface with CO(gas) at T = 373 K shows the formation of CO-islands starting in the (011) regions. Then reaction front moves quickly to the other surface areas without particular delay times for different surface symmetries.

The two reverse titration reactions are rather different. CO(ad) titration with oxygen adsorbed from the gas phase includes three different steps: (i) induction times, (ii) highly specific surface reaction and (iii) front propagation with different rates. CO(gas) reaction with a precovered O(ad) layer starts on nucleous islands around the (011) planes. Then the whole emitter surface is populated by CO(ad) without pronounced surface specificity.

VIBRATIONAL SPECTROSCOPIC INVESTIGATION OF THE GOETHITE THERMAL DECOMPOSITION PRODUCTS

G.N.Kustova, E.B.Burgina, V.A.Sadykov and S.G.Poryvaev

Phys.Chem.Minerals, 18(1992)379-382.

IR and Raman spectroscopic studies of goethite, hematite and intermediates of goethite thermal decomposition were carried out to identify these materials used as catalysts for some chemical reactions. Reported in the literature interpretations of the spectra of poorly crystallized products of goethite thermal decomposition as originated from the surface modes of hematite were discussed. The presence of a small portion of OH-groups in the products at 900-1000°C was assumed to hinder the formation of a perfect hematite structure. A hypothesis concerning C^{6}_{3v} space group of protohematite unrecognized from $D^{6}_{3d}D3d^{6}$ space group of hematite by X-ray diffraction was suggested. The hypothesis explaines both the additional lines in IR and Raman spectra compared to hematite spectra and the same position of peaks in X-ray diffraction picture.

IDENTIFICATION OF TYPE OF HETERO- AND ISOPOLY-ANIONS USING VIBRATIONAL SPECTRA OF THEIR CRYSTAL SALTS

E.N.Yurchenko (State Inst.Applied Chem., St.Petersburg), L.G.Detusheva, L.P.Solov'yeva, G.N.Kustova, S.V.Tsybulya and T.P.Lazarenko

Zh.Strukt.Khim., 33, 3(1992)48-58.

Spectral characteristics of various hetero- and isopoly-anions were revealed via comparative studies of vibrational spectra and crystal structures of molybdenum and tungsten heteropoly compounds. Vibrational spectra were thus shown to be appropriate to analyze the compositions of multicomponent heterogeneous and homogeneous catalysts based on hetero- and isopoly-compounds.

THE CHARACTER OF HYDROGEN INTERACTION WITH COPPER-CONTAINING OXIDE CATALYSTS

State of Copper Chromite and Its Activity for Acetone Hydrogenation Reaction into Iso-Propyle Alcohol

O.V.Makarova, T.M.Yurieva, G.N.Kustova et al.

Kinet.Katal., 34, 3 (1993) 681

The effect of the temperature of pretreatment in hydrogen on catalytic behaviour and state of copper chromite in the catalyst for hydrogenation of acetone to iso-propyle alcohol has been studied. The active state of the catalyst was assumed to result from activation by hydrogen at 180-370 °C. Using the HTXRD and EM data, ca. 50% copper ions were shown to exit from the spinel lattice within this temperature range and to transform into flat particles which become epitaxially bonded to a defect spinel phase. Heating of the catalyst returned it to initial state due to hydrogen extraction.

THEORETICAL ANALYSIS OF VIBRATIONAL SPECTRA OF MOLECULES ADSORBED ON THE SURFACE OF HETEROGENEOUS CATALYSTS

E.V.Burgina, V.P.Baltakhinov and E.N.Yurchenko

J.Electron Spectroscopy and Related Phenomena, 58(1992)11-16.

For the lack of experimental data, spectra simulation via normal coordinate analysis of various adsorption models are useful for interpreting the vibrational spectra of molecules adsorbed on the surfaces of heterogeneous catalysts. An ingenious algorithm for inverse vibrational problems makes it possible to estimate rapidly a number of models and, by comparing an experimental spectrum to the calculated one, to choose a proper model. Key factors which specify changes observed in the vibrational spectrum of a loose molecule after its adsorption on various surfaces (changes of force constants and structure of the adsorbed molecule affected by the surface field, contribution of adsorptive bonds and a surface fragment to the potential energy of the molecule) can be found via calculating the distributing potential energy over the fragments of adsorbed species.

THE EFFECT OF HIGH PRESSURE ON THE INFRARED SPECTRA OF NITRO- AND NITRITO-COBALT(III) AMINE COMPLEXES

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Ber.Bunzen.Phys.Chem. 96, 7(1992)931-937.
Prepr. 4th Japan-Russia Symp. on Mechanochemistry, 1992, Nagoya, Japan, p.33.
Sibirskii Khim.Zh. 3(1992)97-104 (in Russian).

IR vibrational adsorption spectra of Co(III)-amine complexes $[Co(NH_3)_5NO_2]XY$ and $[Co(NH_3)_5ONO]XY$ (XY = Cl_2, Br_2, J_2, $(NO_3)_2$, Cl*NO) were studied at the pressure as high as 20 Kbar. Shifts of valence (symmetric and asymmetric) and of deformational frequencies of NO_2-group were measured. Normal coordinate analysis of $Co(NH_3)_5NO_2$ and $Co(NH_3)_5ONO$ models was made. The effect of kinematic factors on IR vabrational frequencies was discussed. The pressure induced frequency shifts which were observed in the experiments were interpreted on the basis of IR spectra simulation. For the complexes with nitro (via nitrogen) coordination the blue shifts of vibrational frequencies $\delta(NO_2)$ and $\nu^{as}(NO_2)$ were accounted for by a decrease in N-O bond lengths, whereas for those with nitrito (via oxygen) coordination the blue shift of $\nu^{s}(NO_2)$ and the red shift of $\nu^{as}(ONO)$ were attributed to diminuation of the magnitude of O-N-O valence angle at high pressure. The ability of ONO-group to change its geometry, in particular O-N-O angle, was related to the reactivity of an ONO-isomer.

EFFECT OF HIGH PUSSURE ON THE VIBRATION SPECTRUM OF NITROMETHANE MOLECULES: CHANGES IN THE KINEMATICS OF THE VIBRATIONS AS A RESULT OF THE DECREASE OF THE DISTANCE BETWEEN THE MOLECULES

E.B. Burgina, V.P. Baltakhinov, E.V.Boldyreva (Inst.Solid State Chem., Novosibirsk), E.S. Stoyanov, N.Y. Zhanpeisov, G.M. Zhidomirov

J. Molec. Struct., 296 (1993) 53-59

An optimized configuration of nitromethane dimer was calculated with MINDO/3-HB. A decrease of distance between the nitromethane molecules was shown to induce the decrease of O-N-O angle and the increase of N-O bond length. Normal coordinate analysis of nitromethane molecules was carried out. Characteristics of normal vibrations have been analyzed. The kinematic effect of changes in the NO_2 group geometry on the frequencies of symmetric and asymmetric NO_2 stretching vibrations was simulated. Abnormal dependence of ν^{as} (NO_2) of $\nu_{as}(NO_2)$ on pressure was explained with the help of correlation between the force constants and geometry parameters of NO_2-group.

AB INITIO SQM FF CALCULATIONS OF VIBRATIONAL FREQUENCIES OF ACETONITRILE UPON COORDINATION TO LEWIS ACIDS

M.A.Ablaeva, A.G.Pelmenschikov,
G.M.Zhidomirov, E.B.Burgina and
V.P.Baltakhinov

React.Kinet.Catal.Lett. 47, 1(1992)99-104.

Proc.14th Austin Symp. on Molecular Structure, 1992, Austin, USA, p.84.

Zh.Strukt.Khim. 33, 5(1992)44-48 (in Russian).

React.Kinet.Catal.Lett. 48, 2(1992)569-574.

Ab initio calculations of the structure and force constants of molecules of acetonitrile and its complexes with Lewis acids such as $AlCl_3$, AlF_3 and $Al(OH)_3$ were performed. Two groups of scale factors for force constants were found, and experimental spectra of CH_3CN, CD_3CN and CH_3CN-$AlCl_3$ were reproduced by SQM FF calculations. Scaled vibrational spectra of complexes CH_3CN-AlF_3 and CH_3CN-$Al(OH)_3$ were calculated. Theoretical spectra of CD_3CN-$Al(OH)_3$ were compared to experimental data for CD_3CN adsorbed on HZSM zeolite.

NON-EMPIRICAL QUANTUM CHEMICAL CALCULATION OF VIBRATIONAL SPECTRA OF SURFACE METOXY-GROUPS ON ALUMINA AND SILICA

M.A.Ablaeva, G.M.Zhidomirov, E.B.Burgina, V.P.Baltakhinov, A.G.Pelmenschikov, E.A.Paukshtis and L.V.Malysheva

Zh.Strukt.Khim. 33, 5(1992)49-54 (in Russian).

Approaches to choosing a proper model for an adsorbed metoxyl complex have been formulated. *Ab initio* calculations of the structure and force constant matrix were performed. A set of scaled factors for force constants of CH—>3 OH molecules was found. Calculated vibrational spectra were compared to the experimental data in order to identify the frequency ranges of surface metoxy-groups $AlOCH_3$ and $SiOCH_3$.

SCANNING TUNNELING MICROSCOPY AND SPECTROSCOPY FOR CATALYSTS INVESTIGATIONS

Sh.K. Shaikhutdinov, D.I. Kochubey

Submitted to *Zh. Strukt. Khim.*

STM was built on the basis of ultra-high vacuum chamber equipped by AES, MS, electron beam heater and Ar^+-gun. It contained UHV STM-head with automatic tip approach, electronic control, IBM PC AT interface necessary for computer control. Data aquisition and image display software were based on MS DOS 5.0. The atomic resolution was achieved on the highly oriented pyrolytic graphite (HOPG).

The construction allowed, if necessary, to perform the sample surface cleaning and element analysis without chamber removal.

Some carbon samples were studied with STM. A highly-dispersed material SIBUNIT appeared to have a very rough surface with no flat structure larger than 20 Å. With the other graphite obtained on Ni-Al catalyst, the atomic resolution confirmed a typical hexagonal structure for graphite layers.

We have also examined the topography of few small particles supported on pyrolytic graphite.

ELECTRONIC AND LOCAL STRUCTURE TRANSFORMATION OF $BaPb_{1-x}Bi_xO_3$ SUPERCONDUCTIVE OXIDE WITH OXYGEN DEFICIENCY: AN X-RAY ABSORPTION STUDY

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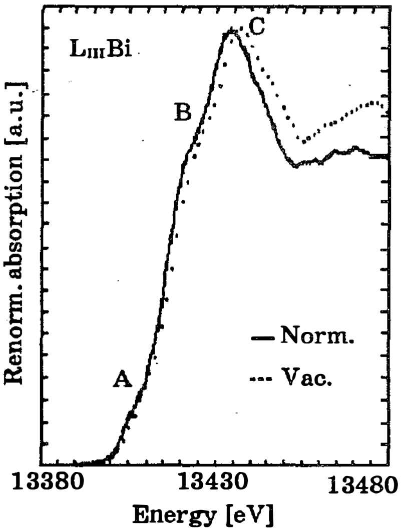
to be published

The oxygen deficiency effect on the electronic structure and local environment of Bi and Pb atoms in $BaPb_{1-x}Bi_xO_3$ was studied with X-ray absorption.

XAFS measurements were performed at the EXAFS line of VEPP-3M (Novosibirsk, Sibirian Synchrotron Center) with an electron beam energy of 2.0 GeV and stored current of 50-100 mA. The Figure presents L_3Bi XANES spectra of $BaPb_{0.75}Bi_{0.25}O_3$ before (solid line) and after (dotted line) annealing in vacuum at 500°C. The observed L_3-edge



shift to higher energy is caused by dielectrization of superconductive phase with x=0.25 upon the oxygen concentration decrease. While annealed, the samples lose their superconducting properties and become semiconductors. Some 2 eV energy band gap of L_3Bi edge shift found in the samples with oxygen deficiency, is in a good agreement with the gap provided by the charge density wave (CDW) in $BaBiO_3$. Both oxygen deficiency and Bi doping ($x \geq 0.35$) increase the Fermi surface nesting. Thus, the energy gap presence suggests the existence of the CDW in Ba-Pb-Bi-O with oxygen deficiency.

EXAFS shows oxygen to interact with Bi^{5+} ions weaker than with Bi^{3+} and Pb^{4+}. Oxygen deficiency provides redistribution of Bi^{3+} and Bi^{5+} states and destroys superconductivity. Thus, Bi-O complexes play a significant role in the coupling mechanism. The oxygen octahedron around Pb atoms remains unchanged upon Bi doping and oxygen stoichiometry change in the sample. The phase transition metal-semiconductor caused by oxygen deficiency is apparently accompanied by structural transformations.

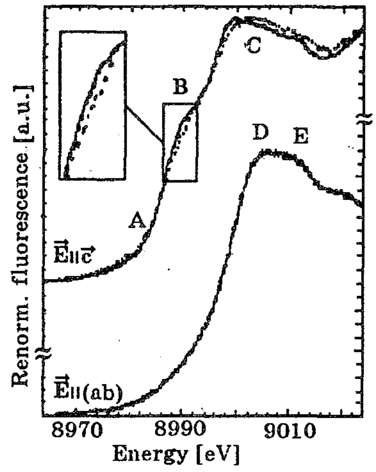
FLUORESCENCE POLARIZED K-Cu XANES OF $Nd_{1.85}Ce_{0.15}CuO_4$ THIN FILMS IRRADIATED WITH He^+ IONS

A.Yu. Ignatov*, A.P. Menushenkov* (Eng. Phys. Inst., Moscow), D.I. Kochubey

Solid State Commun., 84 (1992) 319-321, Abstr. Int. Conf. XAFS-VII, Japan 1992, to be published

With polarized K-Cu XANES, we get a direct evidence that the radiative defects in $Nd_{1.85}Ce_{0.15}CuO_4$ superconductor caused by He^+ ions (E=1.2 MeV) destroy the CuO_2 plane. Charge redistribution in Cu-O-Nd(Ce) chains resulting from the oxygen displacement in the irradiated films is essential for superconductivity destruction.

The polarized K-Cu XANES measurements were carried out at the EXAFS line of VEPP-3m (Novosibirsk, Synchrotron Center). We used $Nd_{1.85}Ce_{0.15}CuO_4$ thin films (ca. 1000 Å) obtained via *in situ* laser deposition on $SrTiO_3$(100). X-ray diffraction measurements showed that films had a pure T'-phase with c axis along the (100) substrate direction. The samples were stepwise irradiated in cyclotron with He^+ ions (E=1.2 MeV) at ambient temperature up to 10^{16} cm^{-2} fluence



which results in T_c temperature decrease to zero. The Figure presents fluorescence K Cu XANES spectra of $Nd_{1.85}Ce_{0.15}CuO_4$ before (solid line) and after (dotted line) irradiation. No significant changes of $E_{||}$ (ab) are observed. With $E_{||}$ c, significant changes occured: B shoulder decreased and C shifted to higher energy.

C shift can be initiated either by changes of the electron state or by slight structure variations, namely by oxygen atom displacement in the elementary unit cell of irradiated compound. C maximum shift is ca. 10%. Since B shoulder corresponds to the Cu^+ state, its amplitude reduction can testify to the decrease of monovalent copper content. Local displacements of oxygen atoms (as they have the smallest mass and activation energy) along the c axis can result in reconstruction of the electron spectra of Cu-Ce-O complexes, while the electronic structure and Cu valence in CuO_2 plane remain the same within the XANES experimental resolution. Polarization data and superconductivity deterioration in the samples irradiated indicate the significant role of Cu-O-Nd(Ce) chain electron structure in coupling on the CuO_2 plane.

EXAFS DATA ON THE STRUCTURE OF IRON DIMERIC CLATHRATE CHELATES

Ya.Z. Voloshin (Karpov Phys.-Chem.Inst., Moscow), A.Yu. Nazarenko (Inst.Gener. Inorg. Chem., Kiev), S.P.Degtyaryov, D.I. Kochubey

EXAFS was used for studying various iron compounds with dioxide ligands. Some of these compounds are supposed to be dimers. EXAFS spectra of iron used for structural analysis of these complexes were complicated by the effects of multiple scattering. The dimer character of these compounds was verified and the general interatomic distances were determined.

STRUCTURAL STUDY OF QUATERNARY FLUORINE GLASSES BASED ON Cd AND Pb

N.V. Guriev (State Opt.Inst. of Glass, St-Peterb.), S.P. Degtyaryov (Eng.Phys.Inst., Moscow), D.I. Kochubey

Using EXAFS spectra of K- and L_3-edges of Cd- and Pb absorptions, respectively, in multicomponent fluorine glasses based on Cd and Pb, we have studied the local neighbouring of the latter at their different percent contents. Since besides fluorine the structure of glass exhibits oxygen as an anion, one of the problems was to find its localization. For Cd surrounding, it it suggested to be either a CdF_4 tetrahedron with Cd-F = 2.24 A or a strongly distrorted octahedron. Cd surrounding is oxygen-free and CdF_4 tetrahedron is a monomer. Pb surrounding is a mixed one, i.e. it is in the form of oxifluoride and again no Pb_n aggregates are found.

STRUCTURE OF AMORPHOUS PRODUCTS OF IRON SULFATE HYDROLYSIS

G.L. Elizarova, L.G. Matvienko, S.G. Nikitenko, D.I. Kochubey

EXAFS spectra of K-edge of iron adsorption were used to study the products of Fe^3 sulfate hydrolysis. Solid samples of various chemical composition were investigated, among them were calcined samples, partially hydroxylated ones and aqueous solutions at ambient temperature and 80°C. The samples of $NaFe_3(OH)_6(SO_4)_2$ molecular formula were shown to have the iron vicinity structure similar to the mineral one. The structure of amorphous complex with $2(Fe_2O_3)(SO_3)x10H_2O$ chemical composition is under study.

STRUCTURE OF $Pd_{501}Phen_{60}(OAc)_{180}$ GIANT CLUSTER

D.I. Kochubey, B.N. Novgorodov

Abstr. Int. Conf. XAFS-VII, Japan 1992,
to be published

EXAFS and some other methods were used to study the $Pd_{561}Phen_{60}(OAc)_{180}$ giant cluster. All methods, including EXAFS for solids gave a cluster model with a metallic nucleus and an organic shell. The metallic nucleus has a HCC structure with a 23+4Å diameter. The curve of radial atom distribution around Pd contains maximums of the first three coordination spheres. The location of maximums and their relative intensity coincide with those of bulk metal. Two discrepancies between this model and the experimental data are observed. First, coordination numbers obtained are by 30% lower than ones expected for the metal particle 23 Å in diameter. Second, RAD curves exhibit a distinct peak of the metal-ligand distance, which is unlikely for the model suggested, since according to the model the peak should possess a very low relative intensity.

New data on cluster solution in acetic acid, CH_3OH, acetonitrile and etc. were obtained. Coordination number for the first Pd-Pd coordination sphere in solutions is similar to that of the solid sample. The peak intensity of the metal-ligand distance increases drastically and there appears a new Pd-Pd distance not fitting the one for metal. All the facts obtained suggest a new model of the cluster metal nuclei different from the previous one.

STRUCTURE OF CdS CLUSTERS IN A AND X ZEOLITES

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To be submitted for publication

The authors have previously developed a technique for the direct CdS cluster synthesis in NaA and NaX zeolites. The optical characteristics of the product synthesized are similar to those of CdS. However, to confirm the synthesis quality, some structural methods should be applied. EXAFS spectra of K-edge absorption of Cd in A and X zeolites and of bulk CdS sulphides with a cubic and hexagonal packings were recorded for this purpose. The specrta exhibit that clusters synthesized in zeolite voids are of the hexagonal CdS structure.

BINUCLEAR ANION COMPLEXES OF Mo(V)

A.N. Startsev, O.V. Klimov, S.A. Shkuropat, M.A. Fedotov, S.P. Degtyaryov, D.I.Kochubey

Polyhedron, 17 (1994) 505-512

The structure of "hydroxide molybdenum(V)" obtained via reduction of MoO^{2-} ion with hydrazine hydrate in aqueous solution was established. It corresponds to the formula $(N_2H_5)_2[Mo_2(\mu_2\text{-}O)_2O_2(OH)_4(H_2O)_2$, (di-$\mu$-oxo-bis(aquadihydroxooxomolybdate(V) dihydrazonium. The products with similar structures were obtained upon MoO^{2-} $NaBH_4$ reduction and $(NH_4)_2MoOCl_5$ hydrolysis. IR-, NMR- and EXAFS spectroscopy were used to characterize diamagnetic complexes appearing upon Mo(V) hydroxide dissolving in oxalic or tartaric acids.

EXAFS FOR STUDYING Ti BUTYLATE HYDROGENOLYSIS

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To be submitted to *Mendeleev Commun.*

EXAFS spectra of K-edge of Ti absorption used for analysis of Ti butylate hydrolysis (the stage of protective coating formation and some chemical process performance) show the initial Ti to be in the form of tetrahedron which retains upon hydrolysis, though OC_4H_9 is substituted by OH group and Ti-Ti distance reduces from 3.5 A to 2.8 Å, which is typical for TiO_2 (anatase).

A NEW MATERIAL FOR RADIOGRAPHY

G.B. Gorin*, K.E. Gunsburg*, N.P.Zvezdova*, (Inst.Phys. State University, Saratov, Russia), D.I. Kochubey

Luminescence methods are placed among the most important X-ray detecting methods. These methods are based either on thermo- or photo-stimulated luminescence energy accumulated under X-ray or X-ray induced luminescence [1,2]. The above methods answer the main demands to X-ray detectors: (i) high quantum efficiency; (ii) wide-range dynamics; (iii) linear responce; (iv) high spatial resolution and (v) short time of pulse registering [3]. Unfortunately, the latent image destroys upon reading and the process of reading cannot be repeated. During the sample storage, the image is also destroyed. In [3] BaFBr-Eu^{2+} was used as a detecting material, which provided a 10% loss of information within a 2 months storage at 0°C, 40% and 87% at 20 and 40°C, respectively.

These shortcomings are caused by the small depths of traps responsible for the luminescence and small activation energies of their destruction. Materials with point defects and higher depths of traps appear to be more promising. They provide luminescence excitation without trap destruction, as the latter can be related to the localized exciting levels. In this case, the information can be read repeatedly and the signal can be accumulated. The storage time becomes unlimited. At the moderate depths of traps there is a possiblity of complete image destruction allowing a repeated utilization of detectors.

The authors managed to find a new class of materials producing luminescence centers with high optical and thermal stability. Those are the alkali-haloid materials with NaCl structure of dumped ions of 3b or 8a groups. These centers remain stable for a one year storage in light at ambient temperature. Centers are destroyed, when heavily heated. Moreover, a large stability of centers allows to perform their luminescence by UV light radiation.

To examine these materials, we have used a monochromatic synchrotron radiation in 6-30 keV range under visible light at ambient temperature. The image contrast was 0.45-0.6, dynamic range - 6 10^3, spatial resolution - 250-300 lin/mm (3-4 micron), the latter is not a limit yet. The life time of the excited center was 10^{-8} s. The minimal doze producing visualization of the stored image was 10^5 protons/(100 microns)^2. The image did not change after a one year storage at room temperature in light and repeated readings.

Thus, the characteristics of new materials for X-ray detecting appeared to be as good as those reported in [1-3]. They provide a repeated reading and a prolonged storage of the image obtained.

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GRAPHITIZED CARBON BLACKS IN THE SERIES OF CARBON SORBENTS

V.I. Zheivot

Carbon, to be published

The generalized data on unmodified and modified graphitized carbon blacks are presented in this communication.

The place of blacks in the series of carbon absorbents is analyzed with regard to both structural (graphitization degree and orientation of hexagonal carbon layers) and adsorption characteristics and with regard to surface chemistry and performance in chromatography.

The family encompases activated charcoals, carbosieves, carbon fibers, carbon-containing adsorbents forming during the catalytic decomposition of hydrocarbons (methane, propane-butane mixture) and composites.

Intermolecular interactions in the adsorbate - graphitized carbon black systems were varied directly by means of carbon black modification. New adsorbents suitable for studying the catalytic reaction products by molecular gas chromatography are presented.

STOICHIOGRAPHHY AND CHEMICAL ANALYSIS OF COMPOUNDS WITH UNKNOWN COMPOSITION

V.V. Malakhov

Zh. Analit. Khim., to be published

Molecular analysis of compounds with unknown composition is discussed with regard to stoichiography as stoichiometry of mass transfer under dynamic conditions. Such processes are the basis for all separation methods applied in analytical chemistry. If a separation method is modified to stoichiography, it allows to determine directly molecular, ionic and phase composition of unknown complex compounds. Two stoichiography laws postulated show its wide potential for advanced analysis. A concept of absolute detector is suggested. Such a detector permits to determine directly the elemental stoichiometric composition and the content of each individual compound present in a multiphase sample. The factors limiting the application of stoichiography methods are discussed. Possible development of stoichiography to a unified field of chemical analysis is considered.

PHASE ANALYSIS OF HETEROGENEOUS CATALYSTS BY STOICHIOGRAPHY OF DIFFERENTIAL DISSOLVING

V.V. Malakhov, A.A. Vlasov

Kinet. Katal., to be published

This work concerns the fundamentals of theory, methodology and instrumental design of a novel standardless chemical method of phase analysis - differential dissolving (DD). DD is based on stoichiography laws, which determine the stoichiometry of mass-transfer under dynamic conditions. Current papers are reporting on some DD applications for the phase analysis of particular heterogeneous catalysts. DD is capable to determine the qualitative and quantitative phase composition of complex catalysts even when their phase composition is not known in advance. The second advantage of this technique is that it provides reliable data on amorphous phases, phases with alternate composition, impurities and admixtures even if their amount in a sample is rather small. It is possibly to use DD for the samples of considerable weight and for the samples weighting several micrograms. DD permits to separate phases efficiently from their mixtures or concentrate them. An individual phase thus prepared can be studied by any method, including X-Ray diffraction. Samples characterization by both DD and X-Ray diffraction is rather promising for the optimization of conditions for studying catalyst phase composition and active component interaction with supports as well.

ICAR PROCESS (IMMEDIATE CATALYTIC ACCUMULATION OF IONIZING RADIATION ENERGY) AS A NEW PROMISING APPROACH TO THE DEVELOPMENT OF CHEMINUCLEAR POWER PLANTS

Yu.I. Aristov, Yu.Yu. Tanashev, S.I. Prokopiev, L.G. Gordeeva, V.N. Parmon

Int. J. Hydr. Energy, 18, 1 (1993), 45-62.

A new thermocatalytic method ICAR for nuclear-to-chemical energy conversion is suggested. The ICAR method is based on a combination of both nuclear and catalytic reactors in the same technological volume by loading the catalyst directly into the active (energy releasing) zone of a nuclear reactor and by heating the catalyst bed "from inside" by dissipation of the radiation energy. Two variations of the suggested method are studied theoretically and experimentally basing on endothermic catalytic reactions of methane and methanol steam reforming as well as on ammonia decomposition. The conditions of the immediate intensive heat release inside the catalyst bed were simulated by means of an electron accelerator. A new type of uranium containing catalysts for steam reforming of methane was synthesized and studied. These special catalysts as well as conventional commercial catalysts used in the ICAR method were shown to ensure a considerable intensification of the energy accumulating chemical reaction and to increase specific power loading of the energy conversion up to 100-150 kW/dm^3. Some advantages and difficulties of the application of the ICAR method are discussed.

INTENSIFICATION OF HYDROGEN PRODUCTION AND OPTIMIZATION OF H2:CO RATIO IN METHANE REFORMING REACTOR WITH A HYDROGEN-PERMEABLE WALL

S.I. Prokopiev, Yu.I. Aristov, V.N. Parmon, N. Giordano (Instituta di Ricerche sui Metodi E Processi Chimici per la Transformazione E L'Accumulo dell'Energia, Messina, Italy)

Int. J. Hydr. Energy, 17, 4 (1992) 275-279.

A combination of the chemical reactor with a hydrogen-permeable membrane is expected to result in the increase of hydrogen production rate. In order to analyze the steady-state operation of the membrane-wall reactor we simulated the process of steam reforming of methane

$$CH_4 + H_2O \longrightarrow CO + 3\ H_2$$

in an isothermal cylindric plug flow reactor ($r = 1\text{-}10$ mm) with a thin ($d = 0.02\text{-}0.10$ mm) palladium wall and a fixed bed of the nickel-based GIAP-3-6N (Russia) catalyst.

Our data show a noticeable increase in the rate of hydrogen formation at T 1000 K and P = 0.1 MPa for reactors with a small radius (rmm). In the membrane reactor high values of both the hydrogen production rate ($\omega = 1\text{-}2\ s^{-1}$) and the methane conversion ($x = 0.6\text{-}0.8$) can be achieved at relatively low temperatures, methane conversion being much higher than thermodynamic equilibrium values without the membrane. Thus, an application of the membrane catalytic reactor is reasonable when the temperature potential of the heat source used for hydrogen production is insufficient to shift the chemical equilibrium towards formation of hydrogen.

The hydrogen-permeable wall allows also to change the composition of syngas produced in particular, to reduce the ratio H_2:CO, which is known to be of a great importance when using syngas for organic synthesis. As is shown, the ratio can be varied within the range of 0-3 by the appropriate choice of temperature, pressure, contact time, reactor radius and membrane thickness.

HIGH-TEMPERATURE CHEMICAL HEAT PUMP BASED ON REVERSIBLE CATALYTIC REACTIONS OF CYCLOHEXANE DEHYDROGENATION - BENZENE HYDROGENATION. COMPARISON OF THE POTENTIALITIES OF DIFFERENT FLOW DIAGRAMS

Yu.I. Aristov, V.N. Parmon, G. Cacciola*, N. Giordano* (Instituta di Ricerche sui Metodi E Processi Chimici per la Transformazione E L'Accumulo dell'Energia, Messina, Italy)

Int. J. Energy Research, 17 (1993) 293-303

In this paper we compare various flow diagrams for high-temperature chemical heat pumps (HTCHP) based on the reversible cyclohexane dehydrogenation benzene hydrogenation reactions. A new technological flow diagram for HTCHP is suggested. The peculiarity of this diagram is a multipurpose use of hydrogen permeable membranes. A comparative thermodynamic analysis of the flow diagrams under consideration is undertaken to examine the influence of various factors on heat efficiency and the coefficient heat pump of performance. It is shown that the use of hydrogen-permeable membranes in principle allows to improve the performance of the HTCHPs and extend the field of their application in comparison with the HTCHPs based on the flow diagrams suggested earlier.

INFLUENCE OF HYDROGEN-PERMEABLE MEMBRANES ON THE EFFICIENCY OF THE HIGH-TEMPERATURE CHEMICAL HEAT PUMP BASED ON CYCLOHEXANE DEHYDROGENATION - BENZENE HYDROGENATION REACTIONS

G. Cacciola*, G. Restuccia* (Instituta di Ricerche sui Metodi E Processi Chimici per la Transformazione E L'Accumulo dell'Energia, Messina, Italy), Yu.I. Aristov, V.N. Parmon

Int. J. Hydrogen Energy, 18, (1993) 673-680.

In this paper we suggested and analyzed the flow diagram for a high-temperature chemical heat pump (HTCHP) based on the reversible cyclohexane dehydrogenation - benzene hydrogenation reactions. The peculiarity of this diagram is a multipose use of hydrogen-permeable membranes. A thermodynamic analysis of the proposed flow diagram was undertaken in order to examine the influence of different factors on the coefficient of heat pump performance and on the pressure in the dehydrogenation reactor. It was shown that the new flow diagram with hydrogen-permeable membranes allows to improve the performance of HTCHPs and to extend the field of their practical application.

A ROLE OF $YBa_2Cu_3O_{7-\delta}$ CERAMICS MICROSTRUCTURE AT NONRESONANCE MACROWAVE ADSORPTION IN THE SMALL MAGNETIC FIELDS

L.L. Makarshin, O.P. Krivoruchko, E.V. Skripchenko, O.V. Lukyanova, N.E. Rudina, E.M. Moroz, V.N. Parmon

Sib. Khim. Zh., vyp. 2 (1991) 43-46

Non-resonance absorption of SHF irradiation was used to study the macrostructure of ceramic superconducting $YBa_2Cu_3O_{7-\delta}$ sample. It was shown that the sample obtained via precipitation of hydroxides exhibits two types of macrostructure, i.e. a thin and superconducting film of ca. 14 μm and particles of d ca. 0.3 μm. These phases are isolated from each other and have the same temperature of the superconducting transition.

EFFECT OF NAPHTHALENE ADSORPTION ON SUPERCONDUCTING PROPERTIES OF YTTRIUM CERAMICS

N.S. Belousov, L.L. Makarshin, V.N. Parmon

Sverkhprovod.: Fiz., Khim., Tekhn., 4, 8 (1991), 1614-1616

With $YBa_2Cu_3O_{7-\delta}$ ceramic samples treated by naphthalene solution in chloroform, the increase of superconducting transition temperature (1-1.5 K), as well as the rise of the critical current (to 20%), were registered at the constant current attenuation rate in the superconducting ring. No effect of anthracene and tetrachloroquinone on the properties of this ceramics was observed.

EFFECT OF ADSORBED NITROXYL RADICAL ON THE TEMPERATURE DEPENDENCE OF THE CRITICAL CURRENT IN THE SUPERCONDUCTING YTTRIUM CERAMICS

N.S. Belousov, L.L. Makarshin, V.N. Parmon

Sverkhprovod.: Fiz., Khim., Tekhn., 6, 3 (1992) 467-469

Nitroxyl radical adsorption (0.2 mol) over the $YBa_2Cu_3O_{7-\delta}$ ceramic provides the increase of critical current at the temperature ranging from 77 to 90 K. The increase of the adsorbed radical concentration decreases the transport critical current. Adsorption of a nonmagnetic analog of the nitroxyl radical does not influence the critical current. Stabilization of Josephson vorteces by magnetic moments localized between the sample granules can most probably be the mechanism of this phenomenon.

IMPROVEMENT AND CHANGE OF SUPERCONDUCTING PROPERTIES OF YTTRIUM CERAMICS CAUSED BY ITS TREATMENT WITH H_2, O_2 and Ar GASES UNDER MILD CONDITIONS

V.V. Kurchev, L.L. Makarshin, V.N. Parmon

in "Production, Properties and Analysis of High-Temperature Superconducting Materials and Products", Ekaterinburg, 1991

If yttrium ceramics is treated with Ar at 80°C under 6 atm pressure, the temperature of superconducting transition appears to rise T_c = 110 K. If time of ceramics treatment exceeds 3 hours, T_c drops.

MULTIFUNCTIONAL CATALYSIS BASED ON VECTORIAL ELECTRON AND ION TRANSFER

K.I. Zamaraev, S.V. Lymar, V.N. Parmon, E.N. Savinov, V.A. Sobyanin

Catal. Science and Technology, 1 (1991) 299-306

The use of liquid and solid electron- and ion-conducting membranes opens new unique opportunities in the design of multifunctional catalytic systems. In such membrane systems one can accomplish rather complicated reactions with high selectivity and minimum energy losses.

In this paper three types of such membrane catalytic systems will be discussed: (i) microheterogeneous vesicle systems for light-to-chemical energy conversion via water cleavage; (ii) systems for gas phase reduction of carbon oxides based on solid proton-conducting membranes; and (iii) systems for methane coupling to C_2 hydrocarbons based on solid O^{2-} conducting membranes and liquid CO^{2-} conducting molten carbonate electrolyte.

GAS-PHASE ELECTROCATALYTIC REDUCTION OF CO_2 TO CO ON CARBON GAS-DIFFUSION ELECTRODE PROMOTED BY COBALT PHTHALOCYANINE

E.R. Savinova, S.A. Yashnik, E.N. Savinov, V.N. Parmon

React. Kinet. Catal. Lett., 46, 2 (1992) 249-254

Cobalt phthalocyanine supported on a carbon gas-diffusion electrode has been found to be an active and stable electrocatalyst for the reduction of CO_2 to CO. Under mild conditions it gives 100% selectivity of this process at current densities of up to 80 mA/cm^2.

