ANNUAL REVIEW

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СО РАН

1994

BORESKOV INSTITUTE OF CATALYSIS
SIBERIAN BRANCH OF RUSSIAN ACADEMY OF SCIENCES

Novosibirsk

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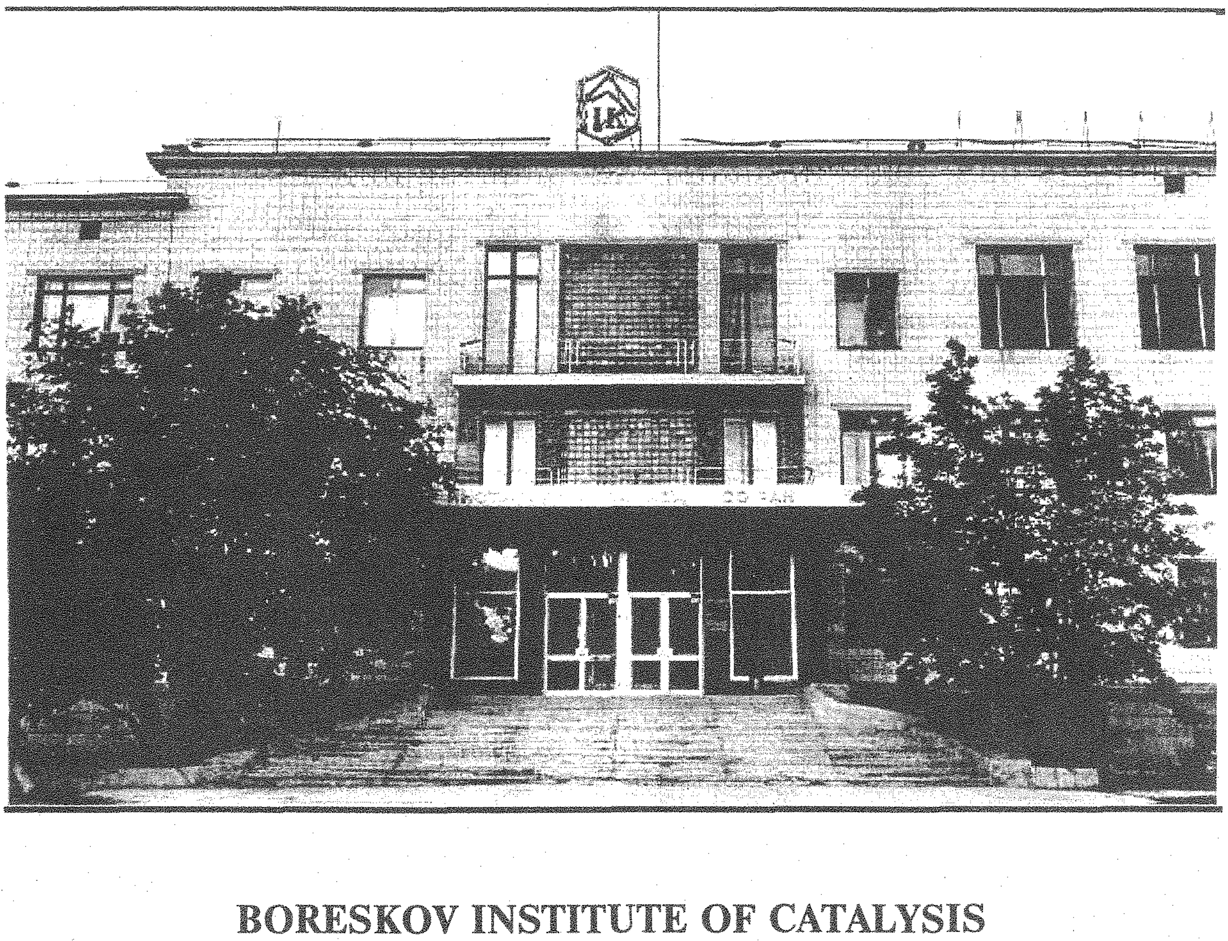

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Dear Colleagues,

This book is the second issue of the new annual reviews of the Boreskov Institute of Catalysis in the main fields of its R&D activity covering year 1994.