INFLUENCE OF COBALT PHTHALOCYANINE DEPOSITED ONTO THE PARTICLE OF MIXED Cd/Cu_xS SUSPENSIONS ON PHOTOCATALYTIC EVOLUTION OF HYDROGEN FROM WATER SOLUTIONS OF Na_2S

E.N. Savinov, Lu Gongxuan (Janzhou Institute of Chemical Physics, Chinese Academy of Sciences, Janzhou, China), V.N. Parmon

React. Kinet. Catal. Lett., 48, 2 (1992) 553-560

Deposition of water-insoluble cobalt phthalocyanine CoPc onto the particles of mixed suspensions of CdS and Cu_xS can increase the rate of photoinduced evolution of H_2 from Na_2S and Na_2SO_3 solutions. At $[Na_2S] = 5\cdot10^{-2}$ M, the rate of photocatalytic reaction is almost doubled at the deposition of $6.4\cdot10^{-10}$ moles CoPc onto $4\cdot10^{-5}$ moles of CdS and of $2.9\cdot10^{-8}$ moles of CoPc onto 10^{-5} moles of Cu_xS. At $[Na_2S] = 10^{-1}$M, which is close to the optimal concentration of Na_2S, the deposition of CoPc is able to provide only a 30% increase of the reaction rate.

KINETIC STUDIES OF PHOTOREDOX REACTIONS SENSITIZED BY DISPERSE CdS AND DESIGN OF SEMICONDUCTOR AND COMBINED SEMICONDUCTOR/ MOLECULAR PHOTOCATALYTIC SYSTEM FOR SOLAR ENERGY CONVERSION

V.N. Parmon, E.N. Savinov, M.I. Khramov, K.I. Zamaraev

Photochemical Conversion and Storage of Solar Energy, 9th Intern. Conf. Beijing, China 1992

Peculiarities of kinetics of photo-redox reactions sensitized by the water suspension of CdS are studied and used for design of semiconductor and combined semiconductor/ molecular photocatalytic systems for the light-to-chemical energy conversion. In particular, under study are: kinetics of electron phototransfer from CdS to molecular oxygen and methylviologen, the influence of the competitive adsorption of reagents and surfactants on the kinetics of photocatalytic reactions, kinetics of photocatalytic H_2 evolution in a mixed semiconductor/molecular system Co phthalocianine/CdS/Cu_xS, kinetics of electron phototransfer across a membrane of a lipid vesicle with CdS as photosensitizer incapsulated in the inner cavities of the vesicle.

OPTICAL RESPONSES FROM A POLYCRYSTALLINE COPPER ELECTRODE UNDER PULSED INFRARED LASER IRRADIATION

Yu.A. Gruzdkov, O.V. Shamardin, V.N. Parmon

J. Chem.Soc.Faraday Trans., 88 (1992) 2705-2711

The study of optical second harmonic generation (SHG) of a polycrystalline copper electrode in the course of its anodic dissolving in aqueous electrolytes has shown two different types of SHG signal. The first type is observed in H_2SO_4 solutions, pH 1, and is caused by molecular adsorption of the electrolyte species on the electrode. The second type is observed in potassium halide electrolytes and is caused by surface copper(I) halide layers formation under anodic potential bias. These types of SHG signal differ in intensity, dependence on excitation power and cyclic reproducibility. A strong non-monochromatic background optical signal was detected in alkaline solutions. The study of the precise nature of this signal indicates that it originates from anodic formation of a thin film of surface copper oxides and a repetitive thermoshock destruction of this film under IR laser pulses.

OXYGEN ISOTOPE EXCHANGE OVER A Pt ELECTRODE IN A CELL WITH SOLID OXIDE ELECTROLYTE

V.A. Sobyanin, V.I. Sobolev, V.D. Belyaev, A.K. Demin, O.A. Mar'ina

React. Kinet. Catal. Lett., 47 (1992) 327-332.

Studies of homomolecular oxygen exchange over a Pt electrode in a electrochemical cell:
$^{16}O_2 + {}^{18}O_2$, Pt|ZrO_2 (10 mol.% Y_2O_3)|Pt, air show that electric current passing through the cell (a flow of O^{2-} anions through the electrolyte) does not change the rate of exchange with respect to its open cicuit value. This fact indicates that the passing electric current does not affect the strength of oxygen adsorption on Pt electrode. Thus the present concept on the nature of Non-Faradaic Electrochemical Modification of Catalytic Activity (Vagenas et al., Catal. Today 11 (1992) 303) is to be specified.

THE EFFECT OF ELECTROCHEMICAL OXYGEN PUMPING ON THE RATE OF CO OXIDATION ON Au ELECTRODE-CATALYST

O.A. Mar'ina, V.A. Sobyanin

Catal. Lett., 13 (1992) 61-70

The effect of electrochemical pumping of oxygen on the rate of carbon monoxide oxidation on Au electrode-catalyst in a solid oxygen conducting electrolyte cell has been demonstrated. The induced change in the reaction rate at the cathodic polarization of Au electrode was by an order of magnitude higher than the rate of O^{2-} pumping from the reaction zone through electrolyte. The anodic polarization of Au electrode-catalyst (O^{2-} pumping into reaction zone through electrolyte) provided pure Faradaic changes in the reaction rate.

THE METHANE OXIDATION ON A GOLD ELECTRODE IN A SOLID ELECTROLYTE FUEL CELL

O.A. Mar'ina, V.A. Sobyanin, V.D. Belyaev

Mater. Sci. Eng., B13 (1992) 153-158

The effect of electrochemical pumping of oxygen on the rate of complete oxidation of methane over Au electrode catalyst in solid oxygen conducting electrolyte cell has been demonstrated. The induced change in the reaction rate upon cathodic polarization of Au electrode appeared to be higher than the rate of O^{2-} pumping from the reaction zone through electrolyte. The anodic polarization of Au electrode (O^{2-} pumping to the reaction zone through electrolyte) caused pure Faradaic changes in the reaction rate.

The enhancement of the Au electrode catalytic activity upon cathodic polarization is most probably related to the increase of coverage with reactive oxygen species, such as O^{-}_{2ads} and O^{-}_{ads}.

THE EFFECT OF ELECTROCHEMICAL OXYGEN PUMPING ON THE CATALYTIC PROPERTIES OF Ag AND Au ELECTRODES AT THE GAS-PHASE OXIDATION OF CH4

O.A. Mar'ina, V.A. Sobyanin, V.D. Belyaev, V.N. Parmon

Catal. Today, 13 (1992) 567-570

The oxidation of methane on Ag and Au electrodes in electrochemical cells such as

gaseous reactants, metal catalysts |ZrO_2
(10 mol.% of Y_2O_3)|, metal, air

has been studied. It was found that the surface oxygen on these electrodes, which was generated from the gas phase and electrochemically, exhibited different properties with respect to oxidation of methane.

OXIDATIVE CONVERSION OF CH4 ON Ni AND Ag ELECTRODE-CATALYST IN A MOLTEN CARBONATE FUEL CELL REACTOR

V.D. Belyaev, V.A. Sobyanin, V.N. Parmon, S. Freni*, M. Aquino* (Instituto CNR-TAE, Salita Lucia, 39, I-98126, S. Lucia (ME), Italy)

Catal. Lett., 17 (1993) 213-221

A fuel cell system with molten carbonates of potassium and lithium used as an electrolyte was applied to oxidative conversion of methane over Ni and Ag electrodes. A possibility of cogeneration of valuable chemicals (C_2 hydrocarbons) and electricity in such a system was demonstrated. With CO_3^{2-} ions (oxygen) transported electrochemically, the rate of formation of C_2 hydrocarbons and their selectivity on Ag electrode were found to be higher than those of oxygen premixed in the gas phase.

THE EFFECT OF ELECTROCHEMICAL HYDROGEN PUMPING ON THE CATALYTIC PROPERTIES OF NI AND Pd ELECTRODE CATALYSTS WITH RESPECT TO ETHYLENE HYDROGENATION

T.I. Politova, V.A. Sobyanin, V.D. Belyaev

Elektrokhim., 28 (1992) 1466-1475

We have shown the effect of electrochemical hydrogen pumping on the rate of ethylene hydrogenation on Ni and Pd electrode-catalysts in the solid-proton-conducting electrolyte cell:

$H_2 + C_2H_4$, Ni(Pd)|C_sHSO_4|Pd, H_2

The electric current passing through the cell was found to alter dramatically and reversibly the catalytic activity of metal electrodes upon C_2H_4 hydrogenation. The induced changes in the catalytic rate were by one-two orders of magnitude higher than the rate of hydrogen pumping through electrolyte.

OXIDATIVE CONVERSION OF METHANE ON Cu AND Ag-Ni ELECTRODES AT ARTIFICIAL UNSTEADY-STATE MODE OF THE SOFC REACTOR OPERATION

V.D. Belyaev, V.A. Sobyanin, O.A. Mar'ina

Studies in Surface Science and Catalysis. "New
Aspects of Spillover Effect in Catalysis for
Development of Highly Active Catalysts". Ed.
T. Inui, Elsevier 1993, 77, p. 213.

A fuel cell system using yttria doped zirconia as electrolyte was applied to the oxidative conversion of methane over Ag-Ni and Cu electrodes. A possibiliity of enhancing the rate and selectivity of C_2 hydrocarbons formation by using such systems at unsteady-state modes of operation was shown.

ON THE NATURE OF NON-FARADAIC CATALYSIS ON METAL ELECTRODES

V.A. Sobyanin, V.D. Belyaev

React. Kinet. Catal. Lett., 51, 2 (1993) 373-382

The non-Faradaic change of the rate of carbon monoxide catalytic oxidation at the polarization of metal electrode-catalysts deposited on a solid oxygen-conducting electrolyte was shown to result from the reaction chain mechanism involving electrochemically generated oxygen species.

OXIDATIVE CONVERSION OF METHANE OVER Pt ELECTRODE IN A FUEL CELL SYSTEM WITH SOLID OXIDE ELECTROLYTE

V.A. Sobyanin, V.D. Belyaev

1st Europ. Congr.Catal. EUROCAT, Montpellier,
France, 1993, Book of Abstracts, 2, p. 730.

A complete oxidation of methane on Pt electrode in a zirconia electrochemical cell was studied. The effect of reactant pressure, temperature, current passing through the cell on the rate of methane oxdative conversion was demonstrated. In particular, it was found that current passing through the cell (O^{2-} anions pumping into reaction zone through the electrolyte) increases significantly the catalytic activity of platinum with respect to its open circuit value. The induced change in the catalytic reaction rate was reversible and by two orders of magnitude higher than that of O^{2-} pumping through electrolyte.

THE EFFECT OF ELECTROCHEMICAL PUMPING OF OXYGEN ON CATALYTIC BEHAVIOR OF METAL ELECTRODES AT METHANE OXIDATION

O.A. Mar'ina, V.A. Sobyanin, V.D. Belyaev, V.N. Parmon

Studies in Surface Science and Catalysiis. "New
Aspects of Spillover Effect in Catalysis for
Development of Highly Active Catalysts". Ed.
T. Inui, Elsevier, 1993, 77, p. 337.
Abstract Handbook. G.-M. Schwab Symposium,
Berlin-Spandau (Johanuesstilt), Germany, 1993.

The deep oxidation of methane was investigated on Ag, Au and Pt electrodes deposited on yttrium stabilized zirconia. The effect of electrochemical oxygen pumping on the rate of methane oxidation on these electrodes has been shown. The enhancement of methane oxidation rates at the electrochemical pumping of oxygen to or from the Ag and Au electrode-catalysts can be explained in the frames of conventional electrochemistry. The change in the catalytic activity of Pt electrode towards CH_4 oxidation during the current passage through the cell is stimulated by the creation of new reaction sites on Pt surface.

PECULIARITIES OF REACTION KINETICS OF METHANE STEAM REFORMING ON NICKEL BASED CATALYSTS

N.N. Bobrov, I.I. Bobrova, V.A. Sobyanin

Kinet. Katal., 34, 4 (1993) 758-761

Kinetics of methane steam reforming on Ni wire and the GIAP-16 commercial catalyst was studied. The data obtained indicate that methane steam reforming on Ni-based catalysts is a particular catalytic reaction with both surface and gas-phase steps.

INFLUENCE OF PREPARATION METHODS ON PROPERTIES OF Ni-MgO CATALYSTS FOR METHANE STEAM REFORMING

A.S. Ivanova, I.I. Bobrova, E.M. Moroz, V.Yu. Gavrilov, A.V. Kalinkin, V.A. Sobyanin

Kinet. Katal. 34, 4 (1993) 758-761

The physico-chemical properties and catalytic activity of Ni-Mg systems prepared via different methods have been examined. The catalyst specific activity was found to remain invariant under various preparation procedure.

IMPROVEMENT OF METHODS AND TECHNIQUES FOR EXPERIMENTAL STUDY OF CATALYTIC PROPERTIES

N.N. Bobrov

Methods for precise kinetic control of catalytic activity in the flow-circulating reactors have been developed for a number of important catalytic processes, such as oxidation of CO, hydrocarbons and SO_2, methane steam reforming, CO steam conversion and hydrogenation, methanol synthesis, partial oxidation, hydrocarbon ammonolysis and etc.

To carry out modern kinetic experiments special highly efficient technical and automatic means have been designed for kinetic studies and control. To obtain precise values of gas adsorption, the volumometric devices working under static and dynamic conditions were built.

These devices and systems are successfully used for design and improvement of catalysts and supports; kinetic studies of the catalytic processes and educational purposes at a High school.

ADVANCED METHODS AND TECHNIQUES FOR CATALYST TESTING

N.N. Bobrov

Novel automatic setups and devices have been designed and used:

- Two CATACON-1.1C setups for the kinetic testing of deep oxidation catalytic activity were created for Monsanto Enviro-Chem (USA) and the Sertification Center "Catalysis" at Boreskov Institute of Catalysis;

- A device for the express measurements of the overall specific surface of catalysts, adsorbents and other dispersed and porous materials.

POROUS CARBON GENERATED ON METAL- AND OXIDE CATALYSTS

V.B. Fenelonov, L.B. Avdeeva, V.I. Zheivot, L.G. Okkel

Kinet. Katal. 34, 3 (1993) 540-544
J. of Catalysis, to be published

Here the properties, mechanisms of generation and prospects of using carbon and carbon-mineral porous systems obtained via coking of metal and oxide catalysts are reviewed. The main four types of systems are notified.

Coking of oxide catalysts yields systems I and II. They possess practically uniform (I) or "mosaik" (II) coating of matrix surface by carbon. Additional activation intensifies the mosaic structure generation and produces microporous carbon in the porous mineral matrix.

Metal catalyst carbonization produces III and IV structures. III-type systems contain a fibrous carbon in the porous space of original matrix; IV contains balls made of carbon filaments with less than 0.01 g of catalyst per gram of carbon.

The adsorption properties of these systems were studied. Peculiarity of systems III (and of some systems IV) is the possibility to produce original "molecular sieves" with large pores (several nm in diameter). The removal of active metal from the carbon filament "head" (via extrusion mechanism) produces such sieves. With IV systems, the surface of carbon filaments can be built exclusively with the side faces of graphite (but not with the basal ones). This provides extremely high values of the Henry coefficient and adsorption heats at a low coating.

The prospects of using these systems as adsorbents and catalysts are under consideration.

FILAMENTOUS CARBON OBTAINED VIA LOW TEMPERATURE CATALYTIC DECOMPOSITION OF ALKANES

V.B. Fenelonov, L.B. Avdeeva, V.I. Zheivot, V.I. Zaikovskii, L.G. Okkel, O.V. Goncharova, G.G. Kuvshinov, V.A. Likholobov

Kinet. Katal., 34 (1993) 545

Submitted to 8th Symp. Scient. Bases for Prep. Heterog. Catalysts, Belgium 1994

A new carbon material presented by filamentous-structured grains has been designed. The material is refered to as CFC (catalytic filamentous carbon). It is produced by the catalytic decomposition of C_1-C_4 alkanes or other hydrocarbons in a vibrofluidized bed at 500-600^{0}C. The yield of 150-330 g per catalyst gram is attained, the content of impurities (whose composition corresponds to that of initial catalyst) being as low as 0.3-0.6%. Thus, the CFC is a virtually pure graphite-like carbon.

Texture. The grains of CFC consist of globules formed by the interlaced carbon filaments; the filaments are several microns in length and 10-15 nm in diameter. The samples have 100-300 m^2 specific surface area, 0.3-0.6 cm^3/g pore volume, and 10-20 nm average pore size.

Structure. A CFC filament is shaped by the graphite basal planes packed like a pile of truncated cones, put on the preceeding one; the interlayer distances are 3.40-3.43 Å. Due to the different cone lengths the exposed filament surface, formed by cone butt-ends, is covered with atomic-sized microroughnesses whose dimensions are divisible by the interlayer distance. Thus, the structure of the exposed surface essentially differs from those of conventional carbon blacks (CB) and activated charcoals (AC) that results in their different adsorbabilities.

Adsorbability. The adsorptive behaviour of the CFC appears to vary from that of currently available carbon adsorbents such as CB, AC, carbon molecular sieves, etc. When compared to CB and AC, a lower adsorption of n-alkanes C_1-C_4 and a higher adsorption of those with more than 4 carbon atoms are observed on the CFC, the difference being more noticeable as the number of C atoms increases. The CFC is far superior (by 4-6 orders of magnitude) to the best known microporous charcoals with respect to adsorption of C_6H_6, C_6H_5Cl, $C_6H_5CH_3$, C_6H_5OH, $C_6H_4(CH_3)_2$ within the concentration range of 10^{-4}-10^{-6} vol.% but ranks below them with regard to adsorption capacity over a higher concentration range.

Therefore, the CFC is a unique adsorbent which seems to be promising for ultrafine purification from various carbon-containing compounds (with no less than 5 carbon atoms) within the concentration range of 10^{-4}-10^{-6} vol.%, for the concentrating of microimpurities needed, e.g., for their analysis, etc.

Besides, a homomesoporous CFC adsorbent is of most interest in the recuperation, gasoline evaporative emission control for cars and etc.

ON AUTHENTICITY OF PORE-SIZE DISTRIBUTION OBTAINED VIA TRADITIONAL TECHNIQUES

D.K. Efremov, V.B. Fenelonov

Pure and Appl. Chem., 65, 10 (1993) 2209-2216
Kinet. Katal. 34, 4 (1993) 625-633

Here we have examined the authenticity of pore-size distribution obtained via some conventional techniques of independent pore interpretation. The investigation presents computer simulated adsorption, capillary condensation, desorption, mercury intrusion and some other processes in model porous lattices built as a large number of spheroidal-shaped voids pasted by toroidal necks.

Special attention was paid to the plausibility of the simulated process. In particular, the cooperative capillary condensation inside the group of neighbouring voids was analyzed on terms of thermodynamics and molecular physics.

The data of prolonged numerical experiments (adsorption isotherms, mercury intrusion curves, etc.) were analyzed with conventional techniques providing evaluation of independent pore size distributions. The values of size distribution, thus obtained, were compared to those for the model porous solids. The discrepancy was considered as well. A more reliable interpretation of results obtained via traditional techniques is given.

OXIDATION OF CYCLOALKENES AND METHYLENECYCLOALKANES BY PALLADIUM(II) COMPLEXES

I.E.Beck, E.V.Gusevskaya, A.V.Golovin, V.A.Likholobov

J. Molec. Catal., 83 (1993) 287-300
J.Molec. Catal., 83 (1993) 301-310

Oxidation of 1-methylcyclobutene (1) and methylenecyclobutane (2) by $PdCl_2L_2$ and $PdCl(NO_2)L_2$ ($L=CD_3CN$) in methylene chloride was studied with ^1H and ^{13}C NMR. Reaction of (1) with $PdCl_2L_2$ leads to the formation of stable ring-opened 1-3-η^3-π-allyl palladium complex (3). When equimolar quantity of $PdCl(NO_2)L_2$ is added to the solution of (3), the allylic oxidation of (3) into CH_3-$CH(NO_2)$-$C(CH_3)$=CHCl proceeds slowly via the intermediate formation of another 1-3-η^3-π-allyl palladium complex (4). When reacting directly with $PdCl(NO_2)L_2$, (1) undergoes a palladium(II) catalyzed ring contraction to cyclopropyl methyl ketone. Kinetic and spectral data indicate the formation of organometallic intermediate: β-nitrotipalladium product of Markovnikov 1,2-cis addition to C=C bond. The reaction of (2) with $PdCl(NO_2)L_2$ yields cyclopentanone. Two intermediates: π-olefin complex of palladium and the product of β-nitritopalladation of (2) in a Markovnikov manner are observed by ^1H and ^{13}C NMR. The selective formation of ring-expanded and ring-contracted carbonyl products from methylenecyclobutane and 1-methylcyclobutene, respectively, is discussed in terms of suggested mechanism.

OXIDATION OF FERROUS IRON SULFATE BY OXYGEN ON Pt/C AND Pd/C CATALYSTS

L.B.Okhlopkova, N.I.Kuznetsova, A.S.Lisytsin, N.I.Gerhert, V.A.Likholobov

Submitted for publication

Pd/C and Pt/C catalysts were found to exhibit a high activity in oxidation of iron suboxide sulfate by oxygen. With metals supported on carbon the process is performed under mild conditions [1] at ambient or even at somewhat higher temperatures and atmospheric pressure. Acidity provides a positive effect on reaction rate even in highly acidic media. This is a peculiarity of this reaction differing from a non catalytic oxidation of Fe(II). The latter can proceed only in basic or neutral media.

The catalytic reaction rate appears to be proportional to oxygen concentration in the gas phase and depends insignificantly on Fe(II) concentration (reaction order is 0.2) and Fe(III) concentration (reaction order is -0.5). The study of kinetic peculiarities and adsorption of iron ions on the surface of Pt/C catalysts has shown, that under reaction conditions the metal surface is covered with adsorbed oxygen, which in its turn adds the ions of suboxide and oxide iron. The surface complexes are in equilibrium with iron ions in solution. In oxygen absence iron ions do not react with the catalyst surface. Reduction of adsorbed oxygen by Fe(II) ions involves protons.

Compounds disposed to the strong adsorption on metal surface provide a considerable inhibiting effect on oxidation of iron(II) sulfate. E.g., introduction of small amount of chloride ions provided a sharp decrease of reaction rate.

Pd/C catalysts loose rapidly their activity under reaction conditions due to dissolving of metal component. Platinum samples are not washed out. The samples which lost partially their activity can be regenerated via reduction.

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EFFECT OF CHEMICAL STATE OF CARBON SUPPORT SURFACE ON PALLADIUM CHLORIDE ADSORPTION

P.A.Simonov, V.A.Likholobov, E.M.Moroz, V.N.Kolomyichuk

Izv. Akad. Nauk, Ser. Khim., to be published

The effect of surface heteroatoms (H, O and Cl) on adsorption of $PdCl_2$ from H_2PdCl_4 solutions has been studied. The latter produces π-complexes of $PdCl_2$ with >C=C< fragments of carbon skeleton.

The surface of carbon supports was modified via 1) oxidation by aqueous solutions of H_2O_2 or $KMnO_4$ with consecutive removal of reaction products, 2) chlorination in Cl_2 atmosphere at 100 °C, 3) exposure to hydrogen flow at 250-350 °C and 4) heating to 600 °C in vacuum.

The type and number of the surface oxygen containing groups was determined with respect to neutralization of HCl, Na_2CO_3, NaOH and NaOEt solutions. The number of sites for $PdCl_2$ adsorption and adsorption equilibrium constants were determined according to [1]. Substructural characteristics of modified supports calculated from the data of a low temperature N_2 adsorption and X-ray analysis (SAXS and WAXS) appear to be very close to those of parental support.

The surface heteroatoms were found to decrease the concentration of sites for the strong $PdCl_2$ adsorption located on the edge planes of carbon crystallites and micropores. The sites of weak $PdCl_2$ adsorption belonging to basal planes appear to be more stable. After destruction of the oxygen containing groups the number of $PdCl_2$ adsorption sites increases again.

The relationships between adsorption site concentration, adsorption equilibrium constants and the number of surface oxygen containing groups were obtained. Accepting groups (–COOH, >C=O and –Cl) appear to increase while donating groups (>C-OH) are found to decrease the strength of the surface π-complexes of $PdCl_2$. This seems to relate to the change of electron density in >C=C< fragments. The surface heteroatoms are assumed to affect the mobility of or $PdCl_2$ molecules clusters and Pd(0) atoms upon reduction of $PdCl_2/C$ to Pd/C during the catalyst preparation.

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RUTHENIUM IONS SUPPORTED ON HETEROPOLYANION: FORMATION, REDOX AND CATALYTIC PROPERTIES

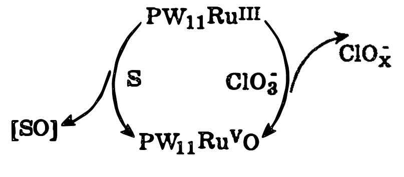
L.I.Kuznetsova, L.G.Detusheva, V.A.Likholobov

Kinet. Katal., 34, 6 (1993) 1017-1019
Izv. Akad. Nauk, Ser. Khim., 8 (1993) 1363

Heteropolycomplex (HPC) of ruthenium(IV) (abbreviated as $PW_{11}Ru^{IV}$) was obtained via reaction of $K_2RuOHCl_5$ with heteropolyanion (HPA) $PW_{11}O_{39}^{7-}$. HPC of ruthenium (II), (III) and (V) were obtained as well via electrolysis of $PW_{11}Ru^{IV}$ solutions and characterized by UV-VIS absorbance spectra. Tetraalkylammonium salts of $PW_{11}Ru^{IV}$ and $PW_{11}Ru^{III}$ were identified with element analysis and IR spectroscopy. pH region of HPC stability was determined via UV-VIS spectroscopy and interaction of $PW_{11}Ru^{IV}$ with ClO_4^-, SO_4^{2-} and Cl^- ions in aqueous solution was studied. For these compounds the Keggin lattice of HPA was assumed not to involve Ru ions. The latter are considered to be bound with the surface oxygen atoms of HPA.

Since Cl^- ions are generated, $PW_{11}Ru^{II}$ is oxidized by perchlorate ions. Kinetics of $PW_{11}Ru^{IV}$ and $PW_{11}Ru^{III}$ oxidation by potassium chlorate was studied at various initial concentrations of HPC, $KClO_3$, ionic strength, pH and temperature. Activation of ClO_4^- ion by $PW_{11}Ru^{II}$ and ClO_3^- ion by $PW_{11}Ru^{III}$ and $PW_{11}Ru^{IV}$ complexes was shown to be possible in aqueous solutions. This seems to be rather important when these ions are used as oxidants in catalytic reactions.

HPC obtained appear to catalyze oxidation of primary alcohol and aldehydes by potassium chlorate to the corresponding carbonic acids with the ~100% yield ($[HPC]=10^{-3}$, $[KClO_3]=0.3\text{-}0.6$ mol/l, pH=2, T=75 °C). In this system acrolein is oxidized to acrylic acid with a 70% selectivity. In the presence of organics $PW_{11}Ru^{IV}$ and $PW_{11}Ru^{V}$ are reduced to $PW_{11}Ru^{III}$ and the scheme of catalytic reaction can be presented as follows:



CATALYSIS BY HETEROPOLY COMPLEXES FOR CYCLOHEXENE OXIDATION AND HYDROGEN PEROXIDE DECOMPOSITION

N.I. Kuznetsova, L.G. Detusheva, L.I. Kuznetsova, M.A. Fedotov, V.A. Likholobov

Kinet. Katal., 33, 3 (1992) 516-523

Heteropolycomplexes (HPC) of formula $[(C_4H_9)_4N]_4H_xPW_{11}M(L)O_{39}$ (M = Ti(IV), V(V), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Ru(IV); L = H_2O, OH^-, O^{2-}) in acetonytrile solutions were prepared and characterized by ^{31}P NMR. These compounds were analyzed at two reactions: (i) hydrogen peroxide decomposition and (ii) cyclohexene oxidation with H_2O_2 ($[HPC]=0.012$, $[H_2O_2]=0.16$, $[C_6H_{10}]=0$ or 0.1 mol/l, 35°C). The catalytic properties of HPC differ from those of parent $PW_{11}O^{7-}$ complex and depend on metal M in HPC.

$PW_{11}O^{7-}$ complex is an active catalyst for cyclohexene epoxidation. Only Fe(III) and Cr(III) containing HPC were active at cyclohexene oxidation, cyclohexenol and cyclohexenon being the main products. UV-VIS and ^{31}P NMR investigations have clearly demonstrated that the catalytic reactions are accompanied by the formation of active oxygen adducts with W(VI) atoms (in PW_{11} complex) or Fe(III) and Cr(III) atoms (in $PW_{11}M$ complexes).

$PW_{11}TiO_{40}^{5-}$ complex behavior is rather unusual. It slowly produces peroxocompound in the presence of H_2O_2 which does not oxidize cyclohexene. In contrast to many others V(V) compounds, $PW_{11}VO_{40}^{4-}$ is inert to H_2O_2. A high stability of these complexes seems to be the reason of their inertness.

ESCA STUDY OF PALLADIUM CATALYSTS DEPOSITED ON VARIOUS CARBON SUPPORTS

A.I.Boronin, A.V.Romanenko, A.B.Shvets, V.A.Likholobov

Appl. Catal., to be published

A set of Pd/C catalysts working in aggressive reaction media for hydrogenation of o-nitrophenol (ONP) solutions and melts of benzoic acid were studied by ESCA technique.

Pd/C catalysts (4-5 wt.%) were prepared via adsorption of H_2PdCl_4 from its aqueous solutions on activated carbons followed by the treatments of suspension with Na_2CO_3 solutions. Then the surface complexes were reduced by sodium formate. The activated carbons of ARD, PN, Degussa trade marks and synthetic activated carbon "Sibunit" with a fraction composition of 100-250 micron were used as supports.

TEM patterns and XPS spectra of initial fresh and treated samples were recorded with JEM-1000CX microscope and "VG ESCALAB", respectively.

Pd 3d spectra of initial catalysts show two main states of Pd: Pd^0 and Pd^{2+} to form on all supports. In a series: "sibunit"-ARD-PN-Degussa the fraction of reduced palladium decreases considerably. This is probably related to the different character of Pd^{2+} compounds and their reduced forms with the surface of various supports.

For reduced Pd forms XPS spectra exhibit lines of a complex structure. Pd 3d and Pd-MNN spectra analysis elucidated various discrete forms of reduced Pd with E_b Pd $3d_{5/2}$ to exist: $Pd^{-\delta}$ (334.5 eV), Pd^0 (335.4 eV) and $Pd^{+\delta}$ (335.8 eV), the contribution of each state varied with the type of support.

Thus, predominant formation of various Pd forms on the surface of active carbons is provided either by the nature of adsorption sites or the effect of reaction medium on Pd particles.

ON THE ORIGIN OF AGGLOMERATES OBSERVED IN HRTEM MICROGRAPHS OF A CATALYST CONTAINING PLATINUM(II) COMPLEXES ANCHORED ON PHOSPHINATED SiO_2: COMPUTER SIMULATION OF HRTEM IMAGES

A.L. Chuvilin, B.L. Moroz, V.A. Likholobov

J. Molec. Catal., 87 (1994) 231-242

Computer simulation has been apllied to interpret "spots on stems" images observed in HRTEM micrographs of a catalyst containing $PtCl_2$ complexes anchored on phosphinated silica. Molecular models of isolated molecules P_2 or $P_2 \cdot PtCl_2$ (P_2-diphosphine ligand covalently attached to the amorphous SiO_2 layer of a 150 Å thickness), aggregates ("islands") of anchored Pt^{II} complexes, $[P_2 \cdot PtCl_2]_n$ (n = 2-5), and metal clusters of Pt_n (n = 1-20) leant on SiO_2 surface via graphite "stem" were constructed. Calculations of HRTEM images were performed on IBM PC with authors' software implementing the standard multislicing procedure. Calculations show no P_2 or $P_2 \cdot PtCl_2$ molecules to be observed even under conditions close to the optimal one. The comparison of real images obtained using JEM-100CX microscope with those simulated for various models shows that experimental HRTEM micrographs exhibit Pt_n metal clusters on graphite "stems". These objects appear to be the products of decomposition of initial

$[P_2 \cdot PtCl_2]_n$ "islands" under the electron beam. The results emphasize the necessity of computer simulation for correct interpretation of HRTEM images, especially when the objects are sensitive to the heat effects of the electron beam.

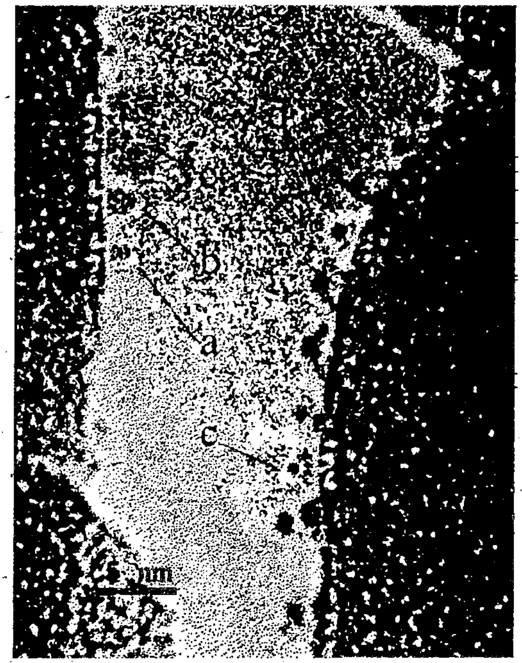


Fig. 1. High-resolution micrograph of the sample containing $PtCl_2$ anchored on phosphinated SiO_2. Bar respresents 5 nm. The print includes computer images (a-d) based on model of $[Pt]_n$/graphite "stem", where n = 5(a), 10(b) and 20 (c,d). The simulated images were calculated at defocus values $D_1 = -120$ nm (a-c) and $D_2 = -192$ nm (d).

$[PdCl_4]^{2-}$ ALKALINE HYDROLYSIS: PRODUCT COMPOSITION STUDY

S.Yu.Troitski, M.A.Fedotov, V.A.Likholobov

Izv. Akad. Nauk 4 (1993) 675-680

The products of $[PdCl_4]$ alkaline hydrolysis were studied with UV spectroscopy and ^{35}Cl, ^{23}Na, ^{133}Cs, ^{17}O NMR. Polynuclear hydroxicomplexes of palladium(II) (PHC) were found to be hydrolysis product.

^{35}Cl NMR showed Cl^- ion evolved into the solution upon hydrolysis to be aquated. Besides, one Cl^- atom per one Pd atom of PHC is absorbed by the PHC molecule.

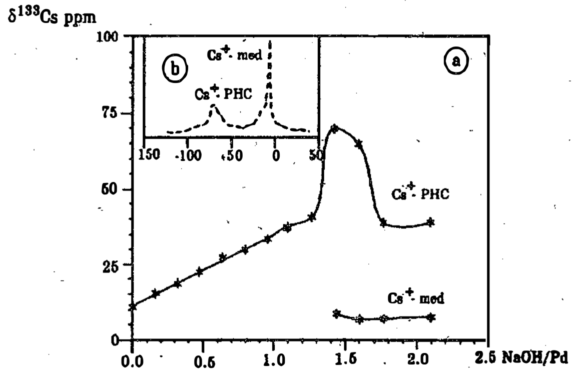
^{133}Cs NMR demonstrated, that two forms of Cs^+ exist in PHC solutions. The first one (wide peak, see Fig.b) is Cs^+ accepted by PHC structure. The second (narrow peak) is Cs^+ surrounded by medium components ($[PdCl_4]^{2-}$, Cl^-, H_2O). The similar data were obtained by ^{23}Na NMR for Na^+.

The concentration of $[PdCl_4]^{2-}$ ions was measured with UV spectroscopy after alkali addition. No noticeable amounts of mononuclear Pd complexes were observed among hydrolysis products. ^{17}O NMR data confirmed these data.

In accordance with the data obtained, the following equation was suggested for hydrolysis process:

$$nNa_2PdCl_4 + 2nNaOH \rightarrow$$
$$[Pd(OH)_2]_n \times nNaCl + 3nNaCl$$

PHC was supposed to possess a thread-like structure consisting of $Pd(OH)_2$ fragments. The compact PHC particles are likely to form via the thread contraction by alkaline metal cations. The induced positive charge is compensated by the aquated Cl^- ions.



a: ^{133}Cs NMR chemical shift changes *vs* alkali amounts in the solution
b: ^{133}Cs NMR spectrum of $NaOH/Na_2PdCl_4$ = 1.5 solution

THE PRODUCTS OF $[PtCl_4]^{2-}$ ALKALI HYDROLYSIS IN AQUEOUS SOLUTIONS

S.Yu. Troitski, M.F. Fedotov, A.L. Chuvilin, V.A. Likholobov

Inorg. Chem., to be submitted

A set of physico-chemical techniques, such as ^{17}O, ^{195}Pt, ^{133}Cs, ^{35}Cl NMR, UV spectroscopy and TEM was used to study the products and mechanism of $[PtCl_4]^{2-}$ alkali hydrolysis in aqueous solutions.

Hydrolysis was found to proceed as follows:

$$[PtCl_4]^{2-} \xrightarrow[1]{} [PtCl_3(H_2O)]^- \xrightarrow[2]{} [PtCl_3(OH)]^{2-} \xrightarrow[3]{} [PtCl_2(OH)_2]^{2-} \xrightarrow[4]{} PHC$$

Here, PHC are the polynuclear hydroxocomplexes of Pt(II), $[Pt(OH)Cl_2]_n$; OH are the bridge ligands in trans positions. In this scheme, stages 1,2 and 3 are fast, while polymerization stage 4 is slow and thus is the rate determining stage. These PHC have a filamentous structure. A filament contains 100 Pt atoms averagely. In solutions the filaments rolled into the compact particles (globules) 25 Å in diameter. Alkali metal ions stabilize these globules efficiently. Recently [1], we failed to study the mechanism of Pd(II) hydrolysis with regard to a monolayer level. Though the observed similarity of the course of Pd(II) hydrolysis and that of Pt(II), as well as analogous structures of their hydrolysis products, allow the conclusion of the same mechanisms for hydrolysis of both Pd(II) and Pt(II) compounds.

1. S.Yu. Troitskii, M.F. Fedotov, V.A. Likholobov, Izv. RAN, Ser. Khim., 4 (1993) 675-680.

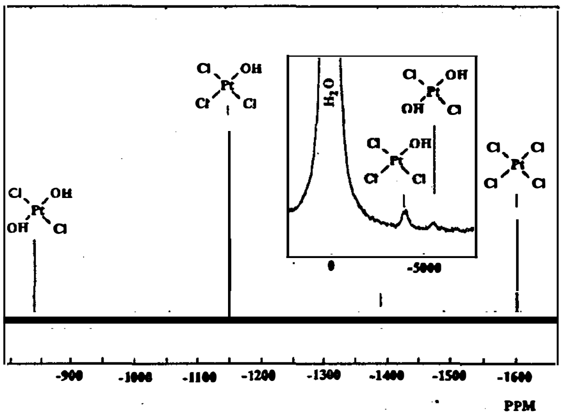


Fig. 1. K_2PtCl_6 hydrolysis products at the addition of 2 NaOH equivalents left for 15 min at 45°C (^{195}Pt NMR data). Inserted is a ^{17}O NMR spectrum of the same solution.

STUDY OF MECHANISM OF THE CATALYTIC PERFORMANCE OF Pt TRIPHENYLPHOSPHINE COMPLEXES IN ETHYLENE HYDROCARBONYLATION

G.N. Ilinich, V.N. Zudin, A.V. Nosov, V.A. Rogov, V.A. Likholobov

Submitted to *J. Molec. Catal.*

We have used multinuclear (^1H, ^{13}C, ^{31}P) HR NMR to study *in situ* the main steps of ethylene hydrocarbonylation proceeding under mild conditions (1 atm, 70°C) in the presence of catalytic systems "P_2PtX_2 (or (P_4Pt)-CF_3COOH/H_2O" ($P=PPh_3$; $X=CF_3COO^-$, CH_3COO^-; $[H_2O] \leq 30$ wt.%). The key reaction intermediates, such as hydride trans-$[HPtP_2X]$, $[HPtP_3]^+$ and trans-$[HPt(CO)P_2]^+$, hydridoethylene trans-$[HPt(C_2H_4)P_2]^+$; ethyl-ethylene trans-$[(C_2H_5)Pt(C_2H_4)P_2]^+$, ethyl-carbonyl trans-$[(C_2H_5)Pt(CO)P_2]^+$ complexes of Pt(II) were identified. The interaction of the above complexes with reactants (H_2, CO, C_2H_4) as well as with CF_3COOH/H_2O solvent was analysed.

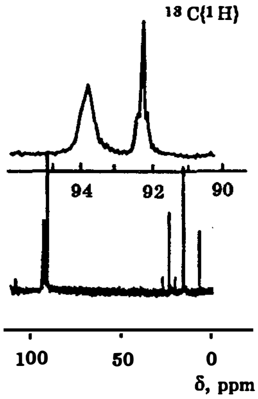


Fig.1. ^{13}C (^1H) NMR spectra of solution containing complexes of trans-$[HPt(C_2H_4)P_2]^+$ (VI) and trans-$[(C_2H_5)Pt(C_2H_4)P_2]^+$ (VII) in CF_3COOH solution at 0°C. Complexes were obtained *in situ* from trans-$HPtP_2X$ and $^{13}CH_2{=}CH_2$ (86% enrichment)

The catalytic properties of Pt(II) hydrides were studied upon both isotope hydrogen heteroexchange and C_2H_4 hydrogenation, which models some hydrocarbonylation stages. Basing on the data of isotope kinetic methods and NMR spectroscopy, we have estimated the stability of various hydrides towards Pt-H bond protolysis and their capability to coordinate ethylene (trans-$HPtP_2X >> [HPtP_3]^+ >$ trans-$[HPt(CO)P_2]^+$.

We have suggested the mechanism of ethylene hydrocarbonylation which includes the subsequent formation of hydride-, hydride-ethylene, ethyl and propionyl intermediates of Pt(II). Insertion of C_2H_4 along the Pt-H bond of trans-$[HPt(CO)P_2]^+$ accompanied by isomerization of trans-$[(C_2H_5)Pt(CO)P_2]^+$ to propyonyl appeared to be the most complex steps of the catalytic cycle. $Sn(OAc)_2$ catalytic dopes (Pt/Sn ≥ 100) increase significantly the rate of the first step and do not affect the second one.

EFFECT OF SUPPORT AND Pd DISPERSION ON STRUCTURAL, ELECTRONIC AND CATALYTIC PROPERTIES OF PALLADIUM IN SELECTIVE HYDROGENATION OF ACETYLENIC HYDROCARBONS.

L.V.Nosova, M.V.Stenin, Yu.A.Ryndin

Appl. Surf. Sci., *55*, 1 (1992) 43.

The supported palladium was found to show an approximately constant turnover number (TON) within a wide range of particle sizes (from 30 Å to 180 Å) in the gas phase hydrogenation of acetylene. This effect appears not to depend on the support nature (SiO_2, γ-Al_2O_3, C). Meanwhile, a decrease of particle size from 30 Å to 10 Å makes TON fall by the order of magnitude.

According to EXAFS data Pd-Pd interatomic distances in small metal particles should be close to those in the bulk metal. However, a positive shift of Pd $3d_{5/2}$ level by 0.7 eV was observed upon the decrease of Pd particle size. The quantitative correlation between TON and the binding energy of Pd core level was derived. The low TON of highly dispersed Pd appears to be caused by a stronger chemisorption of acetylenic hydrocarbons on small electron-deficient clusters than on large particles.

SYNTHESIS AND PROPERTIES OF Pd-Cu BIMETALLIC CLUSTERS, PREPARED VIA ANCHORED METAL COMPLEXES

L.V. Nosova, V.I. Zaikovskii, A.V. Kalinkin, Yu.A. Ryndin

1st Europ.Congr.Catal., EUROCAT, Montpelier, France, 1993, Book of Abstracts v. 2, p. 587

New methods for bimetal Pd-Cu catalyst preparation are suggested. The mechanism of

Cu modifying action on palladium catalytic properties is discussed.

As a precursor of $(Pd+Cu)/Al_2O_3$ catalysts heteronuclear acetate-bridged palladium-copper complex $CuPd(OAc)_4$ was used. It was prepared by Pd(II) acetate heating with Cu(II) acetate in acetic acid. Precursor solution in ethanol easily interacts with dehydrated γ-alumina.

In order to characterize bimetallic and monometallic supported catalysts we have used electron microscopy, chemisorption and XPS methods.

The HT results agree well with the electron microscopy data. The surface mean size of metal particles ranges from 30 to 40 Å for bimetallic catalysts and is less than 10 Å for Pd or Cu on alumina.

According to the XPS data the binding energies of Pd $3d_{5/2}$ level and Cu $2p_{3/2}$ level for monometallic catalysts are very close to those of corresponding bulk metals. A negative shift of core levels of both palladium and copper is reliably registered for bimetallic catalysts reduced *in situ* at 350°C. The Pd/Cu ratio is around 0.8, which is close to the brutto composition of catalysts.

As far as the influence of copper on palladium performance is concerned, the TON of Pd-Cu catalysts in ethane hydrogenolysis (Cu is practically inactive in this reaction) is by 2 orders of magnitude lower than that of supported Pd. The activation energy does not change.

According to experiment, Cu shows negligible activity in vinylacetylene hydrogenation in comparison to supported palladium. Addition of Cu to Pd does not change significantly the TON of palladium but slightly improves the selectivity towards divinyl formation.

Pd and Cu on alumina exhibit an enhanced activity and selectivity at methanol synthesis. The TON have been proved to decrease for all $(Pd+Cu)/Al_2O_3$ catalysts, in comparison to those of monometallic catalysts.

A marked difference in catalytic properties between Cu, Pd and PdCu catalysts shows essential interaction between palladium and copper to occur. Unusual electronic and nonadditive catalytic properties of $(Pd+Cu)/Al_2O_3$ catalysts are caused by the presence of highly dispersed Pd-Cu clusters of homogeneous composition.

SUPPORTED VANADIUM-MAGNESIUM CATALYSTS: NEW POSSIBILITIES TO CONTROL MOLECULAR STRUCTURE OF POLYETHYLENE AND COPOLYMERS OF ETHYLENE WITH α-OLEFINS.

T.B.Mikenas, L.G.Echevskaya, V.A.Zakharov

Proc. 34th IUPAC Intern. Symp. Macromolecules, Prague 1992, p. 52-58.

The possibility to control the molecular structure of polyethylene (PE) and copolymers of ethylene with α-olefins using highly active supported V-Mg catalysts has been studied. The following significant peculiarities of supported V-Mg catalysts have been discovered:

1. PE with a broad molecular mass distribution (MMD) is produced in the presence of V-Mg catalysts unlike the case of the well known Ti-Mg catalysts.
2. PE with a super high molecular mass (10^7) is generated in the presence of V-Mg catalyst at 60-80°C. At the same time this catalyst possesses an extremely high chain transfer constant with hydrogen (35 fold higher than that of Ti-Mg catalyst) and, thus, it allows

to obtain PE with any desired molecular mass (from 10^7 to 10^4) at polymerization in presence of hydrogen.

3. V-Mg catalysts appear to have a higher copolymerizing reactivity in comparison to that of Ti-Mg catalysts (by 3-4 fold) in copolymerization of ethylene with various α-olefins (propylene, butene-1, hexene-1, octene-1, 4-methyl-pentene-1, 3-methyl-butene-1). Moreover, copolymers formed in the presence of V-Mg catalysts are more homogeneous.

Using these data we designed and prepared special modifications of supported V-Mg catalysts for several particular processes: (i) production of PE with a broad MMD via the slurry method; (ii) production of ethylene copolymers with α-olefins of low and superior density via the gas phase method; (iii) production of noncrystalline copolymers with a high content of α-olefins (>20 mol.%) via the solution method.

IRS STUDY OF SURFACE ACIDIC SITES OF HIGHLY DISPERSED MAGNESIUM CHLORIDE SUPPORT FOR Ti-Mg POLYMERIZATION CATALYSTS

V.A.Zakharov, E.A.Paukshtis, S.I.Makhaturilin T.B.Mikenas, E.N.Vitus.

Kinet. Katal., to be published

Direct IRS study of the surface acidic sites of highly dispersed magnesium chloride (adsorbed carbon monoxide served as a reference test molecule) has been performed. Three types of acidic sites were registered on the surface of various magnesium chloride species. These sites are probably responsible for fixing the active polymerization component ($TiCl_4$). The method for quantitative estimation of acidic site concentration has been suggested: IRS analysis of carbon monoxide adsorption and its successive replacement by pyridine. The relationship between the concentration of the surface acidic sites on the activated highly dispersed $MgCl_2$ and the content of $TiCl_4$ binded tightly with the support has been found.

KINETICS OF ETHYLENE HOMOPOLYMERIZATION AND COPOLYMERIZATION WITH HEXENE-1 OVER SUPPORTED Ti-Mg CATALYSTS WITH VARIOUS PARTICLE SIZE

V.A.Zakharov, V.B.Skomorohov, R.A.Hatchinson, (University of Wisconsin, Madison, USA), L.G.Echevskaya

Macromol. Chem., to be published

Kinetic peculiarities of ethylene homopolymerization and copolymerization with hexene-1 over supported Ti-Mg catalysts with various particle size and content of electron donating modifier have been studied. As far as homopolymerization of ethylene is concerned, one can hardly explain the presence of acceleration stage by diffusion restriction of the monomer transfer only. The duration of initial acceleration stage and the level of maximum activity was found to depend on the size of particles and the content of electron donating modifier.

A new method to evaluate the effect of monomer transfer on homopolymerization kinetics and to calculate the effective coefficient of monomer diffusion in a growing polymer particle has been developed. The method is based on the analysis of experimental data on the effect of the catalyst size on molecular mass of polyethylene obtained in the presence of hydrogen.

We observed two general peculiarities of ethylene copolymerization with hexene-1 over various Ti-Mg species: (i) a 2-4 fold increase of maximum activity; (ii) a sharp reduction of initial acceleration stage. The influence of hexene-1 concentration and copolymerization time on the copolymer composition has been studied on catalysts with various particle size. Experiments show copolymerization to run in kinetic region for catalysts with particles less than 20 micron. Particles larger than 30 micron appear to provide diffusion restrictions for ethylene transfer.

NUMBER OF ACTIVE SITES AND PROPAGATION RATE CONSTANTS FOR PROPYLENE POLYMERIZATION ON SUPPORTED Ti-Mg CATALYSTS

G.D.Bukatov, V.S.Goncharov, V.A.Zakharov

Macromol. Chem., to be published

Propylene polymerization on a highly active and stereospecific catalytic system: $TiCl_4/D_1/MgCl_2$-AlR_3-D_2 (D_1 stands for diisobutylphtalate, D_2 stands for phenyltrietoxysilane) has been studied. The number of active sites (C_p^i) and propagation rate constants (K_p^i) for isospecific propylene polymerization were determined via ^{14}CO inhibition. C_p^i value appears to decrease from $1.5 \cdot 10^{-2}$ to $0.7 \cdot 10^{-2}$ mol/mol of Ti and K_p^i value increases from 500 to 2500 l/mol·s when hydrogen is introduced into the catalytic system. C_p^i values obtained by ^{14}CO method in presence of hydrogen seem to be more correct, since without hydrogen active sites are mostly in a dormant state. The effect of hydrogen, phenyltrietoxysilane concentration and polymerization time on C_p^i and K_p^i values is compared with that observed for the system with Ti-Mg catalysts and ethylbenzoate and ethylanisate as D_1 and D_2, respectively.

DETERMINATION OF ACTIVE SITES' NUMBER AND PROPAGATION RATE CONSTANTS FOR ETHYLENE COPOLYMERIZATION WITH HEXENE-1 OVER SUPPORTED Ti-Mg CATALYSTS

V.S.Goncharov, G.D.Bukatov, V.A.Zakharov

Macromol. Chem., to be published

Earlier we have observed a 2-4 fold higher activity of Ti-Mg catalysts in ethylene copolymerization with hexene-1 than in homopolymerization of ethylene. To clarify this phenomenon we determined the number of active sites (C_p) and propagation rate constant (K_p) in copolymerization of ethylene with hexene-1 by a quenching polymerization technique (^{14}CO). C_p value was found to be 2 fold higher in copolymerization than in homopolymerization. So we have performed some additional kinetic experiments, which show α-olefin to be involved in generation of new active sites. According to our data the calculated propagation rate constant K_p also is higher by 1.5-2 fold. We assume this K_p increase to be formal and to relate probably to the decrease of crystallinity of the polymer formed upon copolymerization and to the increase of concentration of ethylene dissolved in this polymer.

ETHYLENE COPOLYMERIZATION WITH α-OLEFINS OVER SUPPORTED NICKEL CHELATE COMPLEXES

V.N.Panchenko, V.A.Zakharov, G.A.Nesterov, L.G.Echevskaya

Vysokomol. Soed., to be published

Copolymerization of ethylene with propene and hexene-1 assisted by catalysts synthesized via interaction of chelate nickel complex, magnesium hydride and modified silica has been studied. Comonomer reactivity ratio of ethylene and hexene-1 was determined. The value of comonomer reactivity ratio appears not to depend on the nature of supports. Copolymerization reactivity of supported nickel complexes was compared to that of Ti, Zr, V and Cr supported catalysts. Ethylene copolymerization with propene on supported nickel chelate complexes is likely to produce terpolymers via reaction with α-olefins on nickel centers.

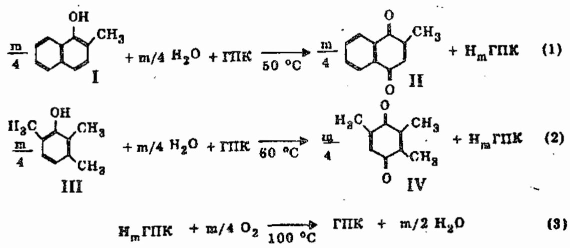
NEW CATALYTIC SYSTEMS FOR SYNTHESES OF VITAMINS OF K- AND E-FAMILIES

K.I.Matveev, E.G.Zhizhina and V.F.Odyakov

Ist Europ. Congr. Catal., EUROCAT, Montpelier, France, 1993, Book of Abstracts, v.1, p.355

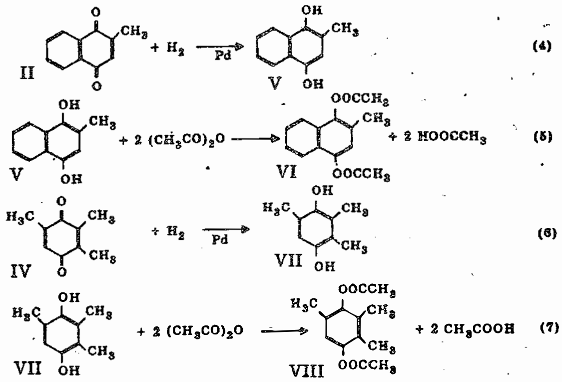
A number of precursors of vitamins of K- and E-families were synthesized using catalysts for oxidation, hydrogenation and acetylation specially developed for these reactions. Methods to employ the new catalysts were proposed. All the organic substrates were oxidized by means of interphase catalysis in a water-immiscible organic solvent, while the catalyst, heteropoly acid (HPA), was in aqueous phase. The reaction proceeded under mild conditions on intensive agitating the solutions. Typically, reaction products remained in the organic layer and were readily isolated from the catalysts by mere phase separation.

Reactions (1)-(3) are the examples of the catalytic transformations under discussion:



Here II and IV (2-methyl-1,4-naphtoquinon being just the vitamin K3 and 2,3,5-trimethyl-1,4-benzoquinon) are the intermediates of the synthesis of vitamins of K- and E-families. Compound II is of importance by itself as the vitamin K3 as well.

Further transformations of II and IV in the above reactions are the steps of hydrogenation and acetylation: (4)-(5) for K- and (6)-(7) for E-families.



Following the methods known in literature, the every reaction was carried out successively in its own right. In our works they all were combined into one technological operation without unstable in air diphenols V and VII to be separated. This is the application of our polyfunctional heterogeneous catalysts for reactions (4)+(5) and (6)+(7) that provide such advantageous combinations of the reactions.

NOVEL CATALYTIC METHODS FOR THE SYNTHESIS OF K AND E VITAMIN HALF-PRODUCTS, AND NEW VITAMINS OF K-GROUP

K.I. Matveev, E.G. Zhizhina, V.F. Odyakov

Sib. Khim. Zh., to be published

We have developed the catalytic methods to perform some stages of vitamin K_1 (VK_1) synthesis. K_1 is the most active vitamin of this group. The main difficulty of such multi-stage synthesis is the absence of economizing and environmentally safe methods for phytol (or isophytol) $C_{20}H_{39}OH$ manufacturing. So, instead of VK_1 synthesis, we suggest to produce the new analogs of vitamin K_3 (vikasol). Such synthesis permits to avoid deficite coumounds at vitamin manufacturing. These vikasol analogs possess better physico-chemical properties, than vikasol itself (it has very high water solubility and low thermostability). New vikasol analogs contain biologically active components, which give to the analogs the properties of polyvitamins or drug-vitamins. It is easier to isolate and store them.

We prepared four vikasol analogs for long term biological tests at industrial poultry farm. Preliminary results of the raising show the biological activity of some vikasol analogs to be significantly higher than that of vikasol and to attain the vitamin K_1 activity. This opens perspectives for designing economizing catalytic method for the synthesis of novel highly efficient vitamins of K group with desired biological properties.

2,3,5-Trimethyl-1,4-benzoquinone (TMBQ) is an important half-product for vitamin E (VE) synthesis. We applied new heteropoly acid catalyst for polymethylphenols (2,3,6- or 2,3,4,6-) oxidation to TMBQ. These catalysts allowed us to use 3-methylphenol (meta-cresol) as a raw material for TMBQ synthesis. The latter is widely available and may be methylated to polymethylphenols by the well known methods. The further synthesis of vitamin E involves the addition of phytyl residue to position 6 in the TMBQ molecule by the methods used at the synthesis of vitamin K_1. Hardly available phytol (or isophytol) makes our further investigations on the catalytic synthesis of VE rather hard.

OXIDATION OF 2,3,6-TRIMETHYLPHENOL IN THE PRESENCE OF MOLYBDOVANADOPHOSPHORIC HETEROPOLYACIDS

O.A.Kholdeeva, A.V.Golovin, R.I.Maksimovskaya, I.V.Kozhevnikov

J. Molec. Catal., 75, 3 (1992) 235-244.

The oxidation of 2,3,6-trimethylphenol (TMP) is both of theoretical and practical interest as a method for preparation of 2,3,5-thrimethyl-1,4-benzoquinone (TMBQ), an intermediate in the synthesis of vitamin E.

Oxidation of TPM by O_2 in the presence of heteropolyacids $H_{3+n}PMo_{12-n}V_nO_{40}$ (HPA-n) in AcOH-H_2O was found to provide up to 86% of TMBQ at a 100% TPM conversion, 2,2', 3,3',6,6'-hexamethyl-4,4'-biphenol (BP) is formed as well. The yield of BP increases at the expense of TMBQ with the increase of H_2O content. BP was shown to be an intermediate in TMP oxidation to TMBQ. VO^{2+} ion formed via dissociation of HPA-n is proved to be a catalytically active species. A stepwise mechanism including TMP oxidation by V(V) producing TMBQ and V(IV) followed by oxidation of V(IV) to V(V) with dioxygen in the coordination sphere of heteropoly anion is suggested.

MECHANISM OF HDS CATALYSIS

A.N.Startsev

Usp. Khim., 61 (1992) 332;
Catal. Rev. -Sci. Eng., to be published

A new method of sulfide HDS catalyst preparation has been worked out. The method is based on the principle of "surface assembly" of the active component direct precursor and includes a successive anchoring of Mo and Ni (or Co) complexes to the support surface. The catalysts prepared via this method exhibit a higher activity in C-S-bond hydrogenolysis in comparison to catalysts prepared by conventional impregnation technique.

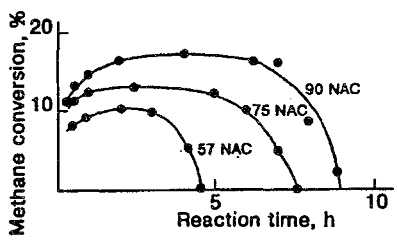
The structure of the active component of HDS catalysts was recognized by EXAFS, RED, XPS, HRTEM techniques. The active component was shown to be crystallized in the structure of a MoS_2 single slab with Ni(Co) atoms localized in the $(10\bar{1}0)$ edge plane at the center of a square formed by four S atoms. The electron density on Ni(Co) atoms is decreased in comparison to that in binary sulfides of these metals due to acceptor properties of a MoS_2 matrix.

The new mechanism of HDS catalysis is proposed and proved on selenophene chemisorption study by *in situ* EXAFS. C-S-bond hydrogenolysis was shown to proceed in the coordination sphere of sulfide bimetal species (SBMS) and not to involve the structure-forming sulfur atoms in catalysis. Adsorption and activation of thiophene molecule occurs on Ni(Co) atoms entering in SBMS composition, while H_2 activation takes place on MoS_2. The nature of synergism and antagonism is explained in the framework of the mechanism proposed.

LOW TEMPERATURE METHANE CRACKING ON NICKEL CATALYSTS

L.B.Avdeeva, O.V.Goncharova, V.I.Zaikovskii

Kinetics of a low temperature decomposition of pure methane on nickel catalyst has been studied. Filamentous carbon was found to be generated at 550 °C. The yield of carbon of such a morphology is shown to depend on the nickel content in the catalyst, the nature of structure generating promotor (oxide of hardly reduced metal) and on kinetic parameters such as temperature and methane flow rate. Kinetics of methane conversion at 550 °C and contact time of 0.03s as functions of nickel content in nickel-aluminum catalysts are presented in the Figure. A complex character of kinetic curves is caused by such carbon deposition on the catalyst, that the latter is not deactivated over a long time period. X-ray and TEM techniques have shown faceted carbon centers growth at the initial stage of the process. These centers are responsible for methane decomposition, formation of carbide carbon on the surface, dissolution and diffusion of this carbon in the nickel particle and its graphite like deposition on a growing carbon filament. Time of the stationary catalyst operation depends on the number of carbon growth centers of a definite size. The loss of catalytic activity is related to mechanical removal of nickel by depositing carbon.



ONION-LIKE CARBON.

EFFECT OF EXPLOSION CONDITIONS ON THE STRUCTURE OF DETONATION SOOTS: ULTRADISPERSE DIAMONDS AND ONION CARBON

V.L.Kuznetsov, I.Yu.Mal'kov (Lavrentiev Institute of Hydrodynamics, Novosibirsk), A.L.Chuvilin, E.M.Moroz, V.N.Kolomiichuk, Sh.K.Shaikhutdinov, Yu.V.Butenko

Carbon, 32, 4 to be published.

Detonation of a number of pure and composite explosives with the negative oxygen balance in a hermetic tank filled with inert gas (N_2, Ar) have yielded the diamond containing solid carbonaceous products (soots). The influence of detonation parameters, namely: 1) the inert gas pressure in the tank decreasing the effective temperature of detonation products and 2) the composition of explosives determining the detonation pressure and temperature, on the nature and the yield of detonation soots have been investigated by TEM, XRD, SAXS, Auger spectroscopy. The soots contain ultra disperse diamond (UDD, 20-150 Å) along with amorphous carbon (40-250 Å), graphite ribbons (with the length less than 200 Å) and spheres (20-40 Å) made of concentric graphite shells (onion-like carbon, which have been registered only in the experiments with low initial inert gas pressure). It was shown that UDD thermally transform into onion-like carbon particles. The detonation parameters have been optimized to increase the UDD yield.

ONION-LIKE CARBON FROM ULTRA DISPERSE DIAMOND

V.L.Kuznetsov, A.L.Chuvilin, Yu.V.Butenko, I.Yu.Mal'kov*, V.M.Titov* (Lavrentiev Institute of Hydrodynamics, Novosibirsk)

Chem. Phys. Lett. 222,(1994) 334-348

A new material containing macroscopic quantities of onion-like carbon (OLC) particles is produced by heat treatment of ultra disperse diamond (UDD) powder (2-6 nm). Annealing products (characterized by high resolution electron microscopy) are presented by: a) quasi-spherical particles with closed concentric graphite shells; b) polyhedron particles with closed shells; c) elongated particles with linked external graphite-like layers and closed quasi-spherical internal shells (Fig.). The intermediates of UDD transformation have been registered. The structural transformation of UDD begins from the surface of diamond particles towards a crystal bulk. The transformation rate of (111) diamond planes to graphite-like sheets is higher than that of other planes.

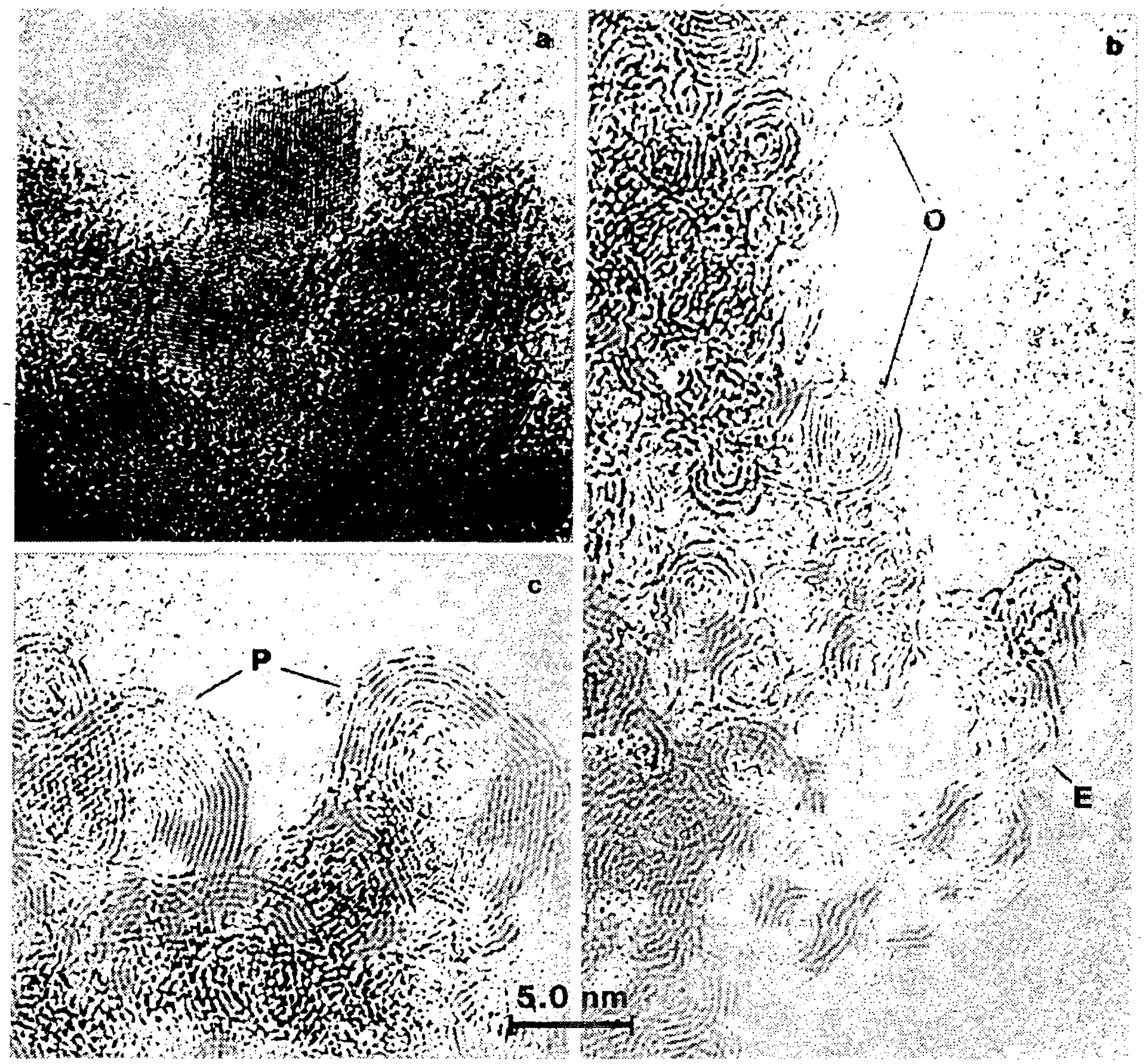


Fig. High-resolution TEM images of original ultra disperse diamonds (a) and their annealing products (b,c, 1500°C). Dark contrast lines (a) and rings (b,c) correspond to diamond crystal planes and graphite-like shells respectively. The distances between lines correspond to the (111) lattice parameter of ultra disperse diamond (a, $d_{111} = 0.2063$ nm) and those between rings (b,c) to the distance between the graphite-like shells ~0.35 nm ($d_{002} = 0.3354$ nm for bulk graphite). Quasi-spherical particles with closed concentric graphite shells (b) are marked O; polyhedron particles with closed shells (c) are marked P; elongated particles with linked external graphite-like layers and closed quasi-spherical internal shells (b) are marked E.

POLYHEDRAL SILSESQUIXANES AS PRECURSORS OF TAILOR-MADE HETEROGENEOUS CATALYST CENTRES

I. Water oxidatin

V.L.Kuznetsov, G.L.Elizarova, L.G.Matvienko, I.G.Lantyukhova and V.N.Kolomiichuk, A.A.Zhdanov and O.I.Shchegolikhina (Institute of Elementoorganic Compounds, Moscow)

J. of Organometallic Chemistry (1994)
JOM 24549 C

Fe-, Ni-, Cu- and Mn-polyhedral oligometallasilsesquioxanes (Fig.) containing $(PhSiO_{1.5})_{12}(MO)_nL$-fragments (where L=ROH, H_2O; n=6 for Fe, Ni, Mn and n=4 for Cu; Ni_4Fe_2- and Ni_4Cu_2-complexes were also used) have been used for the preparation of heterogeneous catalysts to investigate the influence of structural factors on the catalytic properties of the hydroxides of these metals. SAXS have been used for the characterization of the distribution of complexes associates in the solution and on the supports surface. It was found that the complexes distribution on the carbon support (soot) is close to monomolecular. The highest O_2 yields have been obtained with use of Fe/C catalysts.The catalysts prepared on the base Fe_6-complexes were more active than those prepared from Ni_4Fe_2- complexes, in which active Fe-atoms are separated by inactive Ni-atoms. This observation is very important for the mechanism developed by the authors. According to this mechanism for O_2 formation it is necessary to have in active center at least two active metal ions associated each other.

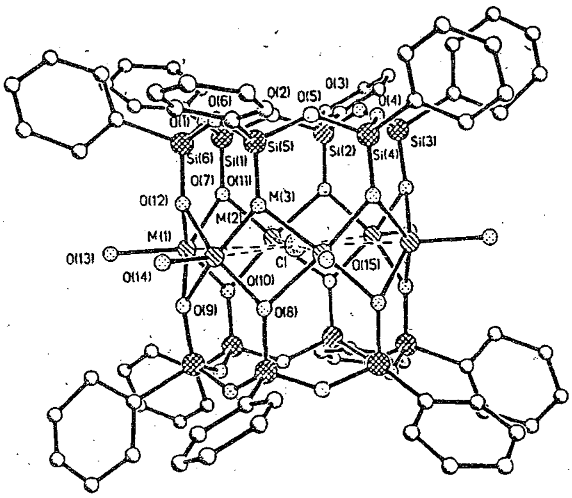


Fig. The molecular structure of $Na^+[(PhSiO_2)_6M_6(O_2SiPh)_6Cl^-](n\text{-}BuOH)_{16}$. Hydrogen atoms and hydrocarbon parts of alcohol have been omitted for clarity (M = Mn,Ni,Fe)

PREPARATION AND PROPERTIES OF SILICA AEROGELS

A.F.Danilyuk, T.A.Gorodetskaya, V.L.Kuznetsov, A.I.Vorobiov* (Inst. of Nuclea Physics SB RAS, Novosibirsk)

The SiO_2 aerogels are used as a radiators of threshold Cherenkov counters for e^+e^- experiments in the γ-meson energy region /1/.

The technology of the aerogel production based on hydrolysis of tetramethoxysilane (TMS) followed by supercritical drying of the forming alkogels have been developed /2/.

The ^{29}Si NMR spectroscopy and SAXS were used to study TMS hydrolysis and condensation reactions in methanol solutions. On the base of theis experiments the optimization of the aerogel production have been done.

The monolitic aerogel blocks with the size 25.25.3 cm and the density 0,1 - 0,4 g/cm^3 and refractive index n = 1,017-1,04 have been prepared. The light scattering lenth is about 2,5 - 3,0 cm at a wavelength l = 436 nm. The average light absorption length is about several meters in the optical range λ=300-600 nm.

The preparation method of the wavelength shifter containing aerogels have been developed. The BBQ dye containing aerogels have high efficiency for the transformation UV-radiation to visible light, which can be easily registrated.

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SCIENTIFIC BASES FOR PREPARATION AND PROCESSING OF CATALYSTS

R.A.Buyanov, O.P.Krivoruchko

A detail analysis of reference literature concerning preparation and processing of catalysts has been performed. The main tendencies and new alternative methods for preparation and processing of catalysts with respect to advances in science have been estimated. The content, structure and boundaries of this field of knowledge were estimated, the scientific bases for catalyst preparation and catalyst processing posited. The problems, concept and methodology of these bases were postulated. The prognosis of the problem development is provided [1].