The Boreskov Institute of Catalysis is well known to the experts in both academic and industrial catalysis not only in Russia and CIS, but also in many western and oriental countries. Since the sixties it remains the largest chemical institution in the Asian part of Russia having many deep and stable traditions and providing research in nearly all fields of catalysis. Its interests spread from the sophisticated purely academic research to the real applied problems, including commercial catalysts and catalytic technologies.

During the last years according to numerous changes in Russia due to its stepwise approach to the market economy, there were also some sufficient changes in the behaviour and life of the Boreskov Institute of Catalysis. However, in spite of general instability in the country, the Institute appeared to be able to survive as a high quality specialized organization. Moreover, the intensity and quality of the research and engineering activity at the Institute became even higher. Hope, the readers will feel it themselves, when comparing the material of this and previous issues of the Annual Review.

The year 1994 was crucial for the life of the Institute in many aspects. The main result of that year can be summarized as follows: even in the unstable outside situation the Institute managed to make the applied research easier for the Russian and foreign industries. This helped financial self-maintenance of the Institute. Also, the Institute gained in research in catalysis fundamentals, thus continuing the old traditions originated from the beginning of the Institute due to a very powerful impulse of its creator and first director academician Georgii K. Boreskov.

Year 1994 was of principle importance for the Institute, since in this year it accepted the highest status for the Russian R&D organizations: according to special act of the Russian Government, the Boreskov Institute of Catalysis became since November 1994 a Federal Research Center of the Russian Federation. The main role in this and current success of the Institute belongs to its second director academician Kirill I. Zamaraev who guided the Institute since 1984 until the beginning of 1995.

This issue is published with a delay in respect to year 1994. This necessitates to comment also some serious steps in the life of the Institute in year 1995. According to the statute of the Russian Academy of Sciences, which is the parent of the Institute, there should be reelection of the directors of its R&D institutes each five years. According to the suggestion of academician Zamaraev supported by the Scientific Council of the Institute, as the new director of the Institute for the next five years since the beginning of 1995 it was elected Prof. Valentin N. Parmon, a corresponding member of the RAS. Academician Zamaraev remained to be the research leader and R&D Director of the Federal Research Center till his untimely decease. So, the new director of the Institute represents the third generation of its specialists. Due to this there were also some other serious changes in the staff of the Board of Directors as well as in the Scientific Council of the Institute, both became much younger. Indeed, this changes are very serious, since now the main research and administrative management in the Institute belongs to much younger generation of the staff. The new management recognizes well all the existing problems taking the maintenance of high activity and productivity of R&D of the Institute in both fundamental and applied areas as the goals of the highest priority.

Hope, that the next issue of the Annual Review of the Boreskov Institute of Catalysis will exhibit its remaining capacity in catalysis, catalyst and catalytic technologies.

February, 1996. Valentin N. Parmon

IN MEMORIAM

Kirill Ilyich Zamaraev (1939-1996)

Professor Kirill Ilyich Zamaraev, IUPAC Past-President, R&D Director of the Boreskov Institute of Catalysis, died on June 26, 1996. Russia and the world have lost a wonderful person, a great scientist and an eminent statesman.

Kirill I. Zamaraev was born in Moscow, Russia, on May 20, 1939 in the family of a famous soviet chemical engineer. He began his professional education at the Moscow Mendeleev Institute of Fine Chemical Technology, then moved to the Moscow Physical-Technical Institute (MPhTI) in order to improve his knowledge of chemical physics. In both these universities his rank as a student was number one.

He received a BSc degree from the MPhTI in 1963 and was awarded a PhD in chemical physics in 1966 and a DSc in physical chemistry in 1972 by the N. Semenov Institute of Chemical Physics (ICP) in Moscow (title of his doctoral thesis was "ESR study of transition metal complexes structure and reactivity"). In 1966-1976 he made his research as a junior research fellow, a senior research fellow and then a head of a laboratory at ICP where he performed a wide set of important basic research in the fields of elementary kinetics of electron spin exchange and tunneling electron transfer on large distances, as well as of ESR and NMR application to the studies of metallocomplex catalysts. At the same time he worked as an assistant professor at MPhTI. Since the beginning of 70th K. Zamaraev was drawn by academician N. Semenov into the studies on photocatalytic conversion of solar energy. In 1974-1975 he has been the first soviet long-term visiting researcher to the Cornel and Stanford Universities as well as the University of Chicago under a Program of scientific exchange in chemistry between the USSR and the USA.