A new fundamental theory of the formation of amorphous hardly soluble sediments of metal hydroxides and their crystallization without solvent participation via the mechanism of "oriented growth" has been accomplished [2,3,4].

The theory consists of three separate sections:

1. Peculiarities and mechanism of hydrolytic polycondensation of aqua-ions in solutions, generation of polynuclear hydroxo complexes in solutions and of condensed polynuclear sediments as well, their structure and properties.
2. Peculiarities and mechanism, thermodynamics and kinetics of evolution of polynuclear hydrogen sediment structures in the aging process. Crystallization via the mechanism of "oriented growth" and generation of secondary crystals with various morphology and other characteristics.
3. Properties and evolution of secondary crystals under various treatment providing products with desired parameters.

The theory appears to be rather good for prognosis. It allowed to perform a controlled synthesis of numerous supports and catalysts with adjusted structure, strength and other characteristics [2,3,4].

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MECHANISMS OF HETEROGENEOUS CATALYST DEACTIVATION

R.A.Buyanov

With respect to a detail analysis of reference literature and in accordance with numerous experimental data all known cases, reasons and nature of instability of catalyst properties have been considered. This analysis permitted to systemize the changes of catalyst properties and to classify phenomena providing these changes (deactivation) as a hierarchical scheme. This natural classification is based on a well known equation of reaction rate: $A=\alpha S\eta$, where α is specific catalytic activity, S is specific surface are and η is a degree of surface utilization. All factors affecting these values have been taken into consideration. As a result, about 12 various factors appear to influence parameter α [1,2]. Classification mentioned above served for the start of a new trend in catalysis and promoted considerably investigations within this trend.

The mechanisms of catalyst deactivation upon coke deposition were studied in detail. Possible principles for the control over coking process were classified and analyzed in [3].

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PECULIARITIES OF METAL AQUA-IONS POLYCONDENSATION, GENERATION AND EVOLUTION OF HYDROXIDE SEDIMENTS IN MOTHER LIQUOR

R.A.Buyanov, O.P.Krivoruchko, E.A.Taraban, M.A.Fedotov.

Zh. Neorg. Khim. 38, 11 (1993) 1849-1854
Zh. Neorg. Khim. 36, 4 (1991) 875-878

Fundamentals and technique for generation of hydroxide and oxide binary systems of two- and three valent metals upon sedimentation and crystallization via the mechanism of "oriented growth" have been developed. Peculiarities of polycondensation of metal aqua-ions in the mixed solutions of salts: Al(III)-M(II), where M(II) stands for Co, Ni, Zn, Ca, and Al(III)-M(III), where M(III) stands for Fe and Cr have been studied [1-3]. Selected systems allowed to determine general regulations of aqua-ion polycondensation and to elucidate the differences related to the chemical nature of a particular component.

The knowledge of these peculiarities and mechanisms is a key to the directed synthesis of hydroxide (oxide) systems [4].

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THEORY OF CATALYTIC CARBON FORMATION IN PROGRESS

V.V.Chesnokov, R.A.Buyanov, N.A.Prokudina, V.I.Zaikovskii, A.I.Boronin

Formation of carbon from hydrocarbons via a consecutive reaction scheme was studied in detail. New mechanisms of coke formation were found: "mechanism of carbide cycle" and "mechanism of compensated decay".

Carbon formation via the "carbide cycle" on metals of iron group includes two stages [1]. The first one is the formation of carbon atoms from hydrocarbons through intermediate compounds of a carbide type. The second stage is the topochemical aggregation of the carbon atoms to graphite phase.

The study of process peculiarities in these two stages provided fundamentals and practical recommendations for the desired control over coke deposition and its conversion to graphite phase of various morphology. Morphology of graphite phase was shown to depend on transfer processes determined mainly by the diffusion of carbon atoms and on dispersion, nature and cutting of metal catalyst as well [2].

With "compensated decay" carbon formation from ethylene on the surface of platinum and iridium (110) monocrystals was found to proceed via the splitting of hydrogen atom from a hydrocarbon producing a series of damaged hydrocarbon species. Cleavage of C-H bond seems to be compensated by the energy of carbon and hydrogen atoms' interaction with those of platinum surface.

Investigation of carbon formation via the consecutive reaction scheme allowed to reveal the nature of active sites promoting the coking of alumina and zeolites. Acid-base pairs, those are coordinatively non saturated aluminum cations and bridge oxygen ion, were shown to serve as the active sites for coke deposition.

All these data provide the control over coke deposition and tell how to reduce catalyst deactivation in plant reactors.

Catalytic carbon formation is applied for the synthesis of materials (supports, adsorbents and composites) with new properties.

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A POSSIBILITY FOR REGULATING THE MORPHOLOGY OF CARBONACEOUS DEPOSITS ON NICKEL-CONTAINING CATALYSTS

V.V. Chesnokov, V.I. Zaikovskii, R.A.Buyanov, V.V. Molchanov, L.M. Plyasova

Kinet. Katal., 35, 1 (1994) 146-151

This paper concerns the regularities and possible control over the morphology of carbonaceous deposits. These deposits generated at the catalytic decomposition of hydrocarbons can be arranged as thin graphite films, straight and spiral filaments, "octopus" carbon formations.

GROWTH OF METHANE PROVIDED FILAMENTOUS CARBON ON A NICKEL MONOCRYSTAL

V.V. Chesnokov, V.I. Zaikovskii, R.A.Buyanov, V.V. Molchanov, L.M. Plyasova

Kinet. Katal., 35 ,1 (1994) 146-151

The catalytic activity of (100), (110) and (111) nickel faces in methane decomposition via the "carbide cycle" mechanism was shown to differ by several folds. Hence, (100) and (110) faces initiate the growth of filamentous carbon, while on (111) face a graphite structure is generated. Earlier carbon atoms were shown to diffuse from one face to another through metal bulk.

A saturation of (100) and (110) nickel faces with carbon causes a rearrangement of metal surface: cut loss, shape smoothing. Thus, the surface of catalyst particle becomes uniform with regard to the catalytic properties of its surface. This violates the transfer of carbon atoms through the metal bulk and results in the whole surface blockage by carbon.

NEW CATALYTIC SYSTEMS FOR SELECTIVE HYDROGENATION

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Dokl. Akad. Nauk, 306, 6 (1989) 1406-1407

New catalytic systems, hydrides of intermetallides of magnesium, were found to exhibit a high activity and selectivity in hydrogenation of unsaturated bonds and functional groups. Some of these hydrides were not recognized as chemical compounds before. Mostly efficient these catalysts are in selective hydrogenation of acetylene derivatives to olefins and dienes, dienes to α-olefins, p-benzoquinone to hydroquinone.

New methods for synthesizing the hydrides of intermetallic compounds have been designed, in essence, mechanochemical activation under the high pressure of a gas medium. New catalysts based on hydrides of magnesium intermetallides generated via these new methods allow to vary the strength, porosity, shape of granules and to select the properties optimal for particular processes.

New technologies for the fine organic synthesis via catalytic reduction with mechanochemical activation are under development.

METAL-CARBON CATALYSTS

V.V. Molchanov, V.V. Chesnokov, R.A.Buyanov

New metal-carbon supported catalysts are designed. Metal in these catalysts binds to carbon via a chemical bond. Thus supported metal is stable to sintering and to carbon formation up to 1000°C. The method of catalyst preparation is non-runoff and allows to vary the content of metal (0.01-50%) as well as its dispersity (10-500 Å). The nature of supported metals can be varied within some limits. The designed synthesis procedure produces mono- and bimetal catalysts.

Metal-carbon catalysts show a high activity at the hydrogenation of unsaturated hydrocarbons. Some catalysts, containing nickel, lead hydrogenation to alkanes at room temperature. A catalyst, providing butadiene hydrogenation to butenes with a 100% selectivity as well as acetylene hydrogenation to ethene (ca. 100% selectivity), was obtained. One can use the catalysts for steam methane conversion and for other oxidation reactions. Future investigation will extend the field of catalyst application.

HETEROGENEOUS CATALYST INFLUENCE IN RADICAL-CHAIN PYROLYSIS OF HYDROCARBONS: MECHANISM AND PHYSICAL MODELS

N.A.Vasilieva, R.A.Buyanov

J. Kinet. Katal. 34, 4 (1993)

The mechanism of heterogeneous catalyst performance in the non branched radical-chain pyrolysis has been studied experimentally and theoretically. The active surface sites were shown to participate in the transfer of a free valency, that is to serve as mediators between hydrocarbon molecules in chain propogation. The mechanism model of the process was suggested [1,2]. It includes homogeneous and heterogeneous components and assumes four types of surface effects on the radical-chain pyrolysis: inhibiting, neutral, accelerating the homogeneous component and accelerating the heterogeneous component. The latter occurs when additional radicals are generated in the bulk, which are responsible for the chain process. This provides a sphere with a high radical concentration around the catalyst granule, the so called CP sphere. Assumption of CP sphere gave a new turn in understanding the nature of diffusion resistance and served as a basis for the physical model of catalytic pyrolysis of hydrocarbons [3]. Peculiarities not typical for fundamental catalysis such as the effect of catalyst amount in a reactor and dilution of raw material on reaction rate were derived from the mechanism model and supported experimentally [4]. The catalysts have been shown not only to accelerate the process but to affect the nature of generated radicals, since a predominant cleavage of C-C or C-H bond in the hydrocarbon molecule depends on the nature of the active site. The physical model appears to support and supplement the kinetic model.

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POLYHEDRON AlO_5: SYNTHESIS AND STUDY OF COMPOUNDS WITH PENTACOORDINATED Al(III) ION

B.P.Zolotovskii, V.M.Mastikhin, R.A.Buyanov, O.P.Krivoruchko, D.P.Klevtsov

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For the first time mechanochemical activation was found to produce Al(III) ion pentacoordinated to oxygen [1]. Thermal treatment of X-ray amorphous products of mechanochemical activation of trihydroxides as well as of amorphous hydroxide sediment was shown to provide a new alumina (π-Al_2O_3), where a part of aluminum cations is also pentacoordinated to oxygen.

Conditions for generation and existence of pentacoordinated Al(III) ions in the layered materials (trihydroxide of Al(III), kaolinite, etc.) were postulated [3].

The mechanism of π-Al_2O_3 formation [4] includes two main stages: (i) interaction between two OH groups located on the edge joint of two hydroxyl octahedrons producing a bridge oxygen and water molecule and (ii) molecular water removal yielding pentacoordinated Al(III) ions, the layered structure of paternal hydroxide remains untouched. π-Al_2O_3 contains paired Lewis sites presented by two neighbor Al(III) cations in coordination 5. π-Al_2O_3 was shown to possess adsorption properties not typical for the "low-temperature" forms of alumina.

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THERMOCHEMICAL ACTIVATION OF CRYSTALLINE HYDROXIDES

R.A.Buyanov, B.P.Zolotovskii, O.P.Krivoruchko

A new type of crystalline hydroxide evolution under non equilibrium conditions at high temperatures, named "thermochemical activation" (TCA), has been discovered [1]. Three factors were shown to be necessary for TCA performance: evolution of some elements (e.g., water, hydroxyl groups, etc.) from the parent structure, rearrangement of the hydroxide crystalline lattice to the oxide one (phase transition) and a possibility to separate these processes in time.

For trihydroxides of aluminum, kaolinite, hydroxialuminates of Me(II) TCA was demonstrated to yield the product with an intermediate non equilibrium lattice structure similar to the parent hydroxide one but without some initial structure elements: hydroxyl groups. Such a non equilibrium structure does not agree with a new chemical composition, possess the excess energy and, thus, a high reactivity.

The product of gibbsite TCA provides a series of solid phase transitions differing from those of all known hydroxides [2]. This product possesses a unique ability to be hydrated and crystallized to pseudoboehmite or baherite under corresponding conditions via the mechanism of "oriented growth" [3,4].

A new wasteless technology based on TCA principle has been developed for producing a wide set of alumina supports, adsorbents and catalysts.

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DEPENDENCE OF THE PHYSICO-CHEMICAL PROPERTIES OF COBALT-CONTAINING CATALYSTS ON THE NATURE OF HIGH-TEMPERATURE SUPPORT

A.S. Ivanova, O.P. Babushok, V.N. Gavrilin, V.M. Mastikhin, V.I. Zaikovskii, A.S. Kalinkin, V.P. Ivanov, A.V. Pashis

Kinet.Katal., 33, 3 (1992) 654-663

We have studied the effect of a high-temperature support (æ, α-Al_2O_3, MO_2-Al_2O_3, where M = Si, Zr) on the formation of cobalt-containing catalysts. The active component was found to interact with the support only in the Co/æ-Al_2O_3 system to form cobalt aluminate. At small cobalt content (ca. 5 mass.%) the reduction degree of this sample by hydrogen is the lowest. At high Co (ca. 17-23 mass.%), the reduction degree does not depend on the support nature and is around 0.6. The average size of cobalt particles decreases in the series: α-$Al_2O_3 \rightarrow ZrO_2$-$Al_2O_3 \rightarrow$ æ-$Al_2O_3 \rightarrow SiO_2$-$Al_2O_3$.

The lattice structure of metal cobalt particles can be either cubic face-centered (CFC) or hexagonal closely packed (HCP) with defects.

PHYSICOCHEMICAL PROPERTIES OF La-Zr-O AND Ce-Zr-O SYSTEMS OBTAINED UPON PRECIPITATION

A.S. Ivanova, E.M. Moroz, G.S. Litvak

Kinet.Katal., 33, 5-6(1992) 1208-1214

We have investigated the effect of preparation conditions, nature and component ratio on the phase composition and surface values of oxide R-Zr-O composites (where R=La,Ce) obtained via precipitation. Precipitation conditions (pH, temperature) do not affect significantly the above properties.

Only R_2O_3 nature and content are determining. Dehydration process and oxide phase formation in lanthanium-zirconium samples terminate at T≥ 700 °C. Complex of a pyrochloric structure, $La_2Zr_2O_7$, is present in the samples containing 33.3 ≤ La_2O_3 < 90 mol.%. Cerium-zirconium samples stay as oxide composites with a CeO_2 structure even upon drying in air. The surface area of lanthanium-zirconium samples is minimum at La_2O_3 ~ 33.3 mol.%; it remains unchanged at 110-700 °C. The surface area of cerium-zirconium samples decreases monotonously with Ce_2O_3 increase at 110 °C and does not depend on the composition within 400-700 °C.

THERMOLYSIS OF HETEROPOLYACID $H_3PMo_{12}O_{40}$ AND CATALYTIC PROPERTIES OF THERMAL DECOMPOSITION PRODUCTS IN OXIDATION OF ACROLEIN TO ACRYLIC ACID

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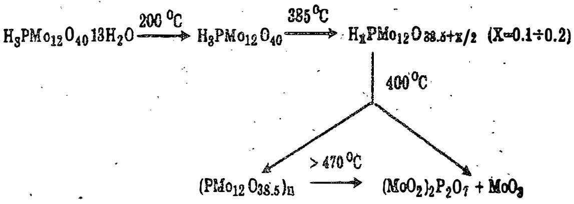
II World Congr., IV Europ. Workshop Meeting "New Develop. Select. Oxidation", Proceedings (editor V.Cortes Corberan & S.Vic. Bellon), 1993.

Thermal instability of PMo HPA providing several different phases under catalytic reaction conditions makes it hard to determine the active component. Here, we investigated PMo HPA thermolysis *in situ* with a high temperature X-ray diffraction, thermal analysis, IR and ^{31}P NMR spectroscopies.

The HPA transformation in air occurs as follows:



Crystallization water is removed at 200 °C. Dehydrated HPA exists in the interval of 200-350 °C. At 385-400 °C it transforms to the phase of a $H_xPMo_{12}O_{38.5+x/2}$ composition with insignificant amount of constitutional water (X is ca. 0.2) retaining discrete polyanions. At T >400 °C the retained constitutional water is lost and rearrangement of discrete polyanions into an oxide structure of ReO_3 type occurs. This oxide phase possesses $(PMo_{12}O_{38.5})_n$ composition and in essence is the anhydride of PMo HPA, which is a structural analog of VMo_3O_{11} generated upon thermal decomposition of VMoSi HPA. Small amounts of $(MoO_2)_2P_2O_7$ and MoO_3 are observed starting from 400-420 °C. Above 470 °C the samples contain only these two phases. The insignificant change of MoO_3 lattice parameters shows the small amount of phosphorus to dissolve in the phase (P:Mo).

The catalytic performance of HPA and the products of its thermal decomposition are presented in the Table.

The products of HPA thermal decomposition appear to be more selective than

№	$T_{calcination}$, °C	$T_{reaction}$, °C	Conversion, %	Selectivity, %				Activity $W\cdot10^9$, $\frac{mol.}{m^2\cdot c}$
				$C_3H_4O_2$	CO	CO_2	$C_2H_4O_2$	
1	110	180	8	21.3	48.4	21.2	9.1	0.04
2	250	250	60	50.0	37.0	6.0	4.5	4.0
3	300	300	60	65.0	32.0	2.2	0.8	7.6
4	350	350	60	68.0	18.0	3.0	0.5	26.2
5	385	350	60	79.0	13.0	2.0	0.5	19.7
6	420	350	60	83.0	13.0	3.6	0.4	16.7
7	530	350	60	86.0	12.0	2.0	-	16.6

paternal HPA: the higher is decomposition degree the more selective is the catalyst.

As shown by the high temperature X-ray studies *in situ* the atmosphere of various gas mixtures affects the composition of products and the temperature of their generation. This can explain a wide variety of data concerning the state of PMo HPA under different reaction conditions.

STOICHIOMETRIC REACTION OF BENZENE WITH α-FORM OF OXYGEN DERIVED FROM N_2O. MECHANISM OF AROMATICS HYDROXYLATION OVER FeZSM-5 ZEOLITES

V.I.Sobolev, A.S.Kharitonov, E.A.Paukshtis, G.I.Panov

J. Molec. Catal., 84 (1993) 117-124

A stoichiometric reaction of benzene with surface α-oxygen produced in N_2O decomposition has been studied on FeZSM-5 zeolites. Reaction products were extracted from the surface and analyzed with chromatographic technique. Reaction was shown to proceed readily at room temperature and to provide a nearly quantitative yield of phenol. This explains the unique catalytic properties of FeZSM-5 zeolites and their ferrisilicate analogs in hydroxylation of aromatics by N_2O.

A mechanism of "monoatomic oxidation" is suggested to explain phenomenon, when participation of a highly reactive α-oxygen results in a partial but not complete oxidation process.

THE EFFECT OF OUTER SURFACE SILYLATION ON THE CATALYTIC PROPERTIES OF FeZSM-11

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Benzene oxidation to phenol by N_2O is among the recently discovered catalytic reactions. Fe-containing zeolites of pentasil type are the most efficient catalysts for this reaction. Their unique properties are associated with the specific Fe-containing active sites (α-sites). To elucidate the location of α-sites in the zeolite matrix (inside channels or on the outer crystal surface), we have studied the effect of the outer surface silylation by polymethylsiloxene on the catalytic activity of FeZSM-11.

SiO_2 deposition does not affect both the zeolite channel system and the micropore volume. Silylation deactivates the outer surface due to its covering by the inert SiO_2. Thus, 15 wt.% SiO_2 deposition (this equals to the 2.5 monolayer coverage with regard to FeZSM-11 outer surface area) decreases the outer surface acidity by 75-80%. This decelerates significantly mesitylene isomerization proceeding over the outer surface of the zeolite, mesitylene conversion drops from 12 to 2%.

At benzene oxidation to phenol, silylation affects neither benzene conversion, nor its selectivity. Thus a major portion of α-sites (if not all sites) is located inside the microporous system of zeolite.

HYDROGENATION OF ACETONE ON COPPER CHROMITE CATALYSTS: STRUCTURE-ACTIVITY RELATIONSHIP

O.V.Makarova, T.M.Yurieva, L.M.Plyasova

Kinet. Katal., 34, 4 (1993) 681

Relationships between structures of $CuCr_2O_4$ and their catalytic activities in acetone hydrogenation have been discovered.

Catalytic measurements were performed in a flow set up and were accompanied by chromatographic analysis of reaction products. The catalyst was reduced in a hydrogen flow in the temperature range of 75-500 °C. Then its activity was determined at 75 °C. High temperature XRD (HTXRD) applied *in situ* provided information about phase composition and structure of catalysts at various stages of their operation.

We have shown, that at various reduction temperatures three definite states of catalyst can be obtained: the first state is obtained at the temperatures up to 180 °C, the second one belongs to the range from 180 °C to 370 °C and the third is registered at temperatures around 450 °C. The first state resembles the paternal catalyst, its XRD pattern corresponds to that of normal $CuCrO_2O_4$ spinel structure. The third state is a mixture of spherical copper particles with chromium oxide. The latter, possessing a structure similar to NaCl and α-Cr_2O_3, is formed upon the temperature increase. The catalytic activity of these two states are near zero and only the second state is rather active. Hydrogen absorption appears to occur on the second state. According to HTXRD and EM data about 50% of copper ions quit the spinel structure and transform into flat particles epitaxially bound with a defect spinel phase. The defect spinel has a cubic structure, where the environment of residual copper ions is distorted from tetrahedron to almost octahedron coordination due to absorbed hydrogen species. Catalyst heating in a helium flow leads to hydrogen desorption and the catalyst returns to its initial state.

Thus, the only active catalyst state is the reversible one containing hydrogen species absorbed by the spinel phase. Therefore, the absorbed hydrogen species seem to be active in acetone hydrogenation. The same conclusion was drawn in [1] for isoprene hydrogenation.

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INTERACTION OF HYDROGEN WITH COPPER CHROMITE SURFACE

A.V.Khasin, I.I.Simentsova and T.M.Yurieva

React. Kinet. Catal. Lett., to be published

Kinetics of surface copper chromite $CuCr_2O_4$ reduction with molecular hydrogen has been studied. H_2 transformation has been shown to proceed with the intermediate participation of copper reduced states, probably Cu^0 formed as a result of surface reaction. The process kinetics has a topochemical character. Reaction rate as a function of surface reduction degree, x, reaches its maximum around $x = 0.5$.

DECOMPOSITION OF ALKANETHIOLS TO DIALKYL SULFIDES AND H_2S

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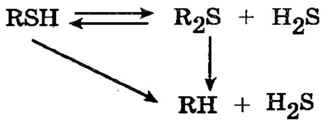
React. Kinet. Catal. Lett., 41 (1990) 357;
React. Kinet. Catal. Lett., 44 (1991) 475

Decomposition of alkanethiols on catalysts of various composition has been studied. At

200-500 °C methanethiol appears to convert quantitatively to dimethyl sulfide on the catalysts under study. 100% selectivity towards diethyl sulfide is observed when ethanethiol conversion attains 50% of its equilibrium value, the selectivity towards diisopropyl sulfide being ca. 30%. The reaction was found to follow a parallel-consecutive scheme:



The mutual inhibition is observed at the conversion of thiols' mixture die to their competitive adsorption on the catalyst.

A stepwise reaction mechanism is suggested: first, the catalyst surface is alkoxylated by thiol, then RO-groups interact with a second molecule of thiol adsorbed on the base sites. Kinetic peculiarities of catalytic decomposition of thiols have been studied under gradientless conditions. The kinetic equation obtained describes rather well the process on a nonhomogeneous catalyst surface.

CATALYTIC SYNTHESIS OF THIOLANE FROM TETRAHYDROFURAN AND H_2S

A.V.Mashkina, V.M.Mastikhin, E.A.Paukshtis, V.Yu. Mashkin, A.V. Nosov, I.V. Desyatov

Appl. Catal., to be published

Tetrahydrofuran recyclization to thiolane (the Yuriev reaction) has been studied in the alumina presence. Thiolane formation at 200-500°C was found to be accompanied by the cracking of both reagent and product thus yielding hydrocarbons and coke deposition on the catalyst surface. Catalysts of various composition were investigated. Lewis acid sites turned out to play a significant role in the thiolane formation, i.e. the rate per one site increases with the strength of this site. Regarding kinetic, IR and NMR data we have postulated reaction mechanism: the interaction between tetrahydrofuran and the catalyst yields an oxo compound which dissociates on Al^{3+}-O^- paired sites. Thiolane forms at the interaction of intermediate alkoxy complexes and H_2S activated on the surface.

EFFECT OF ACID-BASIC PROPERTIES OF CATALYSTS ON THEIR ACTIVITY IN 4-METHYLTHIAZOLE SYNTHESIS

T.S.Sukhareva, L.V.Manuilova, N.D.Parshukova

React. Kinet. Catal. Lett., to be published

We have managed to determine the activity of some catalysts containing various types of acid and basic surface sites in 4-methylthiazole synthesis from methylisopropylidenimine and SO_2.

Catalysts containing strong basic sites and week Lewis sites appear to be the most active and selective, while proton donating catalysts are almost inert. Catalysts with Lewis acid sites accelerate the 4-methylthiazole formation though they are less active than strong basic sites.

4-Methylthiazole yield attains 95% on the basic catalysts.

NEW CATALYSTS FOR SELECTIVE REDUCTION OF NITROGEN OXIDES BY HYDROCARBONS.

V.A.Sadykov, G.M.Alikina, R.B.Bunina, A.S.Ivanova, S.F.Tikhov, A.Ya.Rozovskii (Inst. Petroch. Synth., Moscow), V.V.Lunin (Moscow State Un.), Yu.S.Khodakov (Russian Heat and En. Inst., Moscow)

Selective reduction of nitrogen oxides by hydrocarbons in the excess of oxygen seems to be very promising for NO_x removal from the flue gases of power plants. New systems potentially suitable for this purpose have been tested, propane was used as reductant. Several catalysts were found to possess catalytic properties superior to those of the known catalysts [1]. Though with the systems based on transition metal aluminas and zeolites the conversion into nitrogen is known to decrease sharply at high temperatures and high oxygen concentrations, our catalysts exhibit a monotonous increase of nitrogen production rates up to 600-800 °C and 5-10% of O_2. Pilot tests with flue gases from oil burner demonstrated that within 400-800 °C, flow rate of 10,000-15,000 h^{-1} and NO_x:propane ratio of 1:1 the conversion to N_2 exceeded 95%.

1. 10th Int. Congr. Catal., Budapest, Hyngary, 1992, Preprint and Abstract Book, p.213-215

SUPPORTED Pd: STRUCTURE, KINETICS AND MECHANISM OF LOW-TEMPERATURE OXIDATION OF CARBON MONOXIDE

S.N.Pavlova, V.A.Sadykov, D.I.Kochubei, B.N.Novgorodov, G.N.Kryukova, V.A.Razdobarov

10th Int. Cong. Catal., Budapest, Hungary, 1992. Preprint and Abstract Book, p. 337

According to EM and EXAFS data, the mean Pd-Pd distance, Debye factor and morphology of Pd particles with the average diameter less than 20 Å appear to depend on the support nature (TiO_2, SiO_2, Al_2O_3), epitaxy is developed for the case of Pd/anatase. EXAFS data show the surface layer of Pd particles to be compressed in comparison to those of the core. This phenomenon is explained by rearrangement of (100) and (110) faces into a more densely packed corrugate layers with a local hexagonal coordination of Pd atoms. The surface layer altering and rearrangement is caused by adsorption processes. Thus, the forms of CO and oxygen adsorbed on supported Pd appear to differ from those adsorbed on a massive metal crystal. Due to the presence of defect sites stabilizing the weakly bound forms of CO and oxygen, titration of adsorbed species by the gas phase molecules seem to involve formally impact stages. This is also substantiated by deviations of kinetic parameters (E_a, n_i, TOF) and dynamic features of low-temperature catalytic reaction from the corresponding parameters typical for single crystals faces. Under steady-state conditions and at ambient temperatures the catalytic reaction was proved to occur via interaction of weakly bounded CO and, probably, molecular oxygen.

RELATIONSHIP BETWEEN CO AND NO ADSORPTION SITES WITH DIPOLE COUPLING AND ACTIVE SITES OF IRON OXIDES

S.F.Tikhov, V.A.Sadykov, G.N.Kryukova, V.A.Razdobarov

1st Europ. Congr. Catal. "EUROCAT", Montpelier, France, 1993, Book of Abstracts, v.2, p.764

CO and NO adsorption on various Fe_2O_3 samples was studied with IR spectroscopy to elucidate the chemical nature of the surface active sites of iron oxides.

CO adsorption at 80 K provides absorption bands (a.b.) at 2200-2190, 2180-2170, 2165-2160, 2150 cm^{-1}, their relationship depending on the conditions of sample preparation. After NO adsorption at 300 K a.b. at 1825-1780cm^{-1} were detected. Coadsorption of CO and NO appears to produce carbonyl complexes with a.b. at 2200-2170 cm^{-1} and surface nitrosyls are formed on the same coordinatively unsaturated Fe^{2+} ions. The density of these sites varies from sample to sample and does not exceed several percent of a monolayer. Isotope dilution experiments ($^{12}C \rightarrow {}^{13}C$, $^{14}N \rightarrow {}^{15}N$) demonstrated a red shift of the a.b. due to the weakening of dipole-dipole dynamic interaction of CO (NO) in the adlayer. Since the number of adsorption sites is rather small, these data evidence for their aggregation on the surface. These sites are easily reduced by CO at 300 K to Fe^{1+}-Fe^{0} state (ν_{CO}=2140-1980 cm^{-1}) and reoxidized by oxygen.

The correlation of concentration of the easily reduced sites with the specific activity of catalysts in CO oxidation under steady and unsteady conditions show these sites to be the active ones. TEM data revealed no simple correlation between a.b. intensities and exposition of various crystallographic planes for the systems under study. Therefore, the surface active sites are considered to be the clusters of coordinatively unsaturated cations readily undergoing redox transitions at ambient temperatures. These sites are most likely tp be located in the vicinity of surface steps including those at the outlets of bulk extended defects.

IR SPECTROSCOPIC STUDIES OF MECHANISM OF TOTAL OXIDATION OF PROPANOL-2 ON COPPER OXIDE UNDER CONDITIONS OF CATALYTIC REACTION

N.M. Dobrynkin, A.A. Davydov, A.A. Budneva, V.V. Popovskii, V.A. Rogov, V.F. Serebryakov

Kinet.Katal., 33 (1992) 133-141

The spectrokinetic method was used to investigate the nature of surface species and kinetics of their transformations in the course of propanol-2 oxidation. The structure of intermediate surface species and the sequence of their transformation as well as the kinetic parameters of some individual stages were determined. It was shown that at the conditions of catalytic propanol-2 oxidation the following transformations of surface species occured: iso-propylate —> adsorbed acetone species —> carboxylate —> formate —> carbon dioxide. The oxidation of carboxylate species is the rate determining stage.

STUDY OF ADSORPTION OF ALCOHOLS ON THE SURFACE OF COPPER OXIDE BY TPD AND IR SPECTROSCOPY METHODS

V.A. Rogov, A.A. Davydov, V.F. Serebryakov, N.M. Dobrynkin

Kinet. Katal., 33 (1992) 157-162

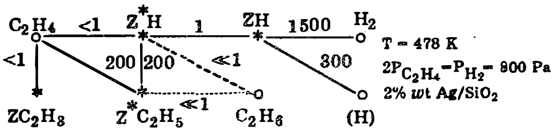
Here we present the IR spectra of methanol adsorbed on CuO at 293-473 K, and TPD spectra of methanol, ethanol and butanol-2. The alcohol adsorption species identified from the TPD patterns appear to correspond to the carbonate-carboxylate structures shown by the IR spectroscopy.

HYDROGEN INDUCED ACTIVATION OF ETHYLENE ON Ag/SiO2 CATALYSTS ELUCIDATED BY ISOTOPE KINETICS.

V.S.Muzykantov, A.A.Shestov, H.Ehwald (Center of Heterogeneous Catalysis, Berlin, Germany)

1st Europ. Congr. Catal. "EUROCAT",
Montpelier, France 1993, Book of Abstracts,
v.2, p. 618

Unlike copper, silver was not known as a suitable catalyst for ethylene hydrogenation. Nevertheless, we succeeded in demonstration of a latent though intensive interaction of ethylene with hydrogen in the presence of a highly dispersed Ag/SiO_2 catalyst. This could be elucidated by means of labeled atoms only. Homoexchange of ethylene (C_2H_4-C_2D_4) attains equilibrium very slowly (400-500 K). Hydrogen addition provides a 10 fold increase of exchange rate. At the same time, H_2 homoexchange and heteroexchange with the surface hydrogen (H) proceed rather fast, while the heteroexchange between hydrogen and ethylene is very slow. Using exact isotopic-kinetic equations [1] for analysis of isotope molecules redistribution observed we were capable to determine the paths and rates of hydrogen transfer upon ethylene activation:



The vertices of this graph correspond to the hydrogen containing species, the weights of its edges are the relative hydrogen transfer rates. The effect of hydrogen on ethylene homoexchange is represented by equation:

$$K = k \cdot P_{C_2H_4} \cdot P_{H_2}^{0.5} \quad (30-3000\ \text{Pa})$$

Differing from a well known Horiuti-Polanyi mechanism our scheme involves two surface species of one-atomic hydrogen: ZH (H_2 exchange) and Z^*H (C_2H_4 activation). Formation of the latter is complicated and so its concentration is extremely low. Therefore, only ethylene homoexchange occurs due to the reversible stage: $C_2H_4 + Z^*H = Z^*C_2H_5$, while hydrogenation can not proceed, since interaction between $Z^*C_2H_5$ and Z^*H is not probable. Thus, the surface processes of both copper and silver are similar, however, their overall catalytic behavior differs distinctly.

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ISOTOPIC STUDIES OF KINETICS AND MECHANISMS OF CATALYTIC DIHYDROGEN ACTIVATION BY PALLADIUM PHOSPHINE COMPLEXES IN ACID SOLUTIONS

V.N.Zudin, V.S.Muzykantov, V.A.Rogov, A.A.Shestov, E.P.Beloborodova, A.V.Golovin, V.A.Likholobov

1st Europ. Congr. Catal. "EUROCAT",
Montpelier, France 1993, Book of Abstracts,
v.I, p. 264

Activation of molecular hydrogen (dihydrogen) by transition metal complexes is an important stage of a number of homogeneous catalytic processes. A means of studying the catalytic dihydrogen activation is the isotope exchange method. With this method, essential information on a mechanism of exchange process (including quantitative assessment of contributions of all the possible types of exchange) can be obtained solely with complete analysis of the observed redistribution of isotope dihydrogen molecules using rigorous equations of isotopic kinetics [1]. In spite of a quite voluminous literature on homogeneous catalytic dihydrogen activation, we appeared to be pioneers in applying the approach mentioned above to the subject, e.g., by studying the regularities of isotope hydrogen exchange in the systems such as : "palladium(II) acetate - phosphine ligand - protic acid - dihydrogen". For all the systems investigated no hydrogen homoexchange ($^*H_2 + H_2 \rightleftarrows 2^*HH$) was found to occur, while two types of hydrogen heteroexchange ($^*H_2 + H^+ \rightleftarrows {}^*HH + {}^*H^+$ and $^*H_2 + 2H^+ \rightleftarrows H_2 + 2^*H^+$) proceeded with various relative contributions (depending on the nature and concentration of phosphine ligand and acid), which were computer calculated. A most adequate mechanism of hydrogen exchange was suggested involving the stages of dihydrogen heterolysis and rearrangements of palladium hydride complexes (identified with ^1H and ^{31}P NMR *in situ*):

$$[P_nPdX]^+ + H_2 \rightleftarrows P_2Pd(H)X + H^+$$

$$P_2Pd(H)X + P \rightleftarrows [P_3PdH]^+ + X^-$$

$$[P_3PdH]^+ \rightleftarrows P_3Pd^0 + H^+$$

here P is phosphine ligand, n=2 and/or 3, X^- is acid anion.

The rates of the stages were calculated and the strategy for estimation of possible isotopic effect was derived.

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OSCILLATION TEMPERATURE AND PRESSURE REGIMES OF EXOTHERMAL REACTION WITH PHASE TRANSITIONS

A.N.Stegasov, H.A.Kuzin, V.A.Kirillov

Teor. Osnovy Khim. Tekhn., 26, 1 (1992) 54-70

Physical and mathematical models describing the oscillation regimes of catalyst grain temperature and reactor pressure are suggested for chemical reactions with a considerable heat generation and liquid-gas phase transition.