In 1976 Professor Zamaraev has been elected as the corresponding member of the Academy of Sciences of the USSR and invited by academician G. K. Boreskov to join the Institute of Catalysis, Novosibirsk, as a Deputy Director. Kirill Ilyich has come to Novosibirsk at early 1977 together with a large team of young chemical physicists, thus largely widening the studies of elementary catalytic reactions on molecular-atomic level through application of modern physical and kinetic instrumental methods of investigation.

In 1984 Prof. Zamaraev became the Director of the Boreskov Institute of Catalysis, and since that time he was the real leader of all research and development activity of this huge (more than 1000 people in staff) Institute.

Since 1986 till 1992 Prof. Zamaraev held a position of the General Director of the large R&D association known as "MNTK "Katalyzator" Group". Since 1985 he was the Chairman of the Scientific Council on Catalysis and its Industrial Applications of USSR (now of the Russian Federation), being the leader of the community of specialists in catalysis of the Russian Academy of Sciences. Since 1977 he was a Full Professor of the Novosibirsk State University having the chair in physical chemistry.

During the last changes in the former Soviet Union Professor Zamaraev was in charge of serious transformations of the Russian science on the way of its adaptation to the society with the market economy. He participated as a leading person at the formation of a large set of Federal Research Centers of Russia, which contain now, together with the Russian Academy of Sciences, the main scientific potential of Russia.

In 1994 the status of the Federal Research Center has been obtained also by the Boreskov Institute of Catalysis. In 1995, according to his own will, Kirill Zamaraev has left position of the Director of the Boreskov Institute of Catalysis, remaining the R&D Director of the Institute. The background of this decision was his sincere desire to spend more time on doing deep fundamental science.

Professor Zamaraev has been honored by the Russian Academy of Sciences and international community of chemists on several occasions. In 1987 he was elected a Full Member of the Academy of Sciences of the USSR (now Russia), in 1990 – a Member of the Academia Europea and a Foreign Fellow of the Indian National Science Academy, in 1995 – a Foreign Fellow of the Korean Academy of Science and Technology. In 1994 he was awarded by the Silver medal of the Royal Chemical Society of Great Britain as a centenary lecturer, in 1994 – by Karpinsky medal of the Chemical Society of Germany.

Since 60th Professor Zamaraev was a member of the International Union of Pure and Applied Chemistry. In 1987-1989 he was the President of the IUPAC Physical Chemistry Division, in 1990-1993 he organized the work of Editorial Advisory Board for Monographs on Chemistry for 21st Century, was a member of the IUPAC Executive Committe and Bureau. In 1994-1995 he held the position of the President of the IUPAC. In January 1996 he became the IUPAC Past-President.

Professor Zamaraev participated in the work of numerous scientific journals - Russian as well as international. He was the Editor-in-Chief of the *Reaction Kinetics and Catalysis Letters*, Regional Editor of the *Journal of Molecular Catalysis*, Member of the Editorial Boards of the journals *Catalysis Reviews, Catalysis Today, Catalysis Letters,* *Topics in Catalysis, Chemistry – A European Journal, Mendeleev Communications, Chemistry for Sustainable Development* and some other journals.

Professor Zamaraev is known for his mechanistic studies of catalysis at the molecular-atomic scale, and in particular for in situ characterization with the use of radiospectroscopy methods, i.e., electron spin resonance (ESR) and nuclear magnetic resonance (NMR). At the initial stage of his work Professor Zamaraev studied by ESR the structure of the transition metal complexes in solution and made a considerable contribution to the strategy of interpretation of complex EPR spectra of powder samples and reliable determination of EPR parameters.

He had discovered and kinetically characterized numerous electron tunneling reactions on large distances. He has performed pioneering experimental studies of reactions of electron tunneling between donor-acceptor pairs frozen in neutral matrices. He has demonstrated the possibility of electron tunneling on the distances of 15-30 Å and explored in detail the kinetics of this phenomenon in the time range from 10^{-6} to 10^{5} s. His fundamental studies of electron spin exchange in solution are also well known.

He was one of the pioneers who used the modern multinuclear solid state NMR for studies of the structure and the active sites on the catalyst's surfaces and intermediates of catalytic reactions in solutions and on solid surfaces.

He paid great attention to the study of chemistry in the second coordination sphere of metal complexes and the role of interfere interactions in the mechanisms of catalytic reactions. He was among the first to study of catalytic reactions in the gas phase by ion cyclotron resonance (ICR).