The physical model considers a periodic change of chemical reaction regimes. The mathematical one is based on differential equations with discontinuous right parts. The effect of model parameters on the amplitude and frequency of oscillations was studied numerically.

ANALYSIS OF PROCESSES IN A TRICKLE CATALYST BED

V.A.Kirillov, A.N.Stegasov

Khim. Prom-st, 3 (1994) 175-182

Processes performed in a trickle catalyst bed have been analyzed along with the influence of gas and liquid flow rate, direction of phase flows, geometry and size of apparatus, physical properties of reagents.

MATHEMATICAL MODELING OF SO_2 OXIDATION IN A TRICKLE CATALYST BED

A.N.Stegasov, V.A.Kirillov

Teor. Osnovy Khim. Tekhnol., 27,4 (1993) 393-398

Mathematical model of SO_2 oxidation on a porous catalyst bed has been suggested. Equations of material balance for the element of catalytic surface were analyzed for various reaction orders.

Non stationary equation of material and heat balance for flow phases and catalyst temperature were suggested to describe continuous and pulse regimes in a trickle catalyst bed. Experimental data obtained upon either continuous or periodic liquid flow were processed and a good agreement of calculations with experiment was obtained. A considerable decrease of the observed reaction rate under the periodic liquid flow was demonstrated.

ANALITICAL METHOD FOR ANALYSIS OF UNSTABLE OPERATION OF REACTORS WITH A LIQUID-GAS PHASE TRANSITION

A.N.Stegasov, A.B.Shigarov, V.A.Kirillov

Teor. Osnovy Khim. Tekhnol., 25, 4 (1993) 524-532

Analytical method for studying operation of reactors with a liquid-gas phase transition has been suggested. In effect, the conservation equations and necessary relations are linearized within stationary profiles, meanwhile linear differential equations obtained undergo Fourier transform and a spectral problem is formulated. The analysis of this problem allows to define the regions of stable regimes of reactor operation.

The generalized results were obtained concerning the regions of non stable stationary regimes provided by pure hydraulic, kinetic or both mechanisms.

Results (non stability of stationary regime, oscillation frequencies) obtained via analytical method or calculated via non linear model are compared.

MATHEMATICAL MODEL OF EXOTHERMAL HYDROGEN PEROXIDE DECOMPOSITION IN A FIXED CATALYST BED

V.A.Kirillov, V.A.Kuzmin, N.A.Kuzin, V.P.Denezhkin, A.N.Stegasov

Teor. Osnovy Khim. Tekhnol., 27, 5 (1993) 508-514

Two- or three-temperature models based on general conservation laws for mass, pulse and energy have been suggested for the process of catalytic hydrogen peroxide decomposition. The processing of experimental data allowed to estimate a set of parameters for mathematical description and to show the validity of physical and mathematical models describing the process under study.

REDUCTION OF NITROGEN OXIDE IN AQUEOUS SOLUTIONS

Z.P.Pai, S.V.Kapterev, N.N.Kundo

Sib. Khim. Zh., 1 (1993) 5-11

The reported kinetic study serves to verify the mechanism of nitrogen oxide interaction with oxygen containing sulfur compounds in aqueous solutions. The rates of NO absorption at 50 °C, pH=5.0, P_{NO}=0.08 MPa in Na_2SO_3 and $(NH_4)_2S_2O_3$ solutions were found to be $2.2\cdot10^{-2}$ mol/l·min and $2.7\cdot10^{-4}$ mol/min·l, respectively. The effect of $(NH_4)_2S_2O_3$ within the range of 0.1-1.6 mol/l on the reaction rate was elucidated. The reaction rate order appears to be the first, when $(NH_4)_2S_2O_3$ concentration is less than 0.8 mol/l and the zero one, when $(NH_4)_2S_2O_3$ concentration exceeds 0.8 mol/l.

The main products of NO interaction with $(NH_4)_2S_2O_3$ solution were determined. According to the data obtained $S_2O_3^{2-}$ ions appear to serve only as donors of SO_3^{2-} ions at nitrogen oxide reduction.

MATHEMATICAL MODEL OF SIMULTANEOUS SULFUR DIOXIDE AND NITRIC OXIDES ABSORPTION

A.Yermakova, V.A.Lebedev, Z.P.Pai

Sib. Khim. Zh., 3 (1993) 92-100

A mathematical model of simultaneous sulfur dioxide and nitric oxide absorption in aqueous solutions of ammonia and phosphoric acid (pH ranges from 3.6 to 6.2) accompanied by chemical reactions has been investigated. The reaction of bisulfite with nitric oxides appears to be fast in comparison to gas and liquid diffusion. The effect of liquid/gas flow rate ratio and of starting pH values on the efficiency of SO_2 and NO removal have been studied with numeric analysis of model differential equations. The normal and default process operation regimes were distinguished. In the first regime a high purity of vent gas may be achieved, but if the liquid/gas flow rate ratio fall below the "critical" value, pH level is altered considerably and SO_2 evolution from the solution occurs.

LIQUID-PHASE CATALYTIC SULFUR PRODUCTION FROM HYDROGEN SULFIDE FOR THE COKE-OVEN GAS CLEANING (REVIEW)

Z. P.Pai, A.Yermakova, N.N.Kundo, V.A.Kirillov, E.I.Andreikov, V.G.Nazarov

Koks Khim., 6 (1993) 36-42

Chemical and technological peculiarities of SLP method (liquid-phase sulfur removal) have been compared to other processes used in coke chemistry. The SLP method allows the processing of concentrated (40-60 vol.%) hydrogen-sulfide gas containing hydrogen cyanide and ammonia admixtures simultaneously with sulfur production.

The article concerns the following topics: conventional methods for sulfur removal; chemical regularities of liquid-phase Claus process; SLP-coke technology and perspectives of its application.

CATALYTIC REDUCTION OF THIOSULFATE AMMONIUM BY HYDROGEN SULFIDE IN THE PRESENCE OF CYANIDE IONS

Z.P.Pai, N.N.Kundo, V.S.Zagainov, E.I.Andreikov

Koks Khim., 7 (1993) 26-29

We have studied the effect of CN^- ions on the reduction of sulfur dioxide absorption products by hydrogen sulfide. $(NH_4)_2S_2O_3$ reduction is one of reactions, which limit the process of sulfur formation at the reduction of HSO_3^{2-}, $S_2O_3^{2-}$, $S_nO_6^{2-}$ ions.

$(NH_4)_2S_2O_3$ reduction at pH = 5.0, T = 50°C and phosphatic buffer conditions was found to produce elementary sulfur and rhodanate. The quantity of rhodanate was equal to that of CN^-. Catalyst IC-27-1 has a positive effect on the rhodanate yield.

CORROSION OF METALS BY CONTACT SOLUTION CONTAINING THE PRODUCTS OF SO_2 AND H_2S ABSORPTION

Z.P. Pai

Koks Khim., 8 (1993) 37-40

The paper presents laboratory corrosion tests of various steels and titan. These tests served to verify if it is possible to use these materials for chemical engineering. Corrosion rate (P, mm per year) was determined by the long-duration test with sample immersion. Sample surface conditions were checked before and after experiment with electron microscope NIOPHOT-2.

Steels OX17H13M2T and X18H10T as well as alloy BT-10 based on titanium appear to be the most stable in aqueous solutions (pH = 4-6) containing the products of SO_2 and H_2S conversion.

MATHEMATICAL SIMULATION OF SLP-COKE PROCESS. ACID GAS CONDITIONING BEFORE ABSORPTION

A. Yermakova, Z.P. Pai

Koks Khim., 8 (1993) 25-31

Here we suggest the ways and schemes for refining the concentrated hydrogen sulfide gas with NH_3 and HCN admixtures to obtain the gas with H_2S/SO_2 ratio of 2:1. This gas is suggested for the direct absorptional-catalytic refining by the SLP method. To prepare the gas desired we propose selective oxidation at high temperatures, cooling and condensation of sulfur, its mixing with the inital acid gas. A software for mathematical simulation of various stages and imitation of all scheme operation has been designed. A balanced model for calculating the stage of selective oxidation is suggested. According to the model, the final products depend on thermodynamic equilibrium at the temperature maintenance under adiabatic conditions. A process scheme of acid gas refining utilizing the Altai coke-plant raw materials is presented.

SULFUR PRODUCTION AT PURIFICATION AND CONVERSION OF HYDROCARBON RAW MATERIALS

Z.P.Pai, A.Yermakova, N.N.Kundo, V.A.Kirillov

Chemistry for Sustainable Development,
to be published.

The liquid-phase purification methods accompanied by sulfur recovery appear to be feasible for processing the low concentrated sulforous exhaust gases or small volumes of concentrated sulfides.

Thus, the liquid phase Claus process seems to be rather promising.

Chemical and technological peculiarites of SLP method (liquid-phase sulfur removal) are considered. The figure presents a general scheme for processing gases containing more than 20 vol.% of hydrogen sulfide and CO_2, H_2O admixtures. The scheme includes such important stages as heating, catalysis and sulfur separation.

CATALYTIC PROCESS OF H_2S AND HCN OXIDATION IN SOLUTION

N.N. Kundo, G.A. Faddeenkova

Proc. 7th Int.Symp. "Heterog.Catal.", Bourgas,
Bulgary,1991, p. 1063-1068

Cobalt phthalocyanines (CoPc) were found to be very active catalysts for H_2S oxidation among the sulfides of transition metals, complex compounds and organic redox systems. The process of gas purification with sulfur recover, basing on CoPc catalysts, was suggested. HCN as a component of coke gas demonstrated a strong inhibitory effect on the process of H_2S oxidation to sulfur, producing inactive cyanide complex with CoPc. Varying catalysts and oxidation conditions, we confirmed the possibility of H_2S oxidation accompanied by the HCN binding to rodanide by polysulfides, which are the intermediate products of H_2S oxidation. A commercial process of H_2S and HCN purification was realized at the coke factory in Kemerovo.

NOVEL APPROACH TO SELECTIVE OXIDATION OF GASEOUS HYDROCARBONS

G.A.Kovalenko, V.D.Sokolovskii

Biotechnol. Bioeng., 39, 5 (1992) 522-528;
React. Kinet. Catal. Lett., 48, 2 (1992) 447-454.
II World Congr., IV Europ. Workshop Meeting
"New Develop. Select. Oxidation", Proceedings
(editor V.Cortes Corberan & S.Vic. Bellon), 1993.

Selective oxidation of hydrocarbons can be performed by some microorganisms possessing the monooxygenase activity.

Biocatalytic activities of some strains of methanotrophic bacteria (which utilize methane as a sole source of carbon and energy for growth) were investigated in partial oxidation of methane and propylene (see the Table). Generation of commercially valuable oxy-products (methanol, propylene epoxide) occurred with a 100% selectivity under mild reaction conditions. The maximal rate of product generation attained 250 nmol of methanol per min per mg of bacterial cells (dry weight)

Table.

Biocatalytic activities of some strains of methane utilizers in methane and propylene selective oxidation.

Microorganism	Biocatalytic activity: initial rate of product generation, nmol/min per mg of cells	
	methanol	propylene oxide
Methylococcus capsulatus IMV 3021	25,9 (max 252,1)	31,6
Methylosinus trichosporium IMV 3011	18,3 (max 49,7)	14,4
Methylomonas sp. GY-J-3	19,5 (max 30,5)	20,7

OXYGEN MIGRATION AT SURFACE REDUCTION IN CATALYSTS FOR SELECTIVE OXIDATION

O.Yu.Ovsitser, V.D. Sokolovskii

Recently we have measured the effective coefficient of oxygen migration at surface reduction and the activation energy for migration for a series of oxide catalysts for selective oxidation of organics (V-Mo-O, Bi-Mo-O, Fe-Sb-O, Bi-Sb-O, Sn-Sb-O, Sn-Bi-O, V-P-O, Ga-Sb-O, Mg-O, Sm-O, Sm-Mg-O). The effective coefficient of oxygen migration was calculated with the oxygen migration rates at different degrees of surface reduction [1]. The effective coefficients of oxygen migration in these catalysts defined at optimal operative temperatures were found to be similar in magnitude [2]. At optimal operative temperatures in all studied systems (except for Mg-O, Sm-O and Sm-Mg-O) the maximum rate of oxygen migration is sufficient to provide selective oxidation via a rapid oxygen migrationion in the surface layers [3].

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ADSORPTION AND REACTION OF METHANE AND OXYGEN OVER MgO, Sm_2O_3 AND Sm_2O_3/MgO

O.V. Buyevskaya, M. Rothaemel*, M. Baerns*
(Ruhr Univ.,Bochum,Germany)

Submitted to *J. Catal.*

The mechanism of catalytic methane coupling is not yet completely understood. In particular, the role of different oxygen species in methane activation and product formation is still a matter of discussion. With this regard, we report on the data, obtained with the transient response technique with a high-time resolution and Temporal-Analysis-of-Products (TAP) reactor. The data concern catalysts, consisting of MgO, Sm_2O_3 and Sm_2O_3 (5 mol.%)/MgO. We applied the pulses ranging from 10^{15} to 10^{17} molecules and thus corresponding to the Knudsen- and molecular- diffusion regimes.

(1) Oxygen interaction with surface of MgO, Sm_2O_3, and Sm_2O_3(5 mol.%)/MgO was studied in the temperatures ranging from 539 to 1035 K. $^{18}O_2$/Ne mixture (1:2) was fed

in pulses onto the catalysts. Before each pulse the catalyst was exposed to oxygen and vacuumed for 10 min. Exchange of $^{18}O_2$ with surface oxygen (^{16}O) was observed and all possible oxygen molecules ($^{18}O_2$, $^{16}O^{18}O$ and $^{16}O_2$) were detected at the reactor outlet. The $^{18}O_2$ conversion per run, i.e., the oxygen exchange activity, decreased from Sm_2O_3 (E_a=78 kJ/mol) via Sm_2O_3(5 mol.%)/MgO (E_a=87 kJ/mol) to MgO (E_a=297 kJ/mol). The activation energy of exchange process increased from Sm_2O_3 to MgO. The exchange occurred stepwise ($^{18}O_2 \rightarrow {}^{16}O^{18}O \rightarrow {}^{16}O_2$) as was derived from the mean residence time of different oxygen-isotope molecule responses. However, the product distribution obtained at various catalyst loadings, i.e. contact times, showed that ($^{18}O \rightarrow {}^{16}O_2$) exchange can go through molecular mechansim on Sm_2O_3.

(2) The influence of methane on the oxygen exchange was studied by a simultaneous pulsing of CH_4/Ne and $^{18}O_2$/Ne mixtures (methane:oxygen ratio =1.1) at the temperatures ranging from 539 to 1035 K over the catalysts. The presence of methane did neither influence the activation energies for $^{18}O_2$ consumption, nor the shape of $^{18}O_2$ responses for all catalysts studied. Therefore, the first step of oxygen activation on the surface is faster than methane activation. Thus the gas-phase oxygen does not react with methane under given reaction conditions. The intensity of the response signals of $^{16}O^{18}O$ and $^{16}O_2$ and their respective mean residence times, however, decreased in the presence of methane. So, the surface oxygen species, resulting from the gas-phase oxygen via dissociative adsorption, probably, participate in reaction with methane before their recombination and sequential desorption as dioxygen. Therefore, only the surface oxygen species are involved in the OCM reaction.

(3) The pathways of lattice and surface-oxygen species ($^{*}O_s$), formed at interaction of gas-phase oxygen with surface Sm_2O_3 and MgO, were investigated with sequential pulses of oxygen and methane at various time intervals between the oxygen and methane pulses (0.02 s to 20 s). On MgO, the surface lattice oxygen was found to be responsible for the formation of C_2 hydrocarbons, while adsorbed oxygen appeared to have a short lifetime on the surface (0.1 s) and took part in the formation of complete oxidation products only. Over Sm_2O_3, active oxygen species $^{*}O_s$ had the lifetimes of more than 5 s and were responsible mainly for methane conversion, producing both C_2 hydrocarbons and CO_x.

(4) The dependence of methane conversion and product formation on the amount of active surface oxygen species $^{*}O_s$ over Sm_2O_3 was determined with sequential pulses of O_2 and CH_4 at T = 984 K at various oxygen pulse intensities and time intervals ranging from 50 to 100 ms. A linear dependence of CH_4 conversion on the amount of $^{*}O_s$ attached to the surface was obtained; methane conversion of up to 39% was obtained (compare with 3% conversion in reaction with lattice oxygen only). For $^{*}O_s$ amounts less than 2.5 10^{16} atoms/m^2, a linear correlation of C_2 product yields with the amount of these oxygen sites was observed. However, for higher coverages the yield to C_2 hydrocarbons decreased, probably due to their consecutive oxidation to CO_x.

(5). In conclusion, the active oxygen site fromation from the gas-phase oxygen is essential for a high Sm_2O_3 activity at the OCM reaction. The data presented show, that the concentration of these sites determines the product distribution, while their lifetime, i.e., reflects the adsorption strength and is of minor importance.

BASE SITES ON THE SURFACE OF OXIDE CATALYSTS RESPONSIBLE FOR OXIDATIVE METHANE COUPLING

A.A.Davydov

Submitted to Chem. Eng.Technology

Using FTIR spectroscopy of adsorbed probe molecules (chloroform and CO_2) we have studied the basic sites of various oxide catalysts for oxidative methane coupling. We have compared various methods. CO_2 probe molecule was shown to exhibit several advantages at the identification of basic sites. We have revealed a correlation between the strength of basic sites and the spectral parameters of surface carbonates. The differences in the spectral responses of carbonates can be ascribed to the different oxygen species, participating in carbonates formation. We have estimated the concentration of the most strong sites.

We have studied also the catalytic activity of the systems. The system's activity appears to depend on the presence and concentration of strong basic sites on the catalyst surface.

IR AND UV STUDIES OF ISOBUTANE ADSORPTION ON HZSM-5 ZEOLITES

A.V.Demidov, I.G.Danilova, A.A.Davydov

Zh. Phys. Khim.,, to be published.

Adsorption and reactions of isobutane on HZSM-5 zeolite at 300-673 K has been studied by combined IR and UV (diffusion reflectance) techniques. Adsorption of isobutane at room temperature appears to be accompanied by formation of complexes weakly bounded with surface Broensted acid sites. Oligomer saturated structures, allyl carbenium ions and coke were found to be produced in isobutane transformation on HZSM-5 at 573 and 673K.

ACID-BASE PROPERTIES AND DIRECTION OF OXIDATIVE TRANSFORMATIONS OF METHANE ON MAGNESIUM-PHOSPHORUS CATALYSTS

V.D.Sokolovskii, Z.G.Osipova, L.M.Plyasova, A.A.Davydov, A.A.Budneva

Appl. Catal., A:General, **101**, (1993) 15-23

Methane conversion direction depending on the change in acidity of magnesium basic oxide due to variations in phosphorus content was studied. With the rise of phosphorus content and acidity augmentation the decrease of dimerization rate and the rise of formaldehyde generation rate were observed.

IR data show acid sites to be present on the surface of catalysts for methane to formaldehyde conversion, no acid sites were registered on the catalysts for dimerization.

Thermal desorption studies, CH_3OH and $(CH_3)_4Si$ interaction with basic (MgO) and acid (Mg-P-O) sites demonstrated, that methyl surface groups provide only dimerization products on both catalysts, while methoxyl groups are the sources for both dimerization and oxidation products.

IR-SPECTROSCOPIC METHODS FOR STUDYING BASIC SITES ON OXIDES SURFACE

A.A.Davydov, M.L.Shepot'ko, A.A.Budneva

Kinet. Katal. 35, 2 (1994) 299-306

A spectral method for studying basic sites of oxide surface based on interaction of these sites with a probe molecule was suggested. The possibility to use chloroform and carbon dioxide molecules as probes for testing the basic surface properties was studied. Spectral parameters of surface compounds formed upon adsorption of these molecules on the surface of oxides were analyzed.

It was shown that chloroform molecule can be used only for estimates of averaged state of surface sites, while CO_2 molecule allows to estimate the general content of basic surface sites and to differentiate them with respect to their type and strength. The surface basic sites of oxides were differentiated by their properties. A spectral parameter for estimating the strength of surface basic sites was suggested.

CHNGE IN CONTENT OF BASIC CENTERS ON THE MgO SURFACE DURING MECHANOCHEMICAL ACTIVATION AND THE EFFECT OF THEM ON THE OXIDATIVE METHANE COUPLING

M.L.Shepot'ko, A.A.Davydov, V.V.Poluboyarov, A.A.Budneva

Submitted to *J. Phys. Chem.*

A new method for generation of strong basic sites on the surface of oxide systems, MgO in particular, via mechanochemical activation (MA) of an oxide was suggested. The basic sites of MgO surface before and after mechanochemical activation were studied by IR technique with CO_2 probe molecule. The change of catalytic properties of the activated system in oxidative methane coupling was investigated.

It was found, that the content and properties of the surface basic sites as well as their catalytic activity change considerably and mutually upon MA.

IR SPECTROSCOPY OF ADSORBED MOLECULAR PROBES (CO, NO): STUDY OF STATE OF TRANSITION METAL CATION ON CATALYST SURFACE. VANADIUM IONS ON THE SURFACE OF VANADIUM CONTAINING CATALYSTS

A.A.Davydov

Kinet. Katal., 34, 2 (1993) 333

Spectral parameters of CO and NO combined with vanadium cations in various redox and coordination states have been studied with IR and ESR techniques. Vanadium cations in redox state +5 do not coordinate with NO and CO, though coordinate with ammonia, while at lower oxidation states they appear to coordinate with NO and CO as well. A decrease of νCO and $\delta_S NH_3$ in V^{n+}-CO and V^{n+}-NH_3 complexes was found to be a function of diminishing vanadium oxidation state. Spectral parameters of mono- and di-nitrosyl complex of nitrogen oxide with vanadium cations V^{4+} and V^{3+} were elucidated.

PROTON ACIDITY OF TRANSITION METAL OXIDES

A.A.Davydov

Zh. Phys. Khim., 67, 9 (1993)1900-1906

Direct experimental data (IR spectroscopy) on proton acidity of transition metal oxides referred to in literature and obtained by author et al. have been reviewed and analyzed. All acid forming oxides and their complex composites were shown to possess a proton acidity determined by the cation of acid forming oxide, its redox degree, presence of other cations in the system, structure of the forming compound. Spectral peculiarities of proton sites of acid forming oxides containing cations in the highest oxidation states are discussed. Ways to modify oxides not forming acids and to produce proton sites on their surface are described.

OPTICAL SPECTROSCOPY STUDY OF VANADIUM OXIDE DEPOSITS ON SUPPORTS

A.A.Davydov

J. Molec. Catal., 81, (1993) 3

With IR, ESDR and ESR analysis the structure and properties of vanadium oxide deposits on the surface of supports were shown to depend significantly on the type of support, vanadium content and preparation conditions (pH, deposition procedure, etc.). Interaction of the deposited component with a support appears to be of chemical nature and to involve both surface hydroxyl groups and coordinatively unsaturated cations of support. We have analyzed potentialities of IR spectroscopy of adsorbed molecular probes to prove the mechanism of oxide vanadium cluster generation and participation of particular support sites in this process. Schematic view of fragments formed on various supports of vanadium oxide compounds is presented.

The chemical properties of formed vanadium-oxide compounds were found to differ considerably with respect to their interaction with simple molecules like NH_3, CO, NO. IR spectral parameters of these molecules, which are specific spectral probes, provide a detail information on the state of the catalyst active component and its properties and structure as well.

A NEW PROCESS OF ISOPROPYL BENZENE PRODUCTION ON A ZEOLITE CATALYST

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Proc. Meeting "Zeolite Catalysis for the Solution of Environmental Problems", Yaroslalvl 1992, Russia

Commercial production of cumene by benzene alkylation with propene on aluminium trichloride is environmentally unsafe since the catalyst should be washed out from reaction products with water. Hence, the acidic water wastes produced are to be utilized or recovered somehow. In addition, a non-selective alkylation provides by-products which should be recycled or used as a fuel.

Boreskov Institute of Catalysis has elaborated and tested in VNIIOS a high silica zeolite catalyst for benzene propylation to produce cumene. Studies were carried out in a high-pressure micropilot flow reactor with a fixed catalyst bed. Reaction conditions were varied as follows: molar ratio of benzene to propene was varied from 2:1 to 6:1, temperature ranged from 443 to 553 K, pressure - from 1.0 to 6.5 MPa, WHSV = 2.3-27.3 g/g·h. Catalyst was tested batchwise during 500 h without regeneration and its activity and selectivity remained unchanged. Optimal process conditions estimated by means of a mathematical model were the following: pressure 1.8-2.2 MPa, reaction temperature - 473-493 K, molar ratio of benzene to propene - 4-5:1, WHSV - 6-7 g/g·h. Under these conditions benzene conversion was equal to

20-22%, while the selectivity towards cumene was 95-97%. The rate of cumene production was 1.4-1.6 g/ml·h. The formation of by-products was negligible, no water wastes were generated.

SOME PECULIARITIES OF THE SYNTHESIS OF NITROGEN-CONTAINING HETEROCYCLIC COMPOUNDS ON ZEOLITE CATALYSTS

N.V. Testova, L.V. Malysheva, O.B. Sukhova, E.A. Paukshtis, K.G. Ione

Nitrogen-containing heterocyclic compounds are widely used in organic chemistry. Recent patents show the possibility to apply zeolite systems in catalytic synthesis of alkylamines from the oxygen-containing compounds and ammonia to produce linear, branched or cyclic amines. However, factors directing the conversion in a desired way have not been studied in detail yet.

To reveal the catalytic behavior of ecologically safe zeolite catalysts, we have examined the effect of porous structure, chemical composition, crystal sizes and properties of acid sites of zeolites on their selectivity in the model reaction of monoethanolamine conversion in ammonia atmosphere.

Monoethanolamine conversion may provide either piperazine and triethylenediamine or heterocyclic aromatics and their alkylderivatives (pyridine, pyrasine, pyrrol) depending on the zeolite type and the composition of acid sites on its surface. The results obtained were correlated with the data on the strength and concentration of the Brönsted and Lewis acid sites on zeolite surface.

The yield of piperazine and triethylenediamine was shown to increase proportionally to the concentration of OH groups with ν_{OH} = 3725 cm^{-1}. These products, thus, appear to form on the external surface of ZSM-5, ZSM-11 microcrystals.

The concentration of Lewis sites affects essentially the direction of nitrogen-containing compound synthesis, since the increase of their number provides the raise in alkylpyrasine concentration and, thus, the decrease of selectivity towards triethylenediamine. The formation of alkylpyrasines proceeds via a mechanism involving hydrogen redistribution reactions.

REGENERATION KINETICS OF THE COKED HZSM-5 CATALYSTS

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1st Europ. Congr. Catal., "EUROCAT",
Montpellier, France, 1993, Book of Abstracts,
v.1, p.201

Catalysts based on HZSM-5, HZSM-11 zeolites are widely applied in petrochemistry nowadays. Actually, the catalyst surface is deactivated due to coke deposition during the synthesis and conversion of hydrocarbons. Thus, regeneration of catalysts via a controlled combustion of coke deposits is required to recover the initial activity of catalysts.

Here, we have studied regeneration kinetics of HZSM-5 based catalysts coked in the course of benzene production from a gas condensate. The studies were performed under non-gradient conditions in a flow reactor with the Mac-Ben balance via registering sample weight loss due to the coke combustion. The dependence of coke combustion rate upon its amount on a catalyst, oxygen content in a gas regenerated and the rate of a gas flow was investigated.

More than 90% of coke deposits were found to burn out at the temperatures lower than 500°C, the remaining coke is burnt out only at 530-550°C. The rate of coke combustion depends on its origin and concentration. Thus, according to the Arrenius kinetics of coke combustion, the effective activation energy was found to vary from 33 to 43 kcal/mol.

The dependence of coke combustion rate on the oxygen partial pressure in the regenerating gas has shown the reaction order to be equal to 0.75 ± 0.15. The reaction order with respect to coke concentration is close to 1.

The kinetic equation for coke combustion modeling regeneration of HZSM-5 based catalysts has been derived.

GAS PHASE NITRATION OF AROMATICS ON ZEOLITE CATALYSTS. ROLE OF ACID SITES AND REACTION PECULIARITIES

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1st Europ.Congr.Catal., "EUROCAT", Montpellier, France, 1993, Book of Abstracts, v.1, p.79

Aromatic nitrocompounds are conventionally manufactured via nitration of aromatic hydrocarbons with the mixture of concentrated nitric and sulfuric acids. This provides huge acid wastes. Thus, application of environmentally safe catalysts and nitrating agents is of key importance today.

Here, nitration of benzene, toluene, ethylbenzene, xylenes, mesitilene and chlorobenzene with nitrogen dioxide over ZSM-5, ZSM-12 and β-zeolites has been studied. The effect of active sites nature, porous structure and surface acidity on the activity and selectivity of catalysts have been investigated.

The rate of nitration was found to increase proportionally to the concentration of strong Brönsted sites on the zeolite surface. The protons of hydroxyl groups appear to provide the same affect in the reaction as those of mineral acids in solutions.

Para-selectivity in nitration appears to be higher on a wide pore β-zeolite but not on ZSM-5 with small pores, as it was observed for other electrophilic reactions like alkylation.

The influence of the substrates basicity on their reactivity on the surface is less, than that in solutions. Nitronium ions on the zeolites surface were registered with FTIR spectroscopy. These ions were found to be in equilibria with H-bonded N_2O_4 on the Brönsted sites.

Energetics of reactants interaction with zeolite Brönsted sites was analyzed. Occupation of sites by the substrates and products was calculated via the Langmuir adsorption model. In the studied temperature range nitration was shown to occur in a pseudo-fluidized bed. The competitive adsorption of reagents with the produced nitrocompounds for an active site proceeds on the surface.

The mechanism of aromatics nitration on zeolites based on the data obtained is suggested.

INFLUENCE OF STRUCTURE TYPE AND ACID PROPERTIES OF ZEOLITES IN DIENE CONDENSATION OF ALLOOCUMENE AND α-METHYLACROLEIN

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1st Europ.Congr.Catalys. "EUROCAT",
Montpellier 1993, France, Book of Abstracts,
v.1, p.82

As it was already shown, one of diastereoisomers of ocinal can be obtained upon allocimene interaction with α-methylacrolein at room temperature in the medium of solvent.

The present work is the study on the activity of β-zeolites modified by cations (Me = Fe,Ni,Zn,Cu,La) and zeolites with different structure (ZSM-5, mordenite, erionite, sodalite) in the reaction discussed.

For a number of β_{Me} zeolites the activity and concentration of obtained products was shown to be determined by the type of a modifying cation. The concentrations of diastereoisomers of ocinal and $2,3\beta,5\beta$-trimethyl-2-(4-methyl-trans-penta-1,3-dienyl) -cyclopentanon depend on the quantity of acid sites of various strength. Taking into account the large size of reacting molecules we should consider not only a particular active site of the zeolite but a complex of sites with various strength and properties. A small admixture of alkaline metals in β-zeolite changes the catalytic properties significantly probably due to optimal distribution and cooperative effect and structure of the active acid sites.

Investigation of zeolites with various structures has shown the catalyst activity to depend on the SiO_2/Al_2O_3 ratio. The highest activity is observed for zeolites with $M<40$. The concentrations of reaction products seem to be determined mainly by the SiO_2/Al_2O_3 ratio and the alkaline content in the structure rather than by acidic properties.

CRYSTALLIZATION OF ZSM-5 ZEOLITES ON SEEDS

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Microporous Cryst., Japan 1993

Zeolites milling in a planetary mill, milled zeolite crystals' dissolving and crystallization on milled seeds have been studied with electron microscopy, NMR, ESR, IR spectroscopies, adsorption methods and thermography.

Disruption of the zeolite crystal structure with a subsequent formation of a multilayered particle of a spherical shape was shown to occur upon crashing. The center is a zeolite nucleus with a spatially periodic structural elements. The intermediate layers possess a deformed structure provided by the lattice disarrangement. The outer amorphous layer is a disordered agglomeration of structural units. The formation of disordered structure is determined by the presence of elements substituting silicon isomorphously in a zeolite and occurs due to the cleavage of silicon-oxygen-element bonds. The resistance of bonds against cleavage varies in the series as follows:

$$Fe(OSi)_4 < B(OSi)_4 < Al(OSi)_4 < Si(OSi)_4.$$

Zeolite milling was found to accelerate the dissolving of its particles, which proceeds in four stages due to the layer structure of the milled zeolite crystal. The effective activation energy of milled zeolite dissolving attained 19 kcal/mol.

ZSM-5 zeolite crystallization as well as the properties of produced crystals have been studied with respect to the properties of milled zeolite particle, which served as crystallization seeds.

The seed appears to promote essentially the process of zeolite formation. The period of crystal growth is reduced to higher extent than that of nuclei formation. The use of the seed allows to regulate the size of produced crystals from 1 to 8 micron without changing their shape and composition. The number of synthesized crystals per one seed particle goes through the maximum upon the increase of the seed milling duration.

The equation is suggested, which describes the kinetics of zeolite crystallization promoted by the seed. The effective activation energies of zeolite crystallization on both milled and not milled seeds are calculated. They are, respectively, 20 and 14 kcal/mol for the nuclei formation and 2-5 and 19 kcal/mol for the crystal growth.

The mechanism of zeolite crystallization on the milled seeds is proposed. A partial dissolving of layered seed particles with their successive splittering into several nuclei is assumed to occur during the nucleation process. Further crystal growth is determined by the rate of silicate oligomers supply from the solution. The rate of crystal growth appears to be independent of the oligomer formation rate.

SYNTHESIS OF ε-CAPROLACTAM FROM CYCLOHEXANONE OXIME ON ZEOLITE

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1st Europ. Congr. Catal., "EUROCAT",
Montpellier, France, 1993, Book of Abstracts,
v.1, p. 80

Various types of solid acids, including zeolites, are considered nowadays as the catalysts for the vapor-phase Beckmann rearrangement of cyclohexanone oxime into ε-caprolactam to improve the conventional liquid-phase process. The weak acid sites of zeolites are assumed to take part in cyclohexanone oxime conversion to ε-caprolactam. Here, we tend to elucidate the nature of these sites with the analysis of catalytic activity and selectivity of various zeolites and some model catalysts.

The rearrangement of cyclohexanone oxime was performed in the inert gas flow at 350°C under atmospheric pressure. The activity of zeolites was found to correlate with acid properties of their external surface. Strong Brönsted sites protonating pyridine and ammonia are not effecient in the desired product formation. The increase of secondary reaction rates is faster than that of ε-caprolactam generation upon the increase of OH group concentration on the external surface.

The catalytic properties of Na- and F-modified silica possessing only weak acid Si-OH groups was studied for the comparison. It was established that even the small variations in acidity affect the rate and selectivity of reaction and the maximum intensity is accounted for the acid sites with PA ≟ 1410 kJ/mol.

IR spectra data of adsorbed cyclohexanone show the rearrangement starting with the proton attack on the reagent C=N bond. The nature of intermediates thus produced is responsible for further reaction routes.

CONVERSION OF INTERMEDIATE COMPOUNDS OBTAINED UPON ALKYLATION OF ANILINE WITH METHANOL ON HNaY

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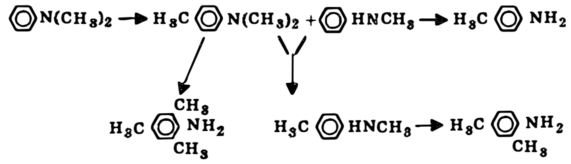
Submitted for publication Int.Symp. Zeolites and Microoporous Cryst., Japan 1993

According to the popular scheme of aniline alkylation by methanol yielding N,C-products on zeolites, orto-toluidine (OT), para-toluidine (PT) and N,N-dimethylaniline (DMA) are the intermediates in C-alkylated product generation.

Here we have studied the conversion and alkylation of these intermediates by methanol on HNaY zeolite to work out in details in the reaction scheme.

The study of OT, PT and DMA conversions gives the following series of activities: DMA > PT > OT. The schemes of OT and PT conversions seem to be similar.

The dependence of reaction products selectivity on DMA conversion suggests the following reaction scheme:



Here, the formation of C-alkylated products occurs via a consecutive conversion of DMA to N-alkylated products with the following isomerization.

Upon PT alkylation by methanol, the activity increases proportionally to alcohol concentration. The selectivities of C-alkylated products (2,4-xylidine and mesidine) pass through their maximum values. When methanol quantity is larger than that of PT, the concentration of N-alkylated products increases.

DMA alkylated with methanol exhibits the increase of selectivity towards mesidine only. However, the increase is not considerable enough in comparison to that in PT alkylation, since the concentration of N-alkylated products is higher in the former case. Concentrations of PT and 2,4-xylidine decrease with the growth of alcohol content in the reaction mixture. Moreover, the alkylation of the latter takes place only after a considerable decrease of PT concentration.

CATALYSTS AND PROCESS FOR ENVIRONMENTALLY SAFE COMBUSTION OF LIQUID FUELS AND TREATMENT OF INDUSTRIAL ORGANIC WASTES

Z.R.Ismagilov, M.A.Kerzhentsev, R.A.Shkrabina, O.A.Kirichenko V.A.Sazonov

CHEMRAWN VIII Chemistry and Sustainable Development - Towards a Clean Environmental, Zero Waste and Highest Energy Efficiency, World Conf., Moscow, 1992, Book of Abstracts, p.23

A process for ecologically favourable catalytic combustion of liquid fuels and purificaton of organic wastes and new catalysts for the process have been developed. The process is accomplished in a fluidized bed of a spherical granulated catalyst in the specially designed reactor referred to as Catalytic Heat Generator (CHG). The method is applied to the combustion of low-calorific fuels and to processing of organic-containing sewages. Heat generated by the combustion can be recovered for technological needs. Efficient and strong catalysts have been developed for the process. A specially designed spherical alumina with high mechanical strength is used as a support. Iron oxide or the mixture of oxides of chromium, magnesium and copper serve as the active components. The catalysts are produced in semi-commercial batches (up to 20 t per a year). Full scale tests have confirmed essential benefits of the developed process if compared to the conventional flame incineration.

MONOLITH SUPPORTS AND HONEYCOMB CATALYSTS FOR PURIFICATION OF EXHAUST GASES FROM INDUSTRY

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CHEMRAWN VIII Chemistry and Sustainable Development - Towards a Clean Environmental, Zero Waste and Highest Energy Efficiency, World Conf., Moscow 1992, Book of Abstracts, p.17.

New monolith supports and honeycomb catalysts for purification of industrial gaseous wastes were developed and studied. Supports with the unique properties: high surface area, mechanical strength and thermostability were designed on the basis of alumina, silica and titanium oxide. The catalysts containing oxides and noble metals were prepared via impregnation and extrusion. Comprehensive physico-chemical studies of the catalysts were carried out.

Interacion of an active component and a support and behaviour of catalysts for environmental protection are discussed.

ECOLOGICALLY FAVOURABLE TECHNOLOGY FOR PRODUCTION OF GRANULATED ALUMINA USING CATALYTIC HEAT GENERATOR

Z.R.Ismagilov, R.A.Shkrabina, N.A.Koryabkina, A.Ya.Bakaev, Yu.K.Vorobiev, M.N.Shepeleva

CHEMRAWN VIII Chemistry and Sustainable Development - Towards a Clean Environmental, Zero Waste and Highest Energy Efficiency, World Conf., Moscow 1992, Book of Abstracts, p.15

An innovative wasteless, sewage-free technology for the production of granulated alumina (as an adsorbent, support or catalyst component) is based on the processing of highly active amorphous alumina which is produced in a reactor of fundamentally new type - catalytic heat generator (CHG) via thermal decomposition of gibbsite. Unique properties of the product obtained allow its transformation into pseudoboehmite. The new technology, unlike conventional ones, involves no steps of gibbsite dissolving and precipitation of aluminium hydroxide of pseudoboehmite structure. A twenty-fold decrease of the reagent amounts, a three-fold reduction of liquid and gaseous wastes, diminuation of total metal weight and dimensions of individual units of the process equipment are achieved with the technology. The granulated α-Al_2O_3 can be produced with various shapes and sizes of granules (spheres of 0.4-10 mm in size, cylinders, rings), parameters of pore structure, 100-300 m^2/g surface area, high mechanical strength.

DEVELOPMENT OF NEW GRANULATED SUPPORTED CATALYSTS FOR PURIFICATION OF AUTOMOTIVE EXHAUST GASES

Z.R.Ismagilov, V.Yu.Aleksandrov, R.A.Shkrabina, G.V.Chernykh, I.P.Andrievskaya

CHEMRAWN VIII Chemistry and Sustainable Development - Towards a Clean Environmental, Zero Waste and Highest Energy Efficiency, World Conf., Moscow 1992, Book of Abstracts, p.13

A new efficient catalyst for neutralization of exhaust gases from internal combustion engines has been developed. A specially designed ring shaped alumina was employed as a support for the catalyst. High mechanical strength and thermostability were demonstrated to characterize the support. An active component (Ce, Pd and Pt in a certain ratio) was loaded via incipient wetness impregnation technique. The proposed impregnation procedure provided an optimum shell-type distribution of noble metals within a 200-300 micron thickness layer. A pilot batch (1 ton) of catalyst was produced. The catalyst was tested in a 1 year run at 10 passenger buses of a local transport company. Average conversions of toxic components were observed to be 80% for CO and 70% (overall) for hydrocarbons. The new catalyst was found to be superior by all parameters to the commercial catalyst ShPAK-0.5.

DIRECT SELECTIVE OXIDATION OF HYDROGEN SULFIDE: CATALYST AND INNOVATIVE PROCESS FOR ENVIRONMENTAL PROTECTION

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CHEMRAWN VIII Chemistry and Sustainable Development - Towards a Clean Environmental, Zero Waste and Highest Energy Efficiency, World Conf., Moscow 1992, Book of Abstracts, p.19
React. Kinet. Cat. Lett., 48, 1, (1993) 55-63

Oxides of Mn, Co, Fe, Cr and V supported on highly strong spherical alumina (γ-, α-, $(\gamma+\chi)$-Al_2O_3 were investigated in the reaction $nH_2S + n/2\ O_2 \rightarrow S_n + nH_2O$ at 423-573 K using the stoichiometric mixture (20% H_2S + 10% O_2). Their catalytic activities affected by the concentration of supported element, modification of the support and reaction temperature were studied. The activities at T> 523 K were shown to vary in the series: Co-O > V-O > Cr-O = Fe-O > Mn-O > γ-Al_2O_3. A significant dependence of activity on the content of the active component was revealed for Co-containing catalysts.

Pilot tests of the catalysts for direct selective oxidation of hydrogen sulfide were shown to provide a high degree of gas purification (conversion of H_2S was ca.99%) at the selectivity of 97-99%.

HOMOGENEOUS-HETEROGENEOUS REACTIONS INVOLVING FREE RADICALS IN PROCESSES OF COMPLETE CATALYTIC OXIDATION. STUDY OF ELEMENTARY REACTIONS OF FREE RADICALS FORMED ON THE OXIDE AND PLATINUM CONTAINING CATALYSTS

Z.R. Ismagilov, S.N. Pak, V.K. Yermolaev

J. Catal., 136 (1992) 197-201;
Catal. Lett., 15 (1992) 353-362

Comprehensive studies demonstrated the oxidative reactions of organics have demonstrated them to proceed according to the homogeneous-heterogeneous mechanism. The mechanism implies surface-generated free radicals to desorb into the gas phase before their interaction with the surface and to take part in the gas phase reactions. The studies of detailed mechanisms of both radical formation and desorption attract a growing interest. Common dependencies of radical generation during n-alcohol and oxygen interaction over some oxide catalysts have been studied with the matrix isolation ESR technique.

EFFECT OF INTERACTION OF ACTIVE COMPONENTS WITH A SUPPORT ON SINTERING AND STABILITY OF OXIDE CATALYSTS SUPPORTED ON ALUMINA

O.A.Kirichenko, M.P.Vorobieeva,V.A.Ushakov

Proc. 10th Int.Congr.Catal., Budapest, Hungary, 1992, v.75, p.2035-2038

Phase composition, sintering kinetics and mechanical strength of some alumina supports and catalysts supported thereon were studied. The sintering kinetics of Zn-Cr, Mg-Cr, Cu-Cr oxide catalysts supported on γ, χ- $(\gamma+\chi)$-Al_2O_3 were found to obey the same equation as that obtained for alumina powders and supports provided that BET area is replaced by the surface area of a solid volume unit. The interaction of a support with the active species results in the formation of solid solutions combining the structures of support and spinel. This changes the catalyst mechanical strength and constants of the sintering kinetic equation. The formation of stable solid solutions based on the structures of γ- and χ-Al_2O_3 enhances the thermal stability of catalyst as compared to that of support.

OPTIMIZATION OF TEMPERATURE REGIMES FOR COMBUSTION OF LIQUID WASTES IN CATALYTIC HEAT GENERATORS

O.A.Kirichenko, M.A.Kerzhentsev, T.L.Susharina

Khim.Tekhnol., to be published

The influence of granule preheating temperature on the thermal shock resistance of spherical catalysts for fuel combustion was studied. New procedure was used to characterize the thermal shock resistance: the catalyst strength against fatigue was measured before and after the heating-cooling cycle. This type of mechanical strength was found not to change upon preheating at the temperatures below 300°C and to decrease at higher temperatures. Pilot-scale testing showed the reduction of waste introduction zone temperature to 190-300°C preventing the total disintegration of granules under exploitation and to diminish NO_x emission.

INTERACTION OF γ-Al_2O_3 AND SUPPORTED COMPONENTS DURING SYNTHESIS OF Al-Fe-O CATALYSTS

O.A. Kirichenko, V.A. Ushakov, V.A.Poluboyarov

Sib. Khim. Zh., 3 (1993) 127-131

Al-Fe-O catalysts were studied with XRD and electron diffuse reflectance spectroscopy. The catalysts were prepared by impregnation of γ-Al_2O_3 with solutions of ferric oxalate complexes and then calcined at 620-1270 K. Variations of intensities in XRD patterns which are accounted for by loading cationic positions in γ-Al_2O_3 tell for the presence of solid solutions in all the samples studied. Associates are also formed where the environment of Fe^{3+} is quite different from that in iron oxides. These are only the samples with Fe content exceeding 5 wt % (Fe_2O_3 at 620 K and α-Fe_2O_3 at 970 K) containing the iron oxide phase. The formation of solid solutions results in a decrease of the phase transition temperatures

$$\gamma \rightarrow \delta \rightarrow \Theta \rightarrow \alpha\text{-}Al_2O_3.$$

The interaction of impregnating solutions with γ-Al_2O_3 occurs through the adsorption of Fe^{3+} oxalate complexes, their hydrolysis is accompanied by precipitation of polynuclear compounds and Al^{3+} removal of (in amounts close to the Fe^{3+} content) into the impregnating solution. The interaction makes isolated Fe^{3+} ions available in the solution and Fe-Al-O solid solutions are formed at 620-820 K. Thus, phase composition and catalytic properties of the supported aluminoferric oxide catalysts can be significantly changed by the control over pH and concentration of impregnating solutions.

ONE-STAGE PROCESS FOR PURIFICATION OF HYDROGEN SULFIDE CONTAINING GASES AT OIL AND GAS PROCESSING PLANTS

Z.R. Ismagilov, N.M. Dobrynkin, S.R.Khairulin

Oil & Gas J., March 7 (1994) 81-82
Zh. Ross. Khim. Ob-va, 37, 4 (1993) 48-54

A one-stage technology for the purification of H_2S-containing gas flows was developed. With the process H_2S-containing gas and oxygen (or oxygen-containing gas mixture) in a ratio providing the following reaction stoichiometry:

$$H_2S + 1/2O_2 \longrightarrow 1/n\ S_n + H_2O + Q$$

are simultaneously fed into the fluidized catalyst bed with highly strong spherical granules. Excess heat generated by the exothermic reaction is utilized using heat exchangers which are immersed into the fluidized bed.

The technology avoids the drawbacks of conventional processes including the concentration limitations with respect to hydrogen sulfide.

The process was performed at the pilot scale and tested in a three months run. Various catalysts were studied; two catalysts, the one chemically similar to $MgCr_2O_4$ supported on γ-alumina and R339, were found to be the most efficient.

The given process appears to be quite efficient under industrial conditions: it provides a one-stage processing of various gases with a high H_2S content. According to the experience accumulated during the pilot scale trials, the design of commercial installations for purification of acid gas, well gas testing units, for purification of associated gases of oil and gas processing plants and for sulfur production has been started.

STUDY OF STRUCTURAL AND MECHANICAL PROPERTIES OF GRANULATED ALUMINA SUPPORTS USING X-RAY MICROPROBES

Z.R.Ismagilov, R.A.Shkrabina, N.A.Koryabkina, J.A.Ovsyannikova

Seventh Int. Symposium on Relation Between Homog. and Heterog. Cat., Tokyo, Japan, 1992, Book of Abstracts, p.504-505

Defects surfaces of porous granulated supports (using alumina as an example) were examined by X-ray spectral microanalysis and the relationship between defects and the mechanical strength of spherical granules was determined. The mechanical strength of the granules depends significantly on their imperfections (micro cracks with a size of > 10^3 nm), which is determined quantitatively from the AlK_α intensity profile. The regularities found are also valid for complex (Mg/Al_2O_3) systems.

THE X-RAY DIFFRACTION METHOD OF THE QUANTITATIVE ANALYSIS OF THE MULTICOMPONENT ALUMINA SYSTEMS

R.A.Shkrabina, E.M.Moroz, T.D.Kambarova

Fourteenth European Crystallographic Meeting, Enschede, the Netherlands, 1992, Book of Abstracts, p.117

The present work deals with the development of the method of the quantitative analysis of the multi component alumina systems.

The method is based on plotting the graduation curves for mixture (mechanical) of standard forms of different hydroxides and oxides of aluminum. For the plotting of the curves of each system the ratio between the intensities of the closest analytical lines of two different phases were used. Using this ratio permits avoiding standartization of pressed powder density, mass of a powder sample etc.

The graduation curves are plotted as a function I /I = f(C), where I and I are the intensities of certain lines of different phases; C is the concentration (wt %) of one of the phases. If phases with regions of coherent dissipation (RCD) > 100 nm are analysed, the ratio of the corrected heights with background subtracted were used; for the systems with RCD 3–100 nm we measured the integral intensity.

X-Ray characteristics of samples were obtained from diffractograms, recorded by a DRON-1,5 apparatus, using CuK_α radiation mono chromated by a graphite monochromator.

The authors have plotted more then ten graduation curves for different mechanical mixtures of hydroxide and oxides of aluminum, permitting them to make qualitative analysis of some multi component systems.

THERMAL STABILITY OF La_2O_3-Al_2O_3 SYSTEM: X-RAY STUDY

Z.R.Ismagilov, N.A.Koryabkina, R.A.Shkrabina, V.A.Ushakov, E.M.Moroz

Appl. Catal., to be published

Thermostability of La/Al_2O_3 system was studied with X-ray diffraction. The procedure of La introduction was shown to influence significantly γ-alumina thermal stablity. The stabilizing effect of La was assumed to be provided by the formation of X-ray amorphous compound with the transient Al_2O_3 form. It is shown that there is an optimal quantity of La, when the phase conversions in the $La_2O_3 \cdot 11Al_2O_3$ system are inhibited. This optimal quantity depends on the initial aluminum oxide preparation as well as on the method of La cation introduction. γ-Al_2O_3 was shown to form at 1100°C. $La_2O_3 \cdot 11\ Al_2O_3$ forms at this temperature only. When $La_2O_3 \cdot 11Al_2O_3$ formation is completed, La stops to affect the system performance, and α-Al_2O_3 starts to form.

MONOLITH HONEYCOMB SUPPORTS AND CATALYSTS

G.B. Barannik, N.N. Sazonova

Proceedings 2nd Meeting,
Novosibirsk, October, 1992

The development of monolithic honeycomb catalysts was started in the Institute of Catalysis at the end of 1980 and their pilot scale production was organized at the Perm Plant of High Voltage Isolators in 1998.

In this collected volume the new results are presented on the preparation, study and application of monolithic honeycomb supports and catalysts in our country in the period after the First All-Union Conference. The results show the chosen direction of investigations to be perspective for the creation of the new generation of home monolithic supports and catalysts and new processes on their basis.

The collected volume is recommended to specialists in catalysis, chemical engineering and environmental protection.

NOVEL THERMOCATALYTIC METHODS FOR PROCESSING AND COMBUSTION OF SOLID WASTES

A.D. Simonov

Papers of REC-93, Switzerland 1993, 146-148

Here we present a novel thermocatalytic method for processing and combustion of solid wastes. The process is based on thermal oxidation of organic component in effluent residues in the fluidized catalyst bed. Carbon-containing solids, thus formed, have a well developed porous structure and provide good adsorption of dissolved toxic products upon waste purification.

The method provides:

- reduction of metal weight of apparatus and a 10-20-fold reduction of the overall expenses as compared to standard combustion methods;
- no heat-resistant materials for construction;
- process performance under autothermal regime at the wettness lower than 80%, with no additional fuel consumption;
- termination or drastic decrease of gas emissions contaminating the organic substances, carbon, nitrogen and sulphur oxides.

THERMOCATALYTIC PROCESSING OF SEDIMENTS AND PURIFICATION OF EFFLUENTS VIA ADSORPTION COAGULATION

A.D.Simonov, N.A.Yazykov, E.I. Yepifantseva, I.V. Wolf, Yu.M. Chernoberezhskii

Chemistry for Sustainable Development,
to be published

In is necessary to provide the optimal conditions for catalyst effect on a solid organic waste to make the catalytic combustion efficient. In many cases we can ahieve this by creating the surface for the catalyst contact with the solid waste, using a fluidized bed of disperse catalyst. In this case we obtain a good mass exchange at sufficiently low temperatures (400-700°C) and efficient interaction of solid organic particles with air, while the intermediate products, evolving due to this interaction, are burnt on the catalyst surface. Meanwhile, nitrogen, combined in the organic waste, is oxidized mainly to molecular nitrogen. Sulfur compounds do not evolve into the gas phase due to the low combustion temperature but remain combined in the mineral fraction of organic waste. With the flame combustion or that performed in the inert bed, the volatile components and CO are burnt in the bulk. Varying the period of particle stay in the catalyst bed by changing the bed height or fluidization rate, we can change the combustion degree, decrease the evolution of volatile components and increase the coke carbonization. The yield of solid product can attain 50-60% with respect to the sediment type. The product tecture investigation shows, that we can obtain adsorbents with high specific surface due to the low process temperature. In the inert bed, where combustion proceeds in the diffusion region, the particle temperature is significantly higher (800-1000°C). Due to this reason, micropores and mesopores burn out, thus decreasing the specific surfaces of products.

UNSTEADY SELECTIVE CATALYTIC REDUCTION OF NITROGEN OXIDES (REVERSE NOx PROCESS)

L.N.Bobrova, A.S.Noskov, Yu.Sh.Matros

Preprint of 8th In. Symp. "Large Chem.Plant.",
Antwerp., 1992

The REVERSE-NOx process and its application for the control over NOx in the waste gases after adsorption columns are presented. Decontamination of gases from nitrogen oxides is performed under unsteady state regimes: SCR reaction occurs in the catalyst bed placed between the layers of inert material. The latter serve as the heat regenerating exchangers under a periodic reverse of gas flow through the packed bed [1]. The REVERSE-NOx process permits to purify the gases autothermally without energy consumption at arbitrary temperature and at various content of nitrogen oxides. A long term operation of industrial plant (since 1989) with a capacity of 10000 m^3/h with the granular catalyst bed confirmed a high efficiency of the new way of gas purification from NOx. At the inlet gas temperature of 30-40 °C and without fuel consumption, the temperature in the catalyst bed attains 300-400 °C. The slip of nitrogen oxides after purification does not exceed 50-80 mg/m^3 while the inlet concentrations is 2-14 g/m^3.

REFERENCES

1. International claim PCT/SU90/00212. The way of gas purification from nitrogen oxides. Yu.Sh.Matros, A.S.Noskov, L.N.Bobrova, E.M.Slavinskkaya.

REVERSE PROCESS FOR NO_X-OFF GASE DECONTAMINATION

A.S.Noskov, L.N.Bobrova, Yu.Sh.Matros

Catal. Today., 17 (1993) 293-300

Reverse process of NO_x selective catalytic reduction (REVERSE-NO_x) consists in the periodic flow reversal of low temperature gas in a fixed bed. The results of process mathematical simulation and experimental testings are discussed. A mathematical model developed accounts for the general parameters of packed bed dynamics and peculiarities of NO_x reduction involving two competitive reactions, NH_3 adsorption and possible formation of ammonia salts. Process performance in various flow-sheets is simulated. Experiments are carried out in pilot and large scale reactors charged with granular and honeycomb catalysts. Reverse process as an energy-saving purification technique has been proved to be particularly efficient for gases characterized by a great fluctuation of inlet NO_x concentration.

STATES MULTIPLICITY IN CATALYTIC REACTOR OPERATED UNDER PERIODIC REVERSE OF THE GAS FLOW MIXTURE.

Yu.V.Ivanov, A.S.Noskov, Yu.Sh.Matros and G.A.Bunimovich.

Teor. Osnovy Khim. Tekhn., 26, 2 (1992) 228-235

Theoretical investigation based on the mathematical model of a catalytic reactor with two parallel exothermal first-order reactions pointed out the multiplicity of regimes provided by the frequent periodic change of the gas mixture filtering direction. The influence of various technological parameters on the charcteristics of a cyclic regime and the change of the regime under multiplicity conditions were studied.

THE INFLUENCE OF VANADIUM CATALYST DYNAMIC PROPERTIES ON THE REVERESE-FLOW SULFUR DIOXIDE OXIDATION PERFORMANCE

G.A.Bunimovich, N.V.Vernikovskaya, V.O.Strots, Yu.Sh.Matros, B.S.Balzhinimaev.

Preprint of Boreskov Institute of Catalysis,
Novosibirsk, 1992, p.51

We have used dynamic kinetic model to study the effect of the elementary reaction steps at SO_2 oxidation in the melt under the periodic gas flow reverse. The possible reasons for discrepancies between the experiment and the data calculated via the steady-state kinetic equation were defined.

PERIODICALLY FORCED SO_2 OXIDATION IN CSTR

V.O.Strots, Yu.Sh.Matros and G.A.Bunimovich.

Chem. Eng. Sci., 47, 9-11 (1992) 2701-2706.

We have used the dynamic kinetic model to simulate the forced periodic operation of CSTR upon SO_2 to SO_3 oxidation. We have revealed a resonance at sinchronous oscillations of SO_2 and O_2 feed concentrations. Note, that a linear system was considered. The reason for such a resonance is a super imposal of dissolving desorption of the reaction mixture components and catalytic steps. The analysis of such a behavior is presented, allowing to build a forcing mode providing the over-equilibrium conversion.

INFLUENCE OF SULPHUR CONDENSATION AND EVAPORATION ON THE CLAUS CATALYST ACTIVITY

A.N. Zagoruiko, V.V. Mokrinskii, V.I.Marshneva, Yu.Sh. Matros

Kinet. Katal., 34 (1993) 1049-1050

Experimental results have shown that during the condensation of sulphur vapors on the catalyst surface the Claus reaction rate in the kinetic region is a linear function of the degree of catalyst pore filling by liquid sulphur.

MATHEMATICAL MODELING OF THE REVERSE-PROCESS FOR MULTISTEP COMPLEX REACTIONS

A.N.Zagoruiko, Yu.Sh.Matros, V.R.Kumar*, B.D.Kulkarni* (National Chemical Laboratory, Pune, India)

Chem. Eng. Sci., 47, 1992, p.4315-4321.

Forced cyclic regimes in the fixed bed reactor undergoing periodic reverses of the gas flow direction for a complex system of three exothermal reaction ($A+B \rightarrow S+D$, $A+B \rightarrow E+D$, $A+E \Leftrightarrow S+D$) were theoretically investigated by means of mathematical modeling.

Analysis of stabilized cyclic regimes showed the possibility to obtain a higher output of aim product S than in conventional reactor.

PECULIARITIES OF FAST HEAT WAVE PROPAGATION IN A CATALYST FIXED BED

A.P.Gerasev, N.A.Chumakova, Yu.Sh.Matros, O.V.Kiselev

Teor. Osnovy Khim. Tekhnol., 27 (1993) 165-172
IV Int. Sem. on Flame Structure, Novosibirsk, 1992. Book of Abstracts, p.145-146.

Unsteady-state processes in the catalyst fixed bed with the quasi-homogeneous model, when a single first-order reaction proceeds, were analyzed. In addition to the well-known slow heat waves, the fast heat waves (or the first type travelling waves) were found to propogate in a sufficiently extensive bed. We have elucidated the factors initiating such waves and the effect of various parameters (kinetic and heat) on their behavior.

FCT METHOD USED TO STUDY THE AUTOSOLITONS STRUCTURE IN HETEROGENEOUS MEDIUM UPON CHEMICAL REACTIONS

V.N.Snytnikov, N.A.Chumakova, N.V.Vernikovskaya

Vychislit. Tekhnologia, Novosibirsk, 2, 4 (1993) 169-176.

The basic features of autosolitons are analyzed for the travelling waves in a dissipative heterogeneous medium with chemical reactions proceeding. The wave velocities appear to fit a limited continuous spectrum. The lower boundary is determined by the bifurcation of the singular point corresponding to the low temperature. The upper spectrum boundary is determined by the total energy emission due to the chemical reaction. Wave solution properties were studied with methods of differential equations theory and numerical FCT method.

STRUCTURES OF AUTOSOLITONS IN HETEROGENEOUS MEDIA

V.N.Snytnikov, N.A.Chumakova, N.V.Vernikovskaya

Proc. NATO ASI on "Unsteady Combustion", Portugal, 1993, p.7

Numerical code for calculating the autosoliton dynamics in the dissipating heterogeneous medium affected by current chemical reactions is suggested. The basic features of automodel solutions, which can be correctly described by numerical model, are analyzed.

Computer simulations of catalytic reactors, operating when the heat fronts (autosolitons) form and propagate, are specified by the solutions of unsteady-state equations for heat- and mass transfer in the multi-phase medium accompanied by the chemical conversion of materials. Studying such physico-chemical systems, we can use the schemes of splitting with regard to spatial variables and processes under study, since they allow to evaluate a large amount of theoretical assumptions without substantial changes of numerical code. A splitting scheme and fluid compensation method are considered as an alternative for calculating the convective transfer in autowave structures.

INDUSTRIAL PLANT FOR UNSTEADY-STATE PURIFICATION OF FLUE GASES FROM ACRYLONITRILE AND CYANIC ACID PRODUCTION

G.V. Vanin, A.S. Noskov, G.Ya. Popova, T.V. Andrushkevich, Yu.Sh. Matros

Catal. Today, 17 (1993) 251-260

The results of research, development and operation of industrial plant for catalytic purification of flue gases from cyanic acid and acrylonitrile under unsteady-state conditions were carried out. The installation was put into operation.

THE IMPACT OF HETEROGENEOUS REACTION KINETICS ON THE PARAMETERS OF COMBUSTION IN A FIXED CATALYST BED

G.V. Vanin, A.S. Noskov, E.S. Borisova, Yu.Sh. Matros

Fiz. Gor. Vzryva, 3 (1993) 139-143

Analytical estimates and numerical calculations of the deep oxidation of organic impurities in a fixed catalyst bed under periodical reversals of filtered gases flows for the irreversible reactions of various order are discussed.

RATE OSCILLATIONS OF CO OXIDATION ON Pt: SIMULATION OF EVOLUTION DYNAMICS

V.I. Savchenko, A.N. Salanov, V.N. Bibin

Kinet. Katal., 34 (1993) 147-193

A model is considered, comparing two parts of the Pt(110) surface in the process of CO oxidation: an original (SN) part, where reaction proceeds in three stages and a modified (SM) part, where reaction proceeds in five-stages and involves two forms of adsorbed oxygen. We also assume beta-oxygen to form on the SM surface only (on Pt(110), defects, initially) its reaction with CO, and absorbed CO(ads). We also take into account diffusion of species between the SN and SM surfaces. Ration SN/SM is determined with respect to beta-oxygen concentration. The calculations describe the dynamics of autooscillation evolution: initial induction period, oscillation birth, increase of their period, birth of oscillations with a very long period (tens of minutes) and "packs" of impulses.

Department of Hydrocarbon Conversion, Omsk

ROLE OF METAL AND ELECTRON DEFICIENT PLATINUM IN POLYFUNCTIONAL MECHANISM OF REFORMING AND DEHYDROGENATION

A.S. Belyi, M.D. Smolikov, D.I. Kiryanov, N.M. Ostrovskii, Yu.K. Demanov, V.K. Duplyakin

Proc. Ist Russia-Japan Joint Symp. of Petroleum, Nature Gas and Petrochemistry, Ju.-Sakhalinsk, 1993, p.146; p.175-176

Here we develop the concepts on the role of electron-deficient platinum (Pt^{δ}) in catalysis of basic reforming processes. Pt^{δ} activity and selectivity appeared to be higher than those of dispersed metal platinum upon three main reactions of aromatic hydrocarbon formation (dehydrogenation of six-membered naphthenes, dehydroisomerization of five-membered naphthenes and dehydrocyclization of paraffin hydrocarbons).

The promoting effect of carbon and sulfur on Pt^{δ} activity in dehydrogenation was registered. Differences in paraffin aromatization mechanisms on zeolite and silica supported platinum and modified alumina are elucidated.

To realize the optimal potentials of Pt^{δ} for a particular reaction, the ligand surrounding of the central atom in the composition of the surface complex and support should be elucidated. Ligands responsible for a considerable change of catalytic properties were found. Development of these concepts allows to posit the ways for reforming catalyst improvement via design and application of catalyst systems which contain platinum ion surrounded by ligands optimal for a particular basic reforming reaction.

EFFECT OF ACTIVE COMPONENT MICRODISTRIBUTION ON THE CATALYTIC REACTION

N.M. Ostrovskii, T.P. Mitsulya, V.K. Duplyakin

Abst. Conf. Chem. Reactor-II, Kharkov 1992, p.81-85; submitted for publication to *Appl.Catal.*

The effect of a new property of supported catalysts - the distribution of the active component among pores with different size (microdistribution) on catalytic reactions was investigated. Microdistribution provides a significant influence on reactions accompanied by the reagent capillary condensation in small catalyst pores.

THEORETICAL FUNDAMENTALS OF CATALYSTS DEACTIVATION KINETICS

N.M. Ostrovskii

Abstr. Conf. "Kinetics-5", Ivanovo 1992, Russia; *Izv. Vuzov*, 7 (1993) 47-59

Equations of deactivation kinetics have been derived from the analysis of basic reaction mechanisms and deactivation stages. General equations for any linear and some nonlinear deactivation mechanisms were pioneerly obtained. The concept of "qualitative" deactivation accompanied by the formation of new active sites was posited. There exists a radical difference between deactivation corresponding to additive and nonadditive changes of active sites. The practical application is considered. The kinetic model of supported platinum deactivation upon its coking via the mechanism of compensated decay was established.

ALUMOPLATINUM CATALYSTS SYNTHESIS FROM Pt(O) CARBONYL

N.B. Shitova, P.E. Kolesov, M.D. Smolikov, A.S. Belyi, E.M. Moroz (Boreskov Inst. Catal., Novosibirsk)

to be submitted to *Kinet. Katal.*

A new synthesis of highly-dispersed (particles are 20 Å and smaller) and thermostable alumoplatinum catalysts was designed via Pt(O) carbonyl interaction with γ-Al_2O_3. As the radial distribution technique shows, a strong interaction between the $[Pt_3(CO)_6]^{2-}$ cluster frame (n=5,6) and alumina producing Pt-O or Pt-Al bonds provides a high thermostability of platinum deposited from its carbonyl.

CATALYTIC POLYMERIZATION OF ACETYLENE OVER PALLADIUM-TIN COMPLEXES

I.E. Kolosova, V.P. Talsi, N.B. Shitova, G.G.Savelieva, V.A. Likholobov (Boreskov Inst. Catal., Novosibirsk)

VMS, A, 35, 8 (193) 1231-1235

The relations between palladium-tin cluster structures and their catalytic properties upon ethylene polymerization have been established. Kinetic and structural data of palladium/tin/chloride complexes suggest that the most active are binuclear palladium clusters. The catalytic system stability evaluated from the polymer yield depends to a great extent on the nature of acetoligand in the SnX_3^- coordination sphere. Yield of polyacetylene formed in palladiumtinchloride system is 25 g per 1 g of Pd which corresponds to the best Latinzher catalyst based on the metals of VIII group. Substitution of Cl by Br in SnX_3^- provides a 3-fold increase of the catalyst stability and polyacetylene yield.

PECULIARITES OF POLYFUNCTIONAL ORGANIC COMPOUND CONVERSION ON THE MODIFIED ZEOLITE CATALYSTS

G.A. Urzhuntsev, V.K. Duplyakin, V.N. Romannikov (Boreskov Inst.Catal., Novosibirsk), S.A. Lange*, P.S. Chekryi* (VNIIOS, Moscow).

Khim. Prom-st, to be published

Methods for modification of zeolite acid sites were developed to obtain the higher yields of desired products of olefin hydration than those obtained over conventional Friedel-Krafts catalysts.

Modification of zeolite acid sites was devised to increase the yield of desired products in olefin hydration as compared to that obtained over conventional catalysts for hydration. The obtained catalysts provide a 85-95% olefin conversion.

The design of zeolite acid properties appeared to be efficient for producing more active catalysts for isoparaffin alkylation, direct amination and n-paraffin isomerization.

MECHANISM OF ZEOLITE CRYSTALIZATION WITH RESPECT TO SYNTHESIS STAGES

T.P. Sorokina, V.P. Doronin, L.Ya. Alt

Zeolite, to be published

^{27}Al and ^{29}Si NMR was used to study the structure of zeolite-phase precursors in intermicellar liquids and stable alumosilicate solutions. All types of aluminium atoms in tetrahedral coordination were detected in alumosilicate ions, thus allowing the correct assignment of lines observed in ^{27}Al NMR spectra. The structure of alumosilicate ions studied within a wide range of gel compositions was shown to depend on the type of the synthesized zeolite (A,X,Y-types).

CATALYST FOR LIGHT PARAFFIN AROMATIZATION ON THE BASIS OF Pt/L ZEOLITE

V.P. Doronin, V.A. Drozdov, A.M. Sergeev, M.D. Smolikov, T.V. Kireeva, T.P. Sorokina

J. Catal., to be published

To elucidate the location of active component over the outer surface of zeolite crystals and inside the pores, as well as the extent of metal plugging through the inner pores volume of zeolite crystals, a new method has been devised. The developed techniques have explicitly shown, that variations in the supporting of active component precursors provide considerable changes in the metal location and the extent of plugging the inner volume of zeolite crystals. Thus, the desired changes of catalytic properties of metal-zeolite catalysts in selective paraffin aromatization can be provided.

RADIAL ATOM DISTRIBUTION TECHNIQUE (RAD)

P.E. Kolosov, E.M. Moroz (Boreskov Inst.Catal., Novosibirsk)

Kinet. Katal. 33, 2 (1992) 435-442.

A new method of "scattering intensity separation" permits to obtain curves of radial atom distribution without monochromator on the scattered beam. The method used in a diffractometer with a coordinated detector saves time proportionally to the amount of simultaneously registered ports.

FORMULATION OF PRINCIPLES FOR FUEL OIL ADSORPTION DEASPHALTING

V.K. Duplyakin, V.P. Doronin, I.S. Ilchuk

The kinetic studies of the petroleum residues transfer in porous structures have culminated in evaluating (i) the significance of various factors for adsorption deasphalting; and (ii) effect of procedure parameters on the quality and yield of deasphaltizate. The basic decision with regard to the flow diagram, power- and stock-intensity of the process was posited.

The data obtained are the fundamentals of adsorption deasphalting of mazouts (ADM) providing the engineering modeling of a large scale pilot plant. Thus, new prospects of ADM application for the nontypical processing of heavy petrols hard for extraction, bituminous rocks and simultaneous petroleum and coal processing to motor fuels have been considered.

PHYSICOCHEMICAL FUNDAMENTALS FOR ENGINEERING OF CARBON MATERIALS

V.K. Duplyakin, O.N. Baklanova, V.V. Shim, G.V.Plaksin

Physicochemical principles have been developed for the production of plastic carbon composites - new construction materials - via extrusion and moulding from synthetic carbon. Pilot batches of extrudates of various shapes (pipe, cylinder, stars, three-leaves), plates and disks, as well as surface-controlled porous solids (wall thickness ca. 0.3 mm) were prepared. Thus, a new type of carbon material engineering has been created. The prospects for utilization of these materials are the following:

- supports of the catalysts for hydrodemetallization of petroleum residues, selective hydrogenation, etc.;
- adsorbents for industrial environmental safety;
- electrodes for electrochemical engineering and fuel elements;
- pharmaceutical sorbents (carbosorbents) for biological liquids purification from toxins.