The works of Professor Zamaraev in photocatalysis and design of catalytic converters of solar energy utilization, as well as on the role of photocatalytic phenomena in the global chemistry of atmosphere, are the contribution to the XXI century science and technology. The approaches developed by Professor Zamaraev towards catalysis research helped to obtain unique results that were important for catalysis fundamentals and applications.

He published 3 monographs and over 300 works in Russian and foreign journals.

Kirill Ilyich was a man of great heartfelt generosity, honesty, decency and kindness. He was a perceptive connoisseur of music and poetry. He really enjoyed the rare moments of contact with nature and he even celebrated his 50-th anniversary with his friends climbing and hiking at the mountains.

This is not only Russian science which have missed one of their front figure but this is the tremendous loss to the international catalysis and chemistry community. He left us unfairly early. He will be missed by his many friends and colleagues.

Prof. V. N. Parmon
Director

Boreskov Institute of Catalysis
Novosibirsk

BRIEF REVIEW OF THE BORESKOV INSTITUTE OF CATALYSIS

The Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences (BIC) is the largest in the world specialized institute working in the field of catalysis. The Institute was founded in 1958. 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, and a significant manager of research. In 1992 his name was assigned to the Institute. Georgii K. Boreskov contributed remarkably to the generation of scientific traditions and style, research trends and activities of the Institute.

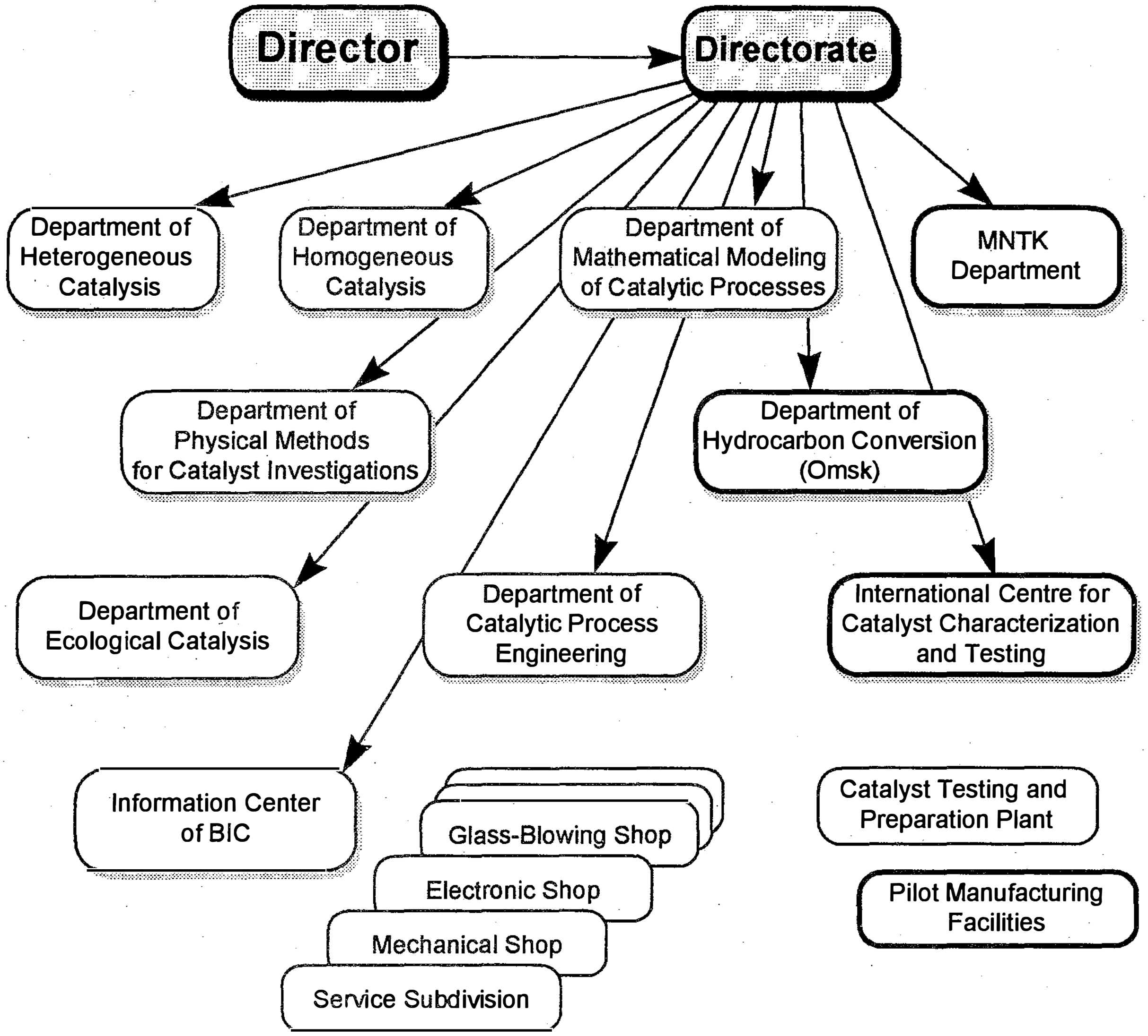
In the former Soviet Union, a successful implementation of large-scale projects in the field of catalysis was closely related with the activity of the Interministerial Scientific-Technological Complex (MNTK according to Russian abbreviation) "Katalizator" ("Catalyst"), founded around the Boreskov Institute of Catalysis by a special decree of the USSR Goverment at the end 1985. R&D Company MNTK "Katalizator" included 26 academic and industrial research and engineering organizations, as well as catalyst producing industrial plants of all the chemical and some metal processing ministries of the former Soviet Union (mostly Russian), pilot plants producing catalysts, etc. MNTK "Katalizator" institutions introduced 90% of advanced technologies to the home industrial catalysis. More than a half of these technologies, commercialized by industry, were designed at the Boreskov Institute of Catalysis, the head unit of MNTK.