HIGHLY-SELECTIVE CATALYSTS FOR PROPANE DEHYDROGENATION

I.B. Yarusov, E.V. Zatolokina, N.B. Shitova, A.S. Belyi, N.M. Ostrovskii

Catal. Today, 13 (1992) 655-658

A new highly-selective platinum-tin catalyst has been designed for propane dehydrogenation. The active site content was estimated. The ways to increase the catalyst stability and to improve its preparation procedure have been developed. Kinetic model of dehydrogenation has been derived.

A COMBINED HYDROFINING AND DEAROMATIZATION OF ENGINE FUELS

N.M. Ostrovskii, K.S. Gulyaev, A.N. Startsev (Boreskov Inst. Catal., Novosibirsk)

Abstr. Conf. "Kinetics.-5", Ivanovo, 1992, Russia,
Izv. Vuzov 7, (1993) 59-64

To obtain the combined process of hydrofining and dearomatization of engine fuels, the kinetics of hydrofining of benzene and aromatics in commercial kerosines on Ni-Mo and Ni-W sulphide catalysts have been studied. The unsteady-state catalyst performance was examined in detail. The reactor model was simulated. The mathematical modeling has explicitly demonstrated the possibility and efficiency of the unsteady-state process.

Advertisement Pages

INTERNATIONAL CENTRE FOR CATALYSTS CHARACTERIZATION AND TESTING:
TWO YEARS OF ACTIVITY

K.I.Zamaraev (Russia), J.M.Thomas (Great Britain) and J.H.Block (Germany)

Introduction

Catalysis is of key importance for the design of new technologies for chemical and petroleum industries. About 90% of chemical products are produced nowadays with the use of catalytic technologies. Modern studies of catalysis are carried out with the use of new sophisticated and very powerful instrumentation. They can be only done by specially trained personnel and are rather expensive. For rapid and reliable characterization of new catalysts internationally accepted methods for the control and certification of their properties are required.

Since 1971 the Coordination Centre for Development of New Industrial Catalysts and Improvement of Catalysts Used in Industry of member countries of the Council for the Mutual Economic Aid has been functioning at the Institute of Catalysis (Novosibirsk). By now the Centre has been transformed into the International Centre for Catalysts Characterization and Testing. The Centre characterizes and tests catalysts on the basis of internationally accepted standards, as well as develops new standards for this purposes. The Centre organizes and carries out projects upon request from various organizations of Russia and foreign countries, as well as joint bilateral and multilateral projects.

Objectives

The Centre provides facilities for comprehensive research in the area of basic and applied catalysis, orginizes and accomplished international projects in the field of catalysis.

Main Directions of Activity

The main directions of the Centre's activity are:

- comprehensive characterization and testing of various catalysts according to internationally accepted standards, including characterization of their chemical and phase composition (in particular, the composition of surface and subsurface layers), point and extended defects, structure of surface species, electronic state of surface atoms, surface area and porous structure, interaction between the active component and support, testing of catalysts activity, etc.;
- comprehensive study of particular commercial catalysts and processes with the aim to give recommendations concerning their improvement;
- carrying out joint studies with russian and foreign partners for development of new catalysts, processes and technologies, as well as for search of new catalytic systems;

- development of standardized equipment and methods for characterization and testing of catalysts, and certification of their physico-chemical and operational properties;
- development of quantum chemical methods for catalysts study together with a package of computational programmes, and the use of these methods and programmes for the interpretation of spectroscopic data;
- development of methods of mathematical modeling of catalytic reactors and processes together with a package of computational programmes;
- organization of training and studies for foreign specialists within the scope of the Centre's activity;
- advertising and representation of foreign companies at exhibitions held in Russia and other regions;
- arrangement of exhibitions, seminars and conferences.

Organization of activity

In its work, the Centre uses the powerful potential of the Institute of Catalysis of the Siberian Division of the Russian Academy of Sciences, which is the biggest in the world specialized institute working in this field. The Institute carries out fundamental and applied studies practically in all fields of catalysis: structural and mechanistic characterization at the molecular level of various catalysts and catalytic reactions, chemistry of catalysts preparation, kinetic studies of catalysis, mathematical modeling and engineering of catalytic reactors and processes, development and commercialization of new industrial catalysts and processes. Sophisticated instrumentation for *in situ* analytical control of catalyst state and reaction mixture composition, including instrumentation for adsorption, kinetic, structural and spectral studies is available at the Institute. All this allows to obtain within short time intervals unique combination of data about the structure of active centers, detailed reaction kinetics and mechanism, and to use these data for purposeful design of new catalysts and catalytic technologies.

At present the Centre carries out joint projects with Universities, Research institutes and industrial companies of the USA, Germany, Great Britain, Spain, Italy and India.

Dec. 31. 1990,
Oil & Gas Journal

Siberian catalyst research center works at world class level

Herman J. Lovink
Akzo Chemicals
International bv
Amersfoort, The Netherlands

The Soviet Union's Novosibirsk catalysis research and development center is one of the largest such facilities in the world. It is in the heart of Siberia on the Ob River some 2,000 miles east of Moscow.

The center's original charter was for fundamental research, but in the past 5 years the scientists there have been looking for practical uses for their findings.

The scientists, to name a few, are Profs. Zamaraev, Parmon, and Ione, and Dr. Startsev. They and their staffs are well known in their fields. They serve on the boards of several international journals.

The fact that Soviet Institutes are state-owned means that their results go to difficult-to-trace patents and journals. Perestroika means, however, that these results should also be commercially applied in competition with everyone else.

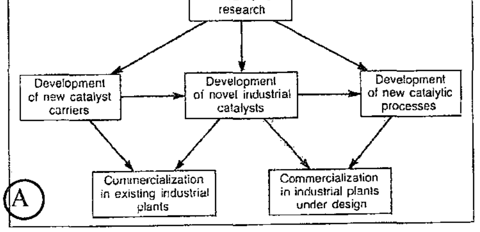
A new group, called "Katalyzator," is trying to commercialize the findings from several institutes, plants, and other laboratories. A whole spectrum of new processes and catalyst improvements in specialty chemicals is now being offered to the Soviet industry as well as to the West.

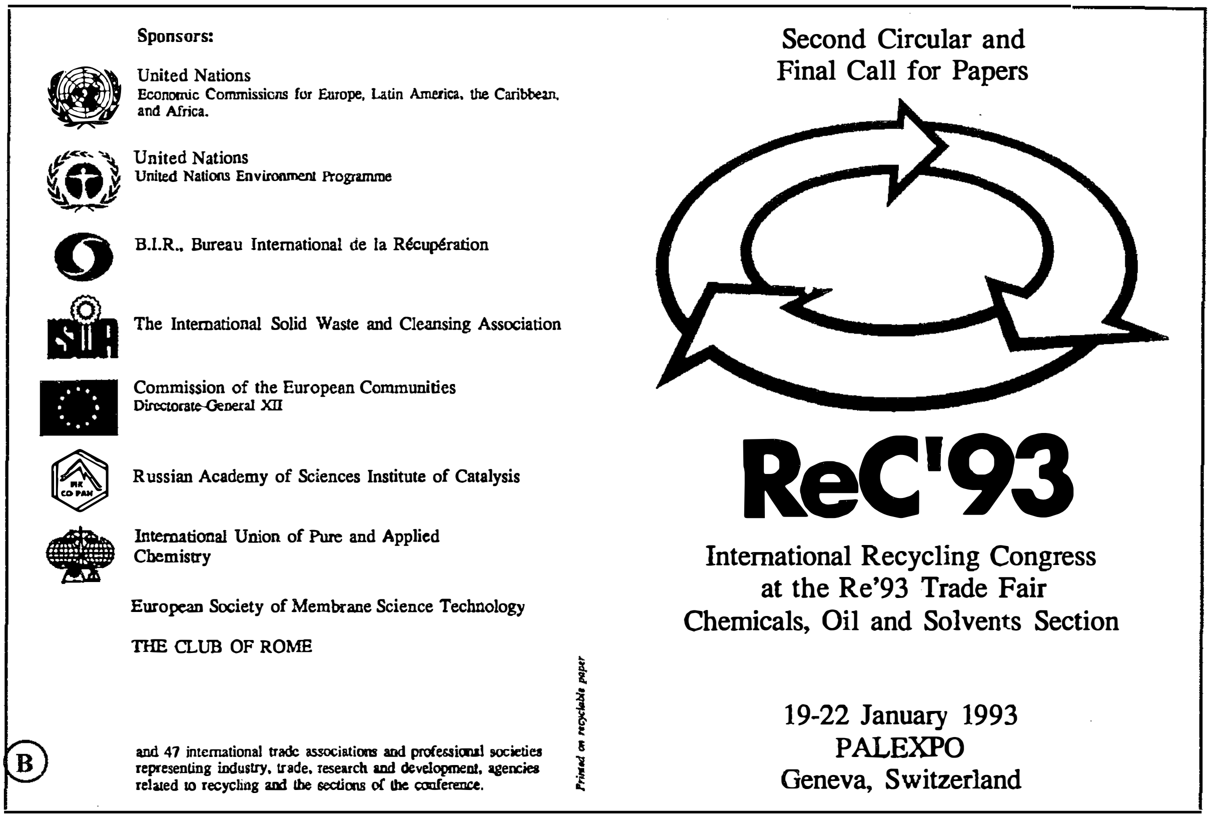
Young managers, more fluent in English, are pushing new developments towards commercialization. With time, we will see more coming out of this working group. Fig. 1 indicates its objectives.

Modern ways of marketing and the know how to do it are in keen demand in the Soviet Union. Opening up to the world outside is of prime importance for Novosibirsk because Siberia is still far away and rather isolated.

Russia is big and so are the number of Institutes and persons engaged in research and development work. Some 2,000 are working at Novosibirsk. Four hundred of them have academic degrees. At present the ratio between fundamental research and applied studies (pilot plant scale) there has been brought down to about 70 fundamental to 30 applied. This ratio in the West is

Catalyst, process development and commercialization strategy





Sponsors:

United Nations
Economic Commissions for Europe, Latin America, the Caribbean, and Africa.

United Nations
United Nations Environment Programme

B.I.R., Bureau International de la Récupération

The International Solid Waste and Cleansing Association

Commission of the European Communities
Directorate-General XII

Russian Academy of Sciences Institute of Catalysis

International Union of Pure and Applied Chemistry

European Society of Membrane Science Technology

THE CLUB OF ROME

and 47 international trade associations and professional societies representing industry, trade, research and development, agencies related to recycling and the sections of the conference.

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Fig.1A and 1B illustrates world recognition of the work carried at BIC.

International Advisory Board

The International Advisory Board of the Centre consist of the following specialists of the world renown.

1.	Zamaraev K.I.	Boreskov Institute of Catalysis, Russia	Chairman
2.	Bal'zhinimaev B.S.	Boreskov Instutute of Catalysis, Russia	
3.	Bell A.T.	University of California, USA	
4.	Block J.H.	Fritz-Haber-Institut, Germany	
5.	Gryaznov V.M.	Peoples Friendship University, Russia	
6.	Lovink H.J.	Akzo Chemical International, Netherlands	
7.	Moiseev I.I.	Kurnakov Institute of General and Inorganic Chemistry, Russia	
8.	Parmon V.N.	Boreskov Institute of Catalysis, Russia	

9.	Rao C.N.R.	Indian Institute of Science, India
10.	Somorjai G.A.	University of California, USA
11.	Tamaru K.	University of Tokyo, Japan
12.	Thomas J.M.	Royal Institution of Great Britain
13.	Van Santen R.A.	Eindhoven University, Netherlands
14.	Vedrine J.C.	Institute de Researches sur la Catalyse, France
15.	Zhidomirov G.M.	Boreskov Institute of Catalysis, Russia

Management

Scientific supervisor of the Centre is Academician Kirill I.Zamaraev, Director of the Boreskov Institute of Catalysis.

Executive Director of the Centre is Professor Bair S.Bal'zhinimaev.

First Results of Activity

As has already been mentioned, the Centre carries out joint projects with the Universities, Research Institutes and Companies of the USA, Great Britain, Germany, Spain, Italy and India.

In this section some results are presented that were obtained within the framework of those projects.

Project 1. Mechanistic Study of Butanols Dehydration on H-ZSM-5 Zeolites and Amorphous Aluminosilicate.

This is a joint project of the Boreskov Institute of Catalysis - BIC (Novosibirsk, Russia) and the Royal Institution of Great Britain - RI (London, United Kingdom). The project leaders are Academician K.I.Zamaraev and Prof.J.M.Thomas. The project is supported by the RAS, Siberian Branch of RAS and the Royal Society of Great Britain. It is carried out via exchange of scientists between BIC and RI. Experimental work is made mainly at BIC. The project was started before the creation of the Centre and now is a part of the Center's activity.

The results are published or prepared for publication in scientific journals (refs. 1a - k in the list of publications).

Figures 2 - 6 present some important experimental data obtained within this project. Figure 7 presents the proposed mechanism of butanols dehydration.

The obtained results are of general importance for acid-base catalysis on zeolites.

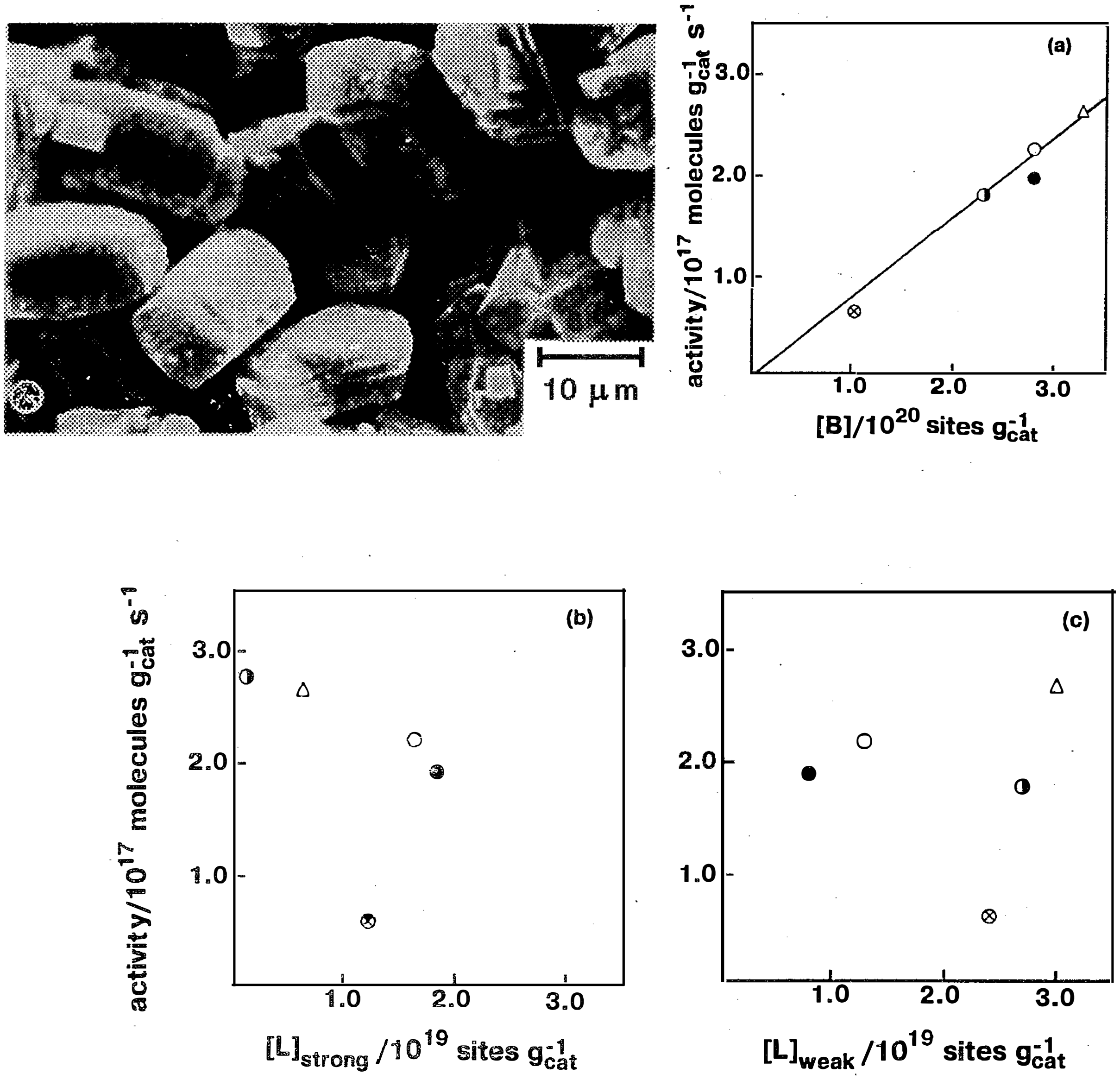

Fig.2. Scanning electron micrograph [1d] for H-ZSM-5 sample and relation [1b] between the activity of ZSM-5 and AAS in iso-butanol dehydration to butene at 397 K and the number of: (a) - Bronsted acid sited [B], (b) - strong Lewis acid sites $[L]_{Strong}$ and (c) - weak Lewis acid sites $[L]_{weak}$.

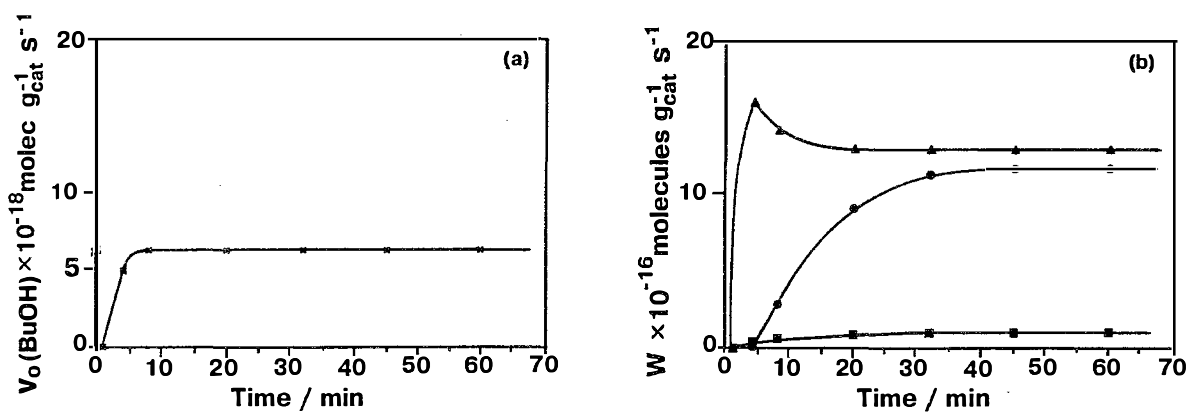

Fig.3. Kinetics of n-butanol consumption (a) and dehydration (b) in H-ZSM-5 (flow microreactor, 399K ▲ - water ● - di-n-butil ether, ■ - butene, x - unreacted n-butanol.

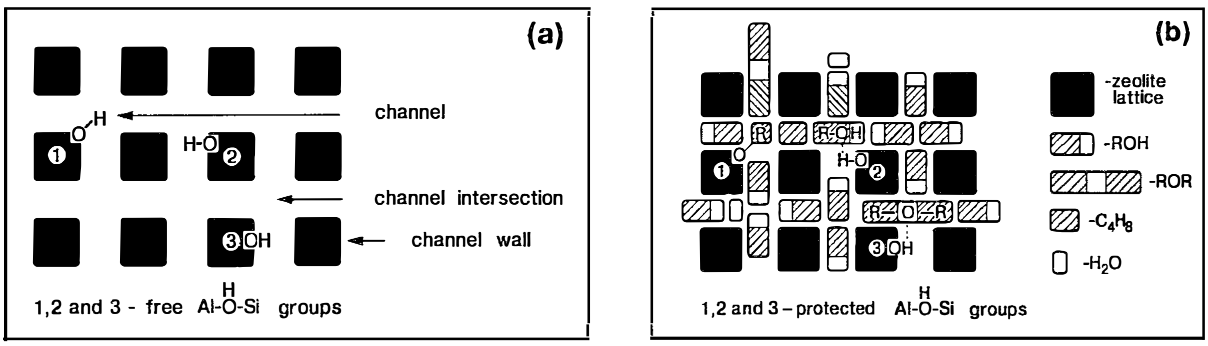

Fig.4. Schematic representation of H-ZSM-5 porous structure - (a) and of molecules of butanols, of reaction intermediates and of products in H-ZSM-5 pores - (b). Polar and non-polar fragments of the molecules are shown as white and dashed areas, respectively.

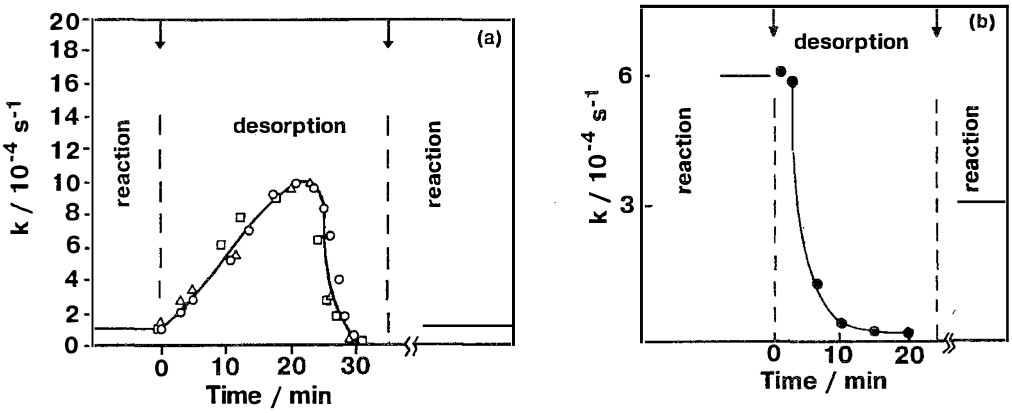

Fig.5. Rate constants of butanols dehydration into butene over H-ZSM-5 under steady state conditions and subsequent desorption of butene when the helium + alcohol flow is switched to the pure helium flow: (a) - sec-butanol at 369 K; (b) - iso-butanol at 397 K. The horizontal lines on the extreme right denote the reaction rate constants after returning to the previous helium + butanol flow.

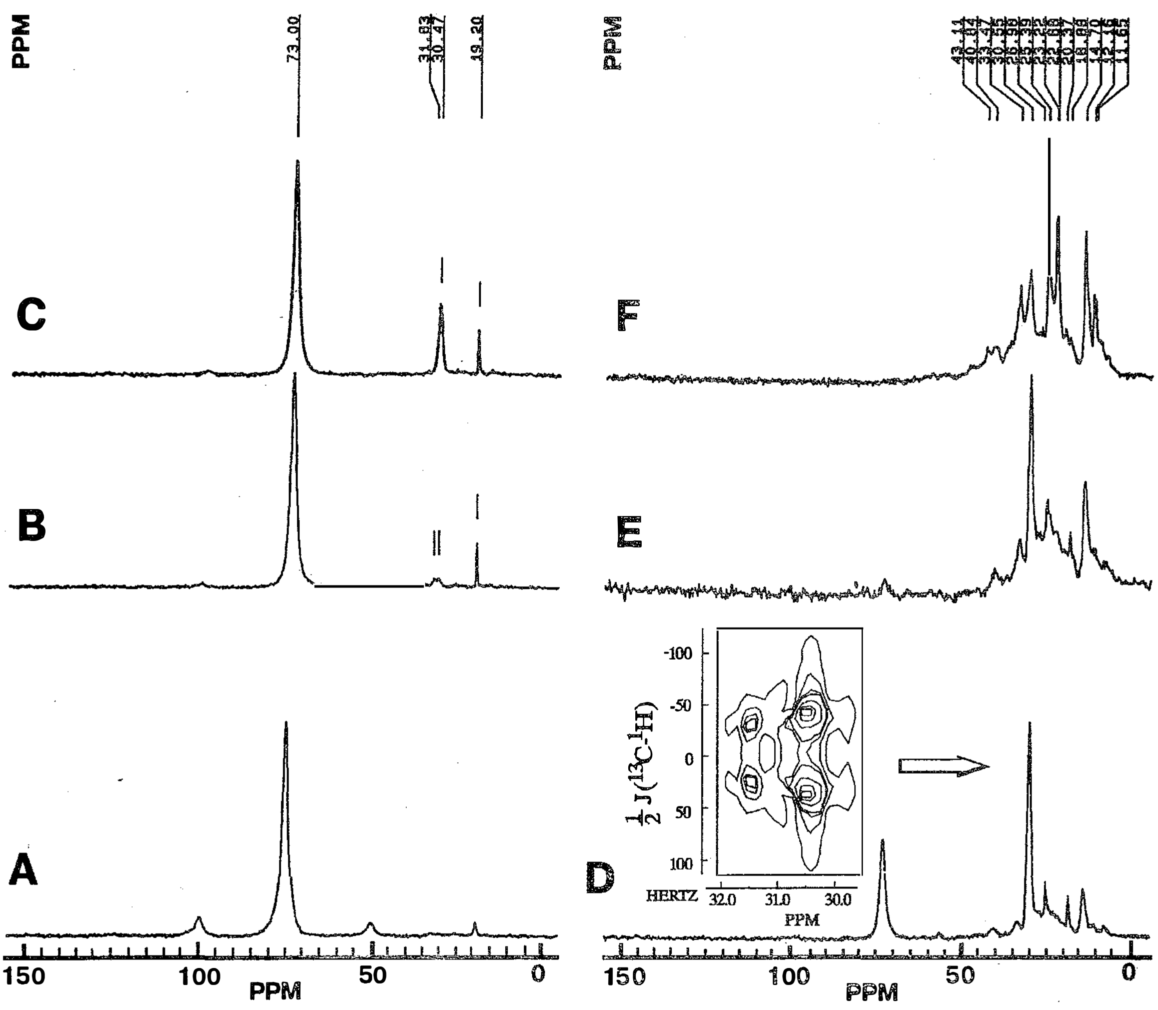

Fig. 6. Variation of the ^{13}C CP/MAS NMR spectrum of $(CH_3)_2CH^*CH_2OH$ adsorbed in H-ZSM-5 upon successive heating of the sample for a certain time at various T: (A) - after adsorption at 298 K, (B) - 70 min at 343 K, (C) - 40 min at 398 K, (D) - 60 min at 413 K (inserted is the contour plot of the 2D J-resolved ^{13}C MAS NMR spectrum in the vinicity of the signal at 30.5 ppm, (E) - 60 min at 423 K, (F) - 60 min at 448 K.

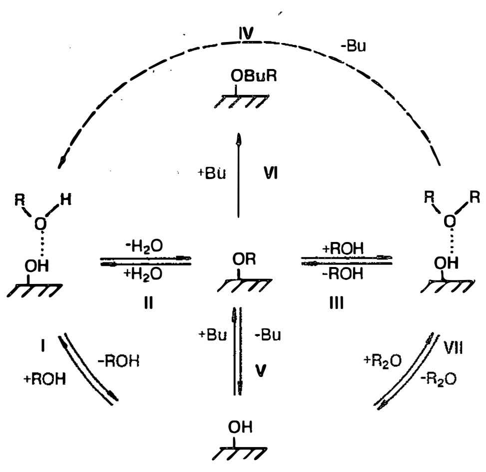

Fig. 7. Mechanism of butanols dehydration

Project 2. Oscillating Phenomena during CO and H_2 Oxidation on Platinum: Study at the Molecular Level.

This is a joint project of the Fritz Haber Institut - FHI (Berlin, Germany) and BIC (Novosibirsk, Russia). Project leaders are Prof J.H.Block (FHI) and Prof.V.V.Gorodetskii (BIC). The project is carried out via the exchange of scientists between FHI and BIC. The experiments are carried out mainly at FHI.

The results are published or prepared for publications in scientific jounals (refs.2a - d in the list of publications).

By way of example, Fig.8 presents the oscillating phenomena that were observed at the atomic scale resolution with the help of the Field ion microscopy (FIM).

This is the first example of observing oscillation behaviour of reaction dynamics with the atomic scale resolution.

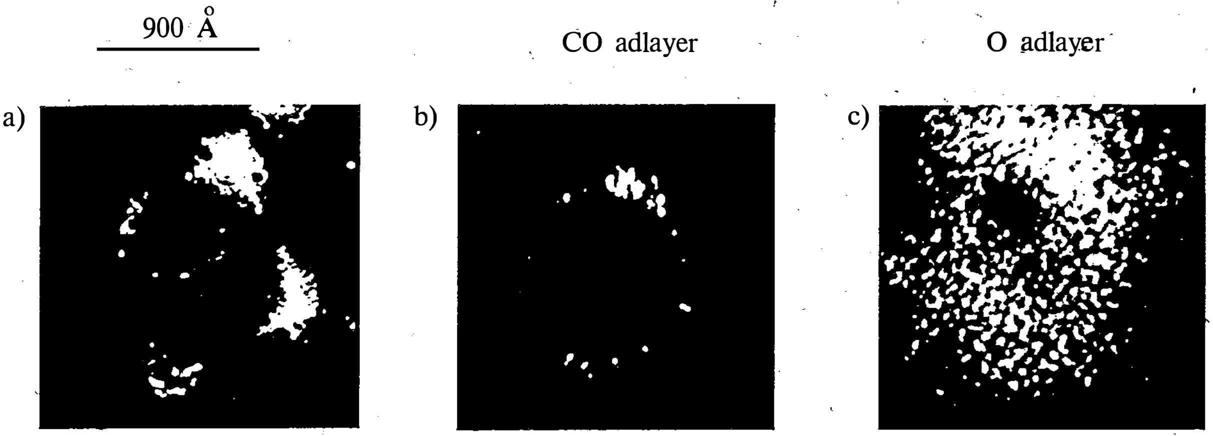

Fig.8. Field ion microscopic (FIM) images of the CO + CO_2 reaction oscillations on a (001) oriented Pt field emitter. (a) Clean surface, FIM He/Ne at 16 kV, $p_{He} = 3x10^{-4}$ mbar, $p_{Ne} = 8x10^{-6}$ mbar, T = 78 K, tip radius 850 A. (b) O_2^+-image, CO_{ad}-surface at 7.8 kV. $p_{O2} = 5x10^{-4}$mbar, $p_{CO} = 5x10^{-5}$ mbar, T = 300 K. (c) O_2^+-image, O_{ad}-surface after «titration reaction». Time of reaction 700 s at 300 K at 7.8 kV, $p_{O2} = 5x10^{-4}$ mbar, $p_{CO} = 10^{-7}$ mbar.

Project 3. Development of the Open-Shell Self-Consistent Field Theory for Highly Symmetric Systems.

This is a joint project of the BIC (Novosibirsk, Russia) and the Institute of the Computational Chemistry, University of Girona - ICCUG (Girona, Spain). Project leaders are Prof.B.N.Plakhutin (BIC) and Prof. R.Carbo (ICCUG).

A post-graduate student from the University of Girona J.M.Oliva is currently working at BIC under this project.

The paper «Open-shell Hartree-Fock energy for molecular structures of icosahedral symmetry» is prepared for publication [3].

The project will result in development of the theory that will allow to make much more reliable quantum-chemical calculations of the molecular structures with the open electronic shell which are important for catalysis.

Project 4. Basic research on the understanding of catalytic action of silver catalysts in ethylene epoxidation.

This is a joint project of the Boreskov Institute of Catalysis (Novosibirsk, Russia) and the Scientific Design Company (Little Ferry, USA).

Project leaders are Prof. Bal'zhinimaev B.S. (BIC) and Dr.Bhise V.S. (SDC).

Fig.9 illustrates some features of the elucidated reaction mechanism at the molecular scale

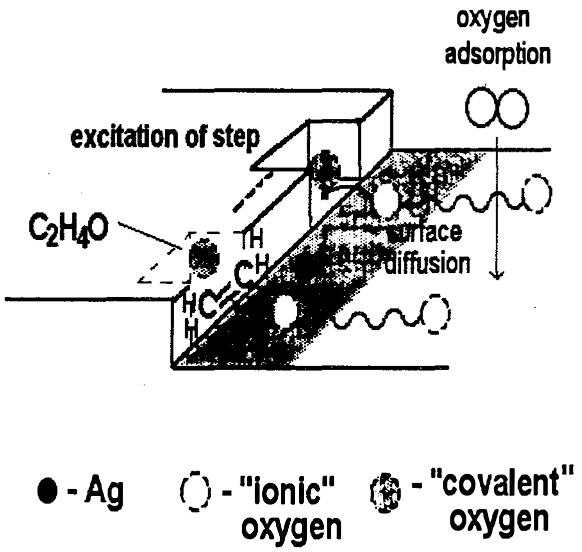

Fig.9. Mechanism of ethylene epoxidation on silver.

PLANS FOR FUTURE

In the future we plan:

1. To continue the ongoing projects with the Universities, Research Institutes and Companies from various countries.
2. To increase the number of joint projects with other Institutions from Russia.
3. To start in 1994 six new projects with the Institute des Researches sur la Catalyse (Lyon, France).
4. To organize in 1995 an International Workshop on Standard Procedures

and Reference Materials for Catalysts Characterization and Testing.

5. To organize regular annual meetings of the International Advisory Board of our Centre at Novosibirsk in 1994 and 1995.
6. To start selecting projects within BIC through the Centre in a competition with the proposals from others institutions from Russia and abroad.

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d. W.Drachsel, V.V.Gorodetskii and J.H.Block (prepared for publication)

3. B.N.Plakhutin, J.M.Oliva and R.Carbo (prepared for publication)

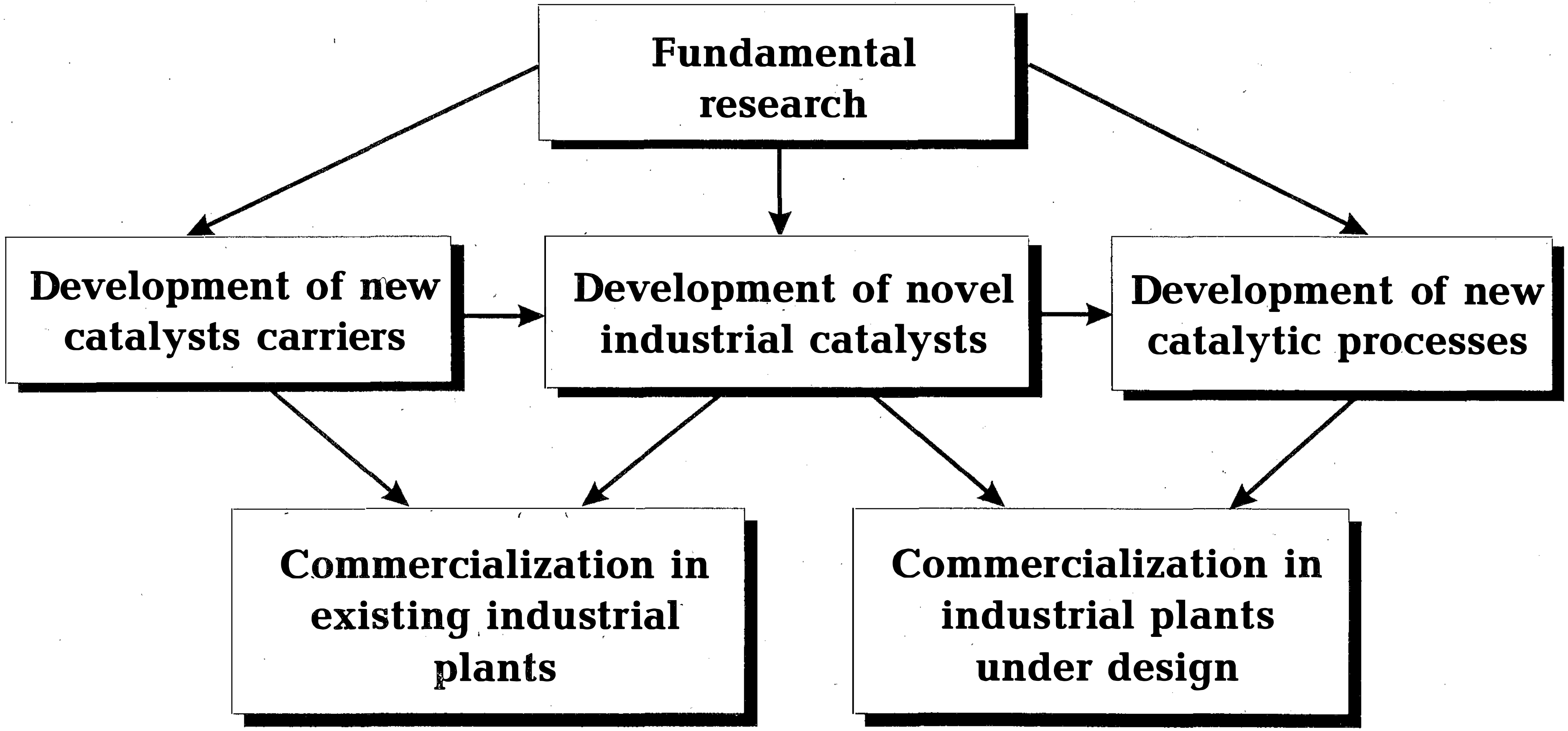
STRATEGY OF FUNDAMENTAL RESEARCH

Elucidation of nature of active species and of mechanism of key catalytic reactions on atomic-molecular level → Prediction of catalytic action

Studies of catalysts structure and mechanisms of their synthesis on atomic-molecular level → Scientific basis of technology of catalysts

Kinetic studies and mathematical modeling of catalytic processes → Development of new and optimization ofexisting catalytic processes

BORESKOV INSTITUTE OF CATALYSIS
STRATEGY OF ELABORATION AND COMERCIALIZATION OF NEW GENERATIONS OF INDUSTRIAL CATALYSTS AND CATALYTIC PROCESSES



Fundamental research

Development of new catalysts carriers

Development of novel industrial catalysts

Development of new catalytic processes

Commercialization in existing industrial plants

Commercialization in industrial plants under design

ORIGINAL BASIC TECHNOLOGIES DEVELOPED IN BORESKOV INSTITUTE OF CATALYSIS

1. **"REVERSE-process" (technologies based on catalytic processes in unsteady state mode).**
2. **"Catalytic Heat Generators" (technologies based on combustion in fluidized bed of catalysts).**
3. **One-stage removal of H_2S from hydrocarbon-containing gases, steam, etc.**
4. **Partial oxidation of aromatics by N_2O.**
5. **Partial oxidation of aromatics under condition of unsteady state of a catalyst.**
6. **Oxidation of methanol to formaldehyde in an adiabatic layer of a catalyst.**
7. **"SOZh" (removal of sulphur compounds through the Clauss process in water solutions).**
8. **Processes assisted by honeycomb and mat catalysts.**
9. **Synthesis of Vitamins K and E.**
10. **Synthesis of Xylidines.**

DEVELOPMENT OF NOVEL INDUSTRIAL CATALYSTS

1. A basic set of catalysts for basic inorganic synthesis
2. A basic set of catalysts for basic and fine organic synthesis
3. A basic set of catalysts for olefins polymerization
4. A basic set of catalysts for oil processing
5. A basic set of catalysts for detexication of flue gases and waste waters of industry, energetics, transport, etc.
6. A basic set of catalysts for treating technological gases

DEVELOPMENT OF NEW CATALYTIC CARRIERS

1. A systematic set of alumina carriers prepared in the frame of a single technology
2. Extremely mechanically stable carriers for fluidized and moving catalyst' beds.
3. A basic set of monolithic carriers (both ceramic and carboneous)
4. Carbon carriers of a high mechanical stability with regulated porous structure
5. Carriers of a high mechanical stability for enzymes immobilization

MAIN DIRECTIONS OF ACTIVITIES FOR SOLUTION OF ECOLOGICAL PROBLEMS AT BORESKOV INSTITUTE OF CATALYSIS

impurity	source of wastes	technologies by the Institute
SO_2	* exhaust gases of metallurgy and chemical industry * natural gases * oil refinery flue gases * exhaust gases of power stations	* REVERSE unsteady state processing of sulfur containing gases for sulfuric acid production**** * new catalysts for Clauss process** * REVERSE Clauss process** * catalytic cleaning of exhaust gases of Clauss process**
H_2S	* flue gases of metallurgy and chemical industry * natural gases * oil refinery flue gases * geothermal gases	* liquid-phase cleaning with production of commercial sulphur*** * new catalysts for Clauss process** * REVERSE Clauss process** * one-step cleaning in a fluidized bed of H_2S containing flue gases of wells** * one-step cleaning of geothermal gases** * one-step cleaning of oil-refinery gases**

Continued

impurity	source of wastes	technologies by the Institute
NO_x	* technological and industrial flue gases * exhaust gases of combustion engines * flue gases of power plants	* REVERSE unsteady-state cleaning*** * honeycomb and granular catalysts for NOx neutralizers (converters)*** * selective catalytic reduction with CO or CH_4*
CO	* technological and industrial flue gases * exhaust gases of combustion engines	* REVERSE unsteady-state cleaning*** * catalytic cleaning in a fluidized bed** * adsorptive-catalytic cleaning*** * honeycomb and granular catalysts for neutralizers**
organics	* technological and industrial flue gases * sewages * products of incomplete combustion of organic fuels	* REVERSE unsteady-state cleaning*** * catalytic cleaning in a fluidized bed** * cleaning with catalytic heat generators*** * cleaning with catalytic air heating mixers***

**** commercial scale
*** semicommerzial scale
** pilot instillations
* laboratory research

LEADING SCIENTISTS OF THE BORESKOV INSTITUTE OF CATALYSIS

ANDRUSHKEVICH Tamara Vitalievna, candidate of chemical sciences,* (1968), Head of the Laboratory of Selective Heterogeneous Oxidation.

T.V. Andrushkevich studies successfully the regulations of catalytic effect of oxide systems on the partial oxidation of organic compounds. The mechanism and kinetics of oxidation and ammoxidation of propylene, acrolein, Ni-containing heterocycles belong to the spheres of her activities. She has established the phase redox mechanism for selective reactions. Thus, the principles of catalyst selection for oxidation of acrolein to acrylic acid were developed on the assumption of the main role of the binding energy of surface intermediates. The role of acid-base and redox properties of the catalysts was recognized. T.V. Andrushkevich contributed considerably to the design of commercial catalysts for the two-stage oxidation of propylene to acrylic acid and for ammoxidation of propylene.

ANIKEEV Vladimir Il'ich, doctor of technical sciences (1992), senior researcher of the Laboratory of Mathematical Modeling of Multiphase Processes.

The domain of his scientific interest includes: mathematical simulation of multiphase processes, catalytic reactors and chemical-technological diagrams; experimental kinetical studies of catalytic processes and catalyst activity; characterization of heat- and mass transfer, studies in the fields of nontraditional power engineering; development of new energy resources and energy saving plants and technologies on the basis of thermochemical catalytic reactions.

V.I. Anikeev has initiated and developed a new scientific direction: application of thermochemical catalytic processes in power engineering. He developed novel catalytic reactor-receivers of the concentrated solar flux and proposed new experimental and theoretical methods for analysing the efficiency of these reactors; guided construction of pilot plants for conversion and transfer of energy based on the closed thermochemical cycle; proposed new schemes of heat-recovery installations; designed the software for numerical calculations and optimization of numerous chemical catalytic processes.

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* Scientific degrees are specified according to the Russian Classification, which correlates with the common one as follows: candidate of chemical sciences (or other sciences) - Ph.D
doctor of chemical sciences (or other sciences) - D.Sc.
Professor (scientific title, provided by certificate) - University Professor

ANUFRIENKO VLADIMIR FEODOSIEVICH, doctor of chemical sciences (1993), Head of research group.

V.F. Anufrienko is a well known expert in ESR spectroscopy. He has revealed a covalent metal-ligand bond in a new family of chelate compounds of copper(II) and suggested a mechanism of a far distant delocalization of unshared electron in the chelate complexes. V.F. Anufrienko has registered the effect of ligand exchange on the ESR spectra of copper(II) complexes in solutions. He was also the first to prove the formation of equatorial forms of copper(II) complexes adducts.

V.F. Anufrienko revealed the effect of a concert arrangement of copper ions and other paramagnetic ions caused by the Jahn-Teller effect in various oxide catalysts. During 20 years of his research activity he described important peculiarities of the ESR spectra of titanium catalysts for polymerization.

V.F. Anufrienko is also known for his fundamental results concerning the ESR of carbons, cokes and carbon mesophase structures.

BALZHINIMAYEV Bair Sadypovich, doctor of chemical sciences, (1991), Head of the Centre for Catalysts Characterization and Testing.

Kinetics of heterogeneous catalytic reactions, reaction and chemical engineering belong to the sphere of his activities. On the basis of detailed knowledge of kinetics and catalytic reaction mechanisms he designs and improves catalysts, processes and techniques of their testings.

B.S. Balzhinimayev has developed experimental procedures for characterizing the kinetics of rapid processes on heterogeneous catalysts. He simulated the unsteady kinetics of ethylene epoxidation, o-xylene oxidation to phthalic anhydride and developed approaches to simulations of highly-selective processes and catalysts via the thorough investigations of the active sites structure, mechanism and reaction kinetics.

BOBROV Nikolay Nikolaevitch, candidate of chemistry (1974), Head of the Laboratory for the Catalyst Activity Testing.

N.N. Bobrov is the expert in experimental kinetic methods applied for catalysis. His nowadays activity concerns: standardization of control over catalysts and supports; equipment for testing the catalyst activity, overall and active surface of catalysts and supports. N.N. Bobrov is occupied as well by the design of the following equipment: express analyzers of gas and gas/vapor compositions, devices for the preparation of reference gas mixtures. His scientific activity concerns kinetics of oxidative conversion of methane and other hydrocarbons. N.N. Bobrov designs the education accessory software for investigation of the formal kinetics of the steady-state heterogeneous processes.

BUYANOV Roman Alekseevich, doctor of chemical sciences (1972), Professor (1976), Honoured Scientist of Russia, the Associate Member of RAS, Lenin prize winner, Head of the Laboratory of Dehydrogenation.

Prof. Byanov R.A. developed a basis for crystallization theory of low-soluble hydroxides via the mechanism of oriented growth and the theory of polynuclear hydroxo complexes formation and that of condensed systems of low-soluble hydroxides in mother liquors. Accounting for the NMR data, he has developed the theory of magnetic mechanism of o-p hydrogen conversion. He studied also the radical-chain mechanism of catalytic pyrolysis. Thus, the role of the heterogeneous initiation, break and propagation of chains over the catalyst surface has been elucidated.

The mechanism of the carbide cycle upon coke deposition and the stage mechanism of carbon oxidation upon catalyst regeneration were investigated by Prof. Buyanov. He studied the reasons of catalyst deactivation and destruction and accomplished their first scientific classification. New mechanisms of activation were applied for preparation and processing of catalysts. A set of commercial catalysts was obtained in his laboratory.

DAVYDOV Anatolii Aleksandrovich, doctor of chemical sciences (1990), Professor (1990), Head of the Laboratory of Selective Conversion of Paraffins.

With IR analysis, Prof. Davydov studies the structure and properties of the surface and surface complexes formed under adsorption of simple and complex molecules on the oxide catalysts and reactions occuring on the surface of solids. He is known for investigation of the mechanism of heterogeneous catalytic reactions; he designs processes and catalysts for the selective paraffin conversion (oxidative methane coupling, oxidative dehydrogenation and ammonolysis of propane and isobutane).

DUPLYAKIN Valerii Kuzmich, doctor of chemical sciences (1990), Director of Omsk Branch of Boreskov Institute of Catalysis.

His research activities include: the catalytic conversion of hydrocarbons, physico-chemical basis and technological design of supported catalysts, development of highly-efficient catalysts for oil refining and petroleum chemistry. V.K.Duplyakin determined the mechanism of anchoring the active component precursors upon the catalyst synthesis, developed the methods of regulation and prediction of the active phase distribution in the catalysts of reforming, hydrofining and hydrogenation. For supported platinum catalysts, he has found the surface compounds playing the role of active sites in dehydrocyclization of paraffins and hydrogenation of aromatic hydrocarbons. With the method of nongradient circular impregnation, he has developed and commercialized new catalysts for reforming and other technologies.

FEDOTOV Martin Aleksandrovich, doctor of chemical sciences (1991), senior researcher.

M.A. Fedotov is a specialist in NMR application for studying the structural and catalytic properties of coordinated compounds of molybdenum, tungsten and metals of Pt group in solutions. He has studied generation of hydroxides from pure and mixed solutions of salts of aluminium and transition elements of the 1st row. He also investigated the structure and the catalytic properties of heteropoly molybdates in solutions and tungstates of various composition possessing ions of transition metals, as well as the structure and catalytic properties of platinum metal complexes in solutions were studied by him. He performs a systematic and thorough investigation of the reagent adsorption and oxygen isotope exchange, hydrogen oxidation and ammonium decomposition on metals. He stated the concept of reaction mechanism and described quantitatively the kinetic results obtained. M.A. Fedotov has investigated the structural factors in the adsorption and catalysis and found a relationship between adsorption and catalytic properties. He elucidated as well the effect of polarization of electrodes contacting with solid H^+ and O^{2-} conducting electrolytes on their catalytic properties in the gas phase heterogeneous catalytic oxidation and hydrogenation.

FENELONOV Vladimir Borisovich, doctor of chemical sciences (1986), Head of the Laboratory for Catalysts Texture Investigation.

In his research activities he studies and simulates the textures of catalysts and adsorbents, mechanisms of their structure formation (building) upon standard synthesis stages, develops the methods of adsorption and mercury porosimetry for studying the structure of pores.

V.B. Fenelonov has developed the physico-chemical principles of the texture generation for a set of standard catalysts and supports via successive technological stages of their synthesis; elucidated the sorption cappilary and colloidal chemical mechanisms of texture formation with the account of geometry variations in the dispersed system. He also developed the methods for interpreting the data of adsorption and mercury porosimetry.

IONE Kazimira Gavrilovna, doctor of chemical sciences(1981), Professor (1988), Head of the Laboratory of Zeolite Catalysts.

Prof. Ione has contributed significantly to the development of scientific basis for catalysis on zeolites; design of zeolite catalysts and zeolite based fine organic synthesis.

She has developed catalytic systems and process principles for producing gasolines with a high octane number, alkyl aromatics and alkyl nitrogen compounds, for the gas phase nitration of alkyl benzenes, etc.

ISMAGILOV Zinfer Rishatovich, doctor of chemical sciences (1988), Professor (1990), Head of the Department of Environmental Catalysis.

Scientific interest of Prof. Ismagilov is focussed on the development of environmentally safe technologies, catalytic methods of waste utilization and environmetal control. The main results of his research activity are: elucidation of the kinetics and mechanism of oxidation of organic substances and the mechanism of heterogeneous-homogeneous free radical reactions; invention of new technologies for purification of waste gases and utilization of liquid and solid residues, recycling; development of new spherical alumina supports and catalysts for gas processing and petrochemistry; development of the process of catalytic combustion; development of honeycomb monolith supports and catalysts for purification of automative exhaust gases and of DeNOX process for purification of tail gases of power plants; invention of new process and catalysts for direct oxidation of hydrogen sulfide to elementary sulfur; engineering for purification of natural gas from hydrogen sulfide.

IVANOV Aleksei Alekseevich, candidate of chemical sciences, Head of the Laboratory of Kinetics and Processes in the Fluidized Bed.

A.A. Ivanov contributed significantly to the studies of catalysts and processes for syntheses of oxygen-, sulphur- and nitrogen-containing compounds. He investigates the mechanism of catalyst action and catalysis under unsteady-state conditions.

A.A. Ivanov has developed a mathematical concept for designing reactors with the fluidized bed and control over effective nonstationary state of catalysts.

A.A. Ivanov has developed the transient response techniques for studying reactions and detailed mechanisms of a series of commercial catalytic processes, i.e. sulphur dioxide oxidation, o-xylol oxidation to phthalic anhydride, butane oxidation to maleic anhydride, acrolein and acrylic acid production from propylene, etc.

KHASIN Aleksandr Viktorovich, doctor of chemical sciences (1989), Leader of the Group of Oxidation on Metals.

A.V. Khasin contributed to investigations of the isotope exchange of oxygen and nitrogen, ammonia synthesis, hydrogen and ethylene oxidation over metals. He gave a quantitative analysis of the kinetics of oxygen isotope exchange on silver and that of nitrogen on iron. He also determined the ratio between the rates of nitrogen isotope exchange and ammonia synthesis, which permitted to predict the synthesis rate on the basis of the isotope exchange data. He investigated the regulations and simulated quantitatively the catalytic ethylene oxidation on silver.

KIRILLOV Valerii Aleksandrovich, doctor of technical sciences (1986), Professor (1991), Head of the Laboratory of Mathematical Modeling of Multiphase Processes.

He is engaged in mathematical simulations of chemical reactors; studies on hydrodynamics of multiphase fluids, phenomena of heat and mass transfer upon chemical and phase conversions and applications of catalysis to ecology and power engineering.

Prof. Kirillov has developed the theory of simultaneous processes of chemical and phase conversions on a porous grain and in the catalyst layer; suggested a set of technologies for liquid phase catalytic purification of industrial gases from the sulphur compounds and nitrogen oxides; solved the problems of thermochemical conversion and storage of solar energy via the use of heterogeneous catalysts.

KOCHUBEY DMITRII IVANOVICH, candidate of physico-mathematical sciences (1977), Head of the Laboratory of Spectral Methods.

D.I. Kochubey contributed significantly to EXAFS studies of ultradispersed metals, cluster oxides and sulfide materials, and to scanning tunnel microscopy on surfaces.

He has developed the following EXAFS techniques: fluorescence transmission, overall photoflow, XEOL (in the International Siberian Centre of Synchrotron Radiation). He directs EXAFS studies of the Centre.

He has developed the technique for characterization of the phase composition of supported metal catalysts under unaerobic conditions and various operation modes.

KOZHEVNIKOV Ivan Vasilievich, doctor of chemical sciences (1983), Professor (1990), Head of the Laboratory of Catalytic Reactions of the Organic Synthesis.

His main recent scientific contributions were made in the field of catalysis by heteropoly compounds (HPC). His laboratory is occupied by research of methods for preparation of HPC, mechanisms of acid and oxidation catalysis by HPC, etc. Numerous noval synthetic methods based on HPC catalysis were developed here. Some innovations were commercialized.

KRIVORUCHKO Oleg Petrovich, doctor of chemical sciences (1990), Head of the Laboratory for Catalysts Preparation.

O.P. Krivoruchko has developed the theoretical principles of heterogeneous catalyst preparation via precipitation, mixing and deposition techniques. He also developed nontraditional methods for the support and catalyst preparation via thermochemical, mechanochemical and radiothermal activation of inert oxygen-containing crystal compounds of various nature. He studies the mechanism and chemical aspects of solid-phase conversions in multicomponent hydroxide and oxide systems.

KUNDO Nikolai Nikolaevich, doctor of chemical sciences (1991), Head of the Laboratory of Catalytic Processes of Desulfurization.

N.N. Kundo is well known for: development of catalytic processes in the gas phase and solutions for detoxication of wastes containing sulfite compounds; search for the catalysts resistant to sulfite compounds; research of catalytic reaction mechanisms.

He has developed the processes for the liquid phase catalytic purification of gases from hydrogen sulfide, yielding elementary sulfur. He pioneered the use of catalysts based on cobalt phthalocyanines for this purpose. The test experiments provided a 95% yield of sulfur and practically complete gas purification from hydrogen sulfide. Heterogeneous catalysts developed on the basis of cobalt phthalocyanine allow to detoxicate wastes from hydrogen sulfide and mercaptanes.

Studuies of H_2S+SO_2 reaction in aqueous solutions resulted in production of efficient catalysts for sulfur generation. The process of sulfur removal from the effluent gases containing sulfur dioxide was designed on the basis of these data.

LIKHOLOBOV Vladimir Aleksandrovich, doctor of chemical sciences (1983), Professor (1985), Head of the Laboratory of Catalysis by Metal Complexes, Head of the Chair "Catalysis and Adsorption" at the Novisibirsk State University.

Prof. Likholobov is a well known specialist in the synthesis of heterogenized complexes of metals and application of these new materials for preparing catalysts, sorbents and compozites. He has developed fundamental and methodological approaches to the synthesis of anchored chemicals by the "tailor-made" method providing a wide spectra of chemical compositions and structures of the catalyst active sites and improving the "chemical accuracy" of the synthesis.

He contributed significantly to the research of processes for activation of dihydrogen, carbon monoxide, dioxygen, olefin molecules by transition metal ions, as well as regularities of ligand rearrangements yielding the products of hydrogenation, oxidation and carbonylation of various organics.

Nowadays he is occupied by the development of methods for the synthesis of the surface-functionalized carbon materials which are catalysts and sorbents of a new generation (they are the key materials for production of dyes and biologically active substrates).

MALAKHOV Vladislav Veniaminovich, doctor of chemical sciences (1988), Head of the Analytical Laboratory.

V.V. Malakhov contributed significantly to the development of such methods as: atomic-emission spectroscopy with inductively related plasma; X-ray-fluorescent spectroscopy; atomic-absorption spectrophotometry; local X-ray microanalysis; chemical methods of elemental and phase analysis; various chromatographic methods, including gas-liquid, gas-adsorption, highly efficient liquid chromatography and supercritical fluid and ionic one; method of chromato-mass spectroscopy for identification of molecular content of samples. V.V. Malakhov has suggested the theory and methodology for concentrating the micro quantities of inorganic and organic chemicals; methods of elemental and molecular analysis of objects of various genesis and application.

He has designed a new chemical method for phase analysis - stoichiographic method for differentiative dissolving, which provides analysis of solids of the unknown phase composition without using the reference samples of individual phases. V.V. Malakhov has designed a new type of polycapillar chromatograph columns, accelerating the chromatographic separation of materials by several orders as compared to the conventional chromatograph columns.

MASHKINA Anna Vasilievna, doctor of chemical sciences (1973), Professor (1988), Head of the Laboratory of Catalytic Conversions of Sulfur-Containing Compounds.

Taking into account the chemical nature of the heterogeneous catalysis, Prof. Mashkina has established a general approach to prediction of catalytic action of materials with respect to sulfur compounds interactions. Her studies of chemical interactions between the reagents and the surface provided the performance of thermodynamically possible but previously uknown reactions and selection of efficient catalysts for specific processes in the hydrogen, oxygen or inert media. She designed catalytic syntheses of methylmercaptane, dimethylsulfide, thiolane, dimethylsulfoxide and sulfolane.

MASTIKHIN Vyacheslav Matveevich, doctor of chemical sciences (1986), senior researcher.

V.M. Mastikhin has contributed to significantly research of catalysts and catalytic reactions by ESR and NMR methods. He has described in detail the state of vanadium catalysts upon SO_2 oxidation. With NMR methods of high resolution in solids he studies heterogeneous catalysts.

MATROS Yurii Shaevich, doctor of technical sciences (1976), Professor (1988), Head of the Laboratory of Mathematical Modeling of Unsteady Catalytic Processes

He has developed a novel research direction in the theory and application of chemical processes and reactors: heterogeneous catalytic processes under simulated unsteady-state conditions (SUSSCs). His theoretical and experimental studies proved the SUSSCs to provide a considerable increase in the efficiency of catalytic processes, i.e. in the activity and selectivity of catalysts, thus saving metal for construction of apparatuses and reducing considerably energy consumption. The novel approach appears to facilitate significantly design of reactors and installations.

MATVEEV Klavdii Ivanovich, doctor of chemical sciences (1970), Professor (1982), Head of the Group for Studying Catalysts and Processes Based on Heteropoly Acids.

Prof. Matveev contributed significantly to the development and study of homogeneous catalysts for oxidation reactions of general and fine organic syntheses. He pioneered in a homogeneous catalysis with heteropoly acids, which resulted in the production of more than 25 catalysts for various reactions of organic synthes. He is the author of 48 patents in USSR and 2 patents in 6 European countries.

MOROZ Ella Mikhailovna, doctor of chemical sciences (1989), senior researcher.

X-ray spectroscopy of highly-dispersed systems is the main field of her research work. She studies the structural and substructural properties of catalysts and supports.

With up to date experimental and numerical methods, E.M. Moroz has developed X-ray methods for studying the multicomponent highly-dispersed materials. The methods are based on integral analysis of the radiation intensity curves of Roentgen rays. Method of radial atomic distribution (RAD) was used to study phase composition, structure and size of crystallites of multicomponent catalysts. The criterion of RAD curves reliability was found. The method of harmonic analysis of diffraction peaks profile was used for definition of crystal dimensions and parameters of crystal distribution and microdistortion. For the first time X-ray analysis was used to determine the structure of low temperature alumina which is of key important for supporting catalysts. E.M. Moroz characterized the mechanism of interaction between these compounds and promoters.

E.M. Moroz investigated structural and substructural characteristics of a series of monometallic supported catalysts Me/(Al_2O_3, C, SiO_2, spinels) (here Me stands for Pt, Ir, Pd, Re, Ni) and bimetallic catalysts of Pt-Me type (here Me stands for Sn, Re, Ru, Ir, Ce, etc.) prepared via various procedures.

NOSKOV Aleksander Stepanovich, doctor of technical sciences (1993), Head of Unsteady State Processes Laboratory.

The main fields of scientific interests are: mathamatical modeling of fixed catalyst bed reactors and forced unsteady state catalytic processes, development and industrial application of catalytic prosseses, effectively used for environment protection (waste gases purification from VOC, SO_2, NO_x).

PANOV Gennadii Ivanovich, doctor of chemical sciences (1985), Associate Member of IUPAC (1989), Head of the Laboratory for Catalytic Synthesis of Oxygen-Containing Compounds.

G.I. Panov is occupied by the problem of isotope application for studying the mechanisms of adsorption and catalysis, as well as ammonium synthesis, nitrogen oxide decomposition, oxidation of hydrocarbons on oxide and metal containing zeolite catalysts. He elucidated the similarity in N_2, O_2 and H_2 activation on the surface of nitrides, oxides and hydroxides of metals, respectively. He proved the oxygen bound in various oxygen-containing molecules to be active in partial oxidation of hydrocarbons. He established a high efficiency of FeZSM-5 zeolites as the catalysts for the one-stage oxidative hydroxylation of. aromatics by nitrogen monoxide.

PARMON Valentin Nikolaeyevich, Associated Member of RAS (1991), doctor of chemical sciences (1984), Professor (1991), Head of the Laboratory of Catalytic Methods of Solar Energy Conversion.

Prof. Parmon has developed and studied a large amount of catalysts and photocatalysts for dihydrogen production from water, thermocatalytic systems and devices for direct conversion of concentrated solar energy and ionizing radiation energy, a new family of materials for chemical accumulation of low-potential heat, systems for CO_2 fixation under mild conditions.

PLYASOVA Ludmila Mikhailovna, doctor of physico-mathematical sciences (1993), Head of the Laboratory of Structural Methods.

With X-ray methods L.M. Plyasova studies polycrystal materails and the structure of oxide catalysts.

She has developed methods for catalyst investigation, studied the processes of phase formation (accompanied by the structural characterization of generated phases) upon preparation and operation of numerous oxide catalysts of partial oxidation of hydrocarbons.

RYNDIN Yurii Alekseevich, candidate of chemical sciences (1977), Head of the Laboratory of Catalysis by Anchored Metal Complexes.

Yu.A. Ryndin is engaged in catalysis by the anchored metal complexes. He studies the nature of active sites of supported metal catalysts via a purposeful synthesis of molecular models of sites from organometallic precursors.

SADYKOV Vladislav Aleksandrovich, candidate of chemical sciences (1978), Head of the Laboratory of Catalysts for Deep Oxidation.

The research interests of V.A. Sadykov include: environmental molecular catalysis, detailed mechanism of heterogeneous reactions of catalytic oxidation and NO reduction, defects of oxide catalysts structures, new routes of catalyst preparations (plasmochemical, hydrothermal, mechanochemical treatments), supported noble metal catalysts promoted by oxides.

V.A.Sadykov studies the discriminative nature of bulk and surface defects of transition metal oxides and its role in the oxidation catalysis; derives new mechanisms of the low-temperature CO oxidation on oxides and supported catalysts. He has elaborated a set of cheap, highly active and thermostable catalysts for environmental control on the basis of wastless technologies.

SAVCHENKO Valerii Ivanovich, doctor of chemical sciences (1985), Professor (1988), Head of the Laboratory of Metal Catalysts.

Using up-to-date physical methods for studying the surface, i.e. diffraction of slow electrons, Auger-, and photoelectron spectroscopy, mass-spectrometry and mathematical modeling of catalytic processes, Prof.Savchenko performs physico-chemical analysis of heterogeneous systems; studies kinetics of adsorption and catalytic reactions, mechanisms of chemisorption and catalysis on metals.

In accordance with the research of variously oriented monocrystals of a series of metals, he established the correlation between the energy and kinetics of adsorption and oxidative catalysis, as well as between the surface structure of metal catalysts and its methamorphose under the influence of the reaction media and the catalyst properties.

SIMONOV ALEXANDER DMITRIEVICH, candidate of chemical sciences (1970), Head of Laboratory of Reactors for Catalytic Head Generators. He is an expert in heterogeneous oxidative catalysis; technology of catalytic detoxication of flue gases and sewages.

A.D. Simonov studies the catalytic burning and processing of solid fuels. At present he pays a particular attention to the processes of catalytic utilization of solid organic wastes and vegetable feedstocks; development of technology and equipment for bringing these processes to practice and technology commercialization. He is the author or co-author of more than 70 scientific publications.

SOBYANIN Vladimir Aleksandrovich, doctor of chemical sciences (1991), Head of the Laboratory of Catalytic Processes in Fuel Cells.

The fields of his research activities are: surface science, adsorption and catalysis by metals, catalysis and electrocatalysis in facilities with solid electrolytes.

V.A. Sobyanin has thoroughly studied the reagent adsorption and isotope exchange of oxygen, hydrogen oxidation and ammonia decomposition on metals. He elucidated reaction mechanism and quantitatively described the kinetic data. With the data obtained he determined the structural factors in adsorption and catalysis, interrelations between adsorption and catalytic properties, the problem of "pressure drop". He studied the polarization effect of electrodes contacting with solid H^+ and O^{2-} conducting electrolytes on their catalytic properties in the gas-phase geterogeneous-catalytic oxidation and hydrogenation.

SOLOVIEVA Lidiya Pavlovna, doctor of geology-minerological sciences (1991), senior researcher.

L.P. Solovieva uses X-ray diffraction based on monocrystal data for studying inorganic compounds; designs mathematical basis for X-xay diffraction calculations.

Nowadays she is concerned with the study of polycrystal structures, development of precise investigation tecniques with the use of synchrotron radiation. She has also established the program systems for elucidation of structural problems via mono- and polycrystal diffractional data. With monocrystal data, she has interpreted the structures of more than 30 minerals and their synthetic analogues. A series of polycrystal materials were structurally interpreted with the Rietweld method by L.P. Solovieva as well.

TALSI Eugenii Pavlovich, doctor of chemical sciences (1991), senior researcher.

The field of his scientific interests includes: NMR and ESR *in situ* studies of key intermediates of homogeneous catalytic oxidation and oxidative coupling. Two types of palladium superoxide complexes with different modes of $O_2^{\bar{\cdot}}$ coordination of to palladium (σ or π) were found. Superoxide complexes (σ-mode) appear to oxidize quantitatively ethylene to ethylene oxide.

With ^{95}Mo, ^{51}V, ^{59}Co, ^{17}O and ^{1}H NMR and EPR metal complexes formed upon catalytic oxidation of alkanes by organic hydroperoxides and hydrogen peroxide were characterized. Alkylperoxo and peroxo complexes of Mo, V and Co were detected and studied *in situ.*

E.P. Talsi studied relations between the catalyst structure and selectivity upon the oxidative coupling of 2,6-dimethylphenol in the presence of copper-amine complexes. Six types of Cu(II) complexes were detected and their role in the catalytic process was shown.

Kinetics and mechanism of Schiff base formation from aniline and derivatives of salycylic aldehyde coordinated to Cu(II) and Zn(II) were studied by ESR and NMR. E.P. Talsi found that metal atoms can change the rate of this reaction in two ways: (a) via stabilization of its intermediate (carbinolamine); (b) via acting as a substituent in the aromatic ring of salicylic aldehyde.

YERMAKOVA Anna, doctor of technical sciences (1986), senior researcher of the Laboratory of Multiphase Processes.

A. Yermakova is an expert in mathematical modeling of chemical processes and apparatuses. She has developed fundamental and experimental approaches to mass-transfer studies in three-phase systems (gas-liquid-solid), modeling of macrokinetic complex chemical reactions. She has established a new set of numerical methods for identification and analysis of kinetic models adapted for IBM PC. Nowadays she is engaged in designing a mathematical model of a new complex liquid-phase catalytic purification of process gases from admixtures of sulfur dioxide, nitrogen oxides, arsenic oxides and developing of new simulating computer models of engineering schemes of chemical processes.

YURIEVA Tamara Mikhailovna, doctor of chemical sciences (1984), Professor (1990), Head of Laboratory of Catalytic Conversion of Carbon Oxides.

Prof. Yurieva is an expert in heterogeneous catalysis with oxides, she studies the mechanism of the oxide catalytic action in redox reaction. Prof. Yurieva has studied the regularities of oxide generation and dependence of their catalytic properties on the structure of environment of metal ions determined experimentally. In accordance with a developed method for the low temperature catalyst preparation Prof. Yurieva has designed a set of catalysts for various processes: alcohol dehydrogenation, synthesis of methanol and C_2-C_6 alcohols, alkylation of amines, fine purification of hydrocarbons from CO, low temperature and one-stage steam conversion of CO.

ZAKHAROV Vladimir Aleksandrovich, doctor of chemical sciences (1982), Professor, Head of the Laboratory of Catalytic Polymerization.

The research interest of Prof. Zakharov is the catalytic polymerization of olefins: synthesis and study of solid catalysts of various types (supported organometallic systems, Ziegler-type supported catalysts), investigation of kinetics of catalytic polymerization, synthesis and analysis of structures of polyolefins and copolymers based on olefins.

ZAMARAEV Kirill Il'ich, Full Member of RAS (1987), Member of the Academia Europaea (1990), Doctor of chemical sciences (1972), Professor (1977), Director of the Boreskov Institute of Catalysis, General Director of MNTK KATALIZATOR, Head of the Chair of Physical Chemistry at the Novosibirsk State University.

Prof. Zamaraev is a well known specialist in the areas of catalysis kinetics of chemical reactions in condensed media, photochemistry and magnetic resonance spectroscopy.

He has carried out detailed studies on the mechanisms of spin exchange between paramagnetic species in solutions. With direct experiments he has proved the possibility of electron transfer reactions in condensed media to occur at large distances via electron tunneling between the reacting particles. He has observed numerous reactions of this type involving trapped electrons, organic and inorganic ion radicals, metal complexes, excited molecules, electron donor and electron acceptor sites on solid surfaces, and carried out both experimental and theoretical studies of the kinetics of these reactions.

Prof. Zamaraev has characterized with various spectroscopic techniques, in particular with EPR, NMR and EXAFS, the structure of numerous homogeneous and heterogeneous catalysts and elucidated the mechanisms of their action by observing reaction intermediates. Prof. Zamaraev has carried out extensive work in the areas of photochemistry, photocatalysis and solar-to-chemical energy conversion. He has developed efficient thermocatalytic convertors based on reversible endothermic chemical reactions.

ZHDANOV Vladimir Petrovich, doctor of chemical sciences (1988), Professor (1988), senior researcher

The main field of his scientic interest is the theory of elementary rate processes on solid surfaces. Prof. Zhdanov has studied in detail vibrational relaxation of adsorbed particles via excitation of phonons and electron-hole pairs; dynamics of surface diffusion; adsorption and desorption including nonequilibrium and nonadiabatic effects; the influence of lateral interactions between adsorbed particles and adsorbate-induced changes in the surface on the kinetics of surface diffusion, adsorption, desorption and elementary chemical reactions.

ZHIDOMIROV Georgii Mikhailovich, doctor of physical-mathematical sciences, Professor (1965), Head of the Laboratory of Quantum Chemistry.

Prof. Zhidomirov contributed significantly to the fundamentals of quantum chemistry, elaboration and modification of semi-empirical quantum chemical calculation methods, quantum-chemical studies of spectroscopic parameters (NMR, ESR, IR, electron spectroscopy, XANES, EXAFS),, theory of magnetic resonance (NMR,ESR) from spectral patterns, theory of electron spin echo phenomena, theoretical surface science and molecular theory of heterogeneous catalysis.

ZOLOTOVSKII BORIS PETROVICH, Doctor of chemical sciences (1993), Head of Laboratory of Adsorbents and Supports.

B.P. Zolotovskii designs new alumina adsorbents and catalyst supports. In particular, he studies the catalysts for gaseous sulfur recover (the Claus processes). Some of his adsrobents, supports and catalysts are used at industrial scale.

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