In November 1994, the Institute received the status of the Federal Research Center (FRC) of Russia. FRC BIC was charged to perform the programs related to fundamental and applied studies, which are financed from the federal budget, including the design of catalysts and catalytic technologies of a new generation; data base formation in the field of catalysis; certification of catalysts and catalytic technologies and, at last, the training of highly-skilled researchers in the field of catalysis.

The list of personnel of the Institute inscribes 1056 people in Novosibirsk and 192 people in Omsk, among them ca. 400 researchers, including 1 full member and 2 corresponding members of the Russian Academy of Sciences, about 41 doctors of sciences (professors) and 201 candidates of sciences (PhD). The scientists of the Institute work in 33 research laboratories and 16 research groups in Novosibirsk and 4 laboratories and 7 research groups in Omsk. Service, Managing and Engineering Departments of the Institute support and promote its research activity. In Omsk the pilot plant of the Institute for manufacturing adsorbents and catalysts is located. Since 1984 until 1995 Prof. K. I. Zamaraev was the Director of the Boreskov Institute of Catalysis, and Prof. Valerii K. Duplyakin guides the Omsk Branch of the Institute. The scientific Council of the Institute is its brain center. Beside the heads of Laboratories and Departments, leading researchers are the members of the Council as well.

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

Structure


Director
Directorate
Department of Heterogeneous Catalysis
Department of Homogeneous Catalysis
Department of Mathematical Modeling of Catalytic Processes
MNTK Department
Department of Physical Methods for Catalyst Investigations
Department of Hydrocarbon Conversion (Omsk)
Department of Ecological Catalysis
Department of Catalytic Process Engineering
International Centre for Catalyst Characterization and Testing
Information Center of BIC
Glass-Blowing Shop
Electronic Shop
Mechanical Shop
Service Subdivision
Catalyst Testing and Preparation Plant
Pilot Manufacturing Facilities

processes, development and commercialization of new industrial catalysts and processes. Sophisticated instrumentation for the *in situ* analytical control of the 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 a unique combination of data about the structure of active centers, detailed reaction kinetics and mechanism, and to use these data for a purposeful design of new catalysts and catalytic technologies.

MAIN DIRECTIONS OF THE INSTITUTE RESEARCH ACTIVITY

Scientific-research activities of the Federal Research Center "Boreskov Institute of Catalysis" (FRC BIC) encompass a broad spectrum of problems, from the development of theoretical concepts on the nature of catalytic action of model catalytic systems to the design of technologies and catalysts for various industrially vital processes. This methodology, laid at the Institute foundation, allows it to preserve the world level of the fundamental studies in catalysis and to keep up with the leading foreign and home companies involved in the improvement and design of new catalysts and processes on their basis.

The wide range of objects studied at the Institute, starting from traditional heterogeneous and homogeneous catalysts, which form the basis for the large-scale chemical productions (sulphur production, ethylene epoxidation, hydrogenation and oxidation of hydrocarbons, etc.) to nontraditional catalytic systems for the fine organic synthesis and the synthesis of biologically active (pharmaceutical) materials, the great experience of the co-workers and traditional systematic approach in the definition and solving of problems enable to crack fast the above problems. As an example, these are the key results obtained in 1994 in various fields:

Problems in Fundamental Catalysis

The Important Studies Related to Quantum Chemistry are Performed:

- An important stage of the quantum-chemical study of active sites in Ti-containing catalysts for the olefin polymerization by the nonempirical SCF MO LCAO method is accomplished.
- A detailed quantum-chemical study of the whole cycle of catalytic water oxidation to molecular oxygen was first performed on the hydroxides of some transition metals.
- A preliminary semi-quantitative analysis of the plausible role of heterogeneous photocatalytic processes proceeding on solid and liquid aerosols under the solar radiation in the Earth atmosphere is completed. It appears that the photocatalytic processes proceeding even on the background amounts of earth aerosols can really contribute to the global atmospheric photochemistry; the role of photocatalytic processes in dust clouds is even higher. Experiments confirming this suggestion are of prime importance for further development of the concepts on the global chemical processes in the Earth atmosphere.

Atomic-Molecular Studies of Catalytic Reaction Mechanisms and Catalytic Properties of Heterogeneous Catalysts by Physico-Chemical Methods are in Progress:

- The catalytic action of silver in ethylene epoxidation has been studied. This reaction is a classical example of the typical selective reaction and, on the other hand, it serves as the basis for the commercial production of ethylene oxide. Using the XPS, isotopic-kinetic analysis and UPS in the visible range, the silver samples were studied in a series: massive monocrystal - real supported catalysts. The electrophylic state of oxygen, localized on the defect areas of silver surface, was found to take an active part in the ethylene oxide generation. The scheme of the electrophilic oxygen formation is suggested, the concept what are the epoxidation active sites, situated over the interface of defect and regular silver, is stated.
- ^{17}O NMR spectroscopy was used to study ZSM-5 and ZSM-11 zeolites where aluminium is substituted amorphously for titanium (titania-silica TS-1 or TS-2). They are active for both the phenol oxidation with hydrogen peroxide to hydroquinone and propylene epoxidation. For the first time, titanium peroxocomplex of a $Ti(OMe)_2(O_2)L_1L_2$ (L_1L_2 - H_2 or MeOH) plausible structure was observed and characterized. It is active in the oxidation of sulphides and cyclohexane.
- The mechanism of the C-H bond activation in C_1-C_5 paraffins on the oxide catalyst surface was followed regarding the nature and properties of the surface active sites. It has been found that the nature and the coordination state of cations and anions in the ion pair control the C-H bond activation. It increases with the increase of both the cation accepting ability and oxygen basicity.
- For the first time the formation of unusual liquid-like particles was observed during the interaction of iron subgroup metals with amorphous carbon under simultaneous heating in vacuum and electron radiation, when the heating temperature was 500 - 900°C, much lower than the melting point of pure metals or their eutectics. The formation (conditions) and behaviour (dynamics) of thus formed particles on the carbon support were registered by video during *in situ* experiments in the electron microscope.

Much Progress is Made towards the Improvement and Design of New Physico-Chemical Methods for Catalysts Study:

A concept of stoichiography-stoichiometry of the unsteady-state mass exchange proceeding under dynamic conditions, such as the dissolving of the object in concern, was developed. The stoichiography transforms the methods of separation to that enabling the direct definition of molecular-, ion- and phase composition of complex materials with the unknown molecular composition. Two stoichiography laws, providing this transformation, were formulated. The stoichiography allows to develop new techniques for the phase analysis of solid materials of various nature.

Scientific Principles of Catalysts and Supports Preparation:

- ❑ A new method for preparing Mo/Al_2O_3 supported catalysts was developed. Their catalytic behaviour in the hydrogenolysis of oxygen-containing organics and olefin metathesis is more superior to that of traditional catalytic systems prepared via impregnation.
- ❑ The reactivity of solids, such as crystal hydroxides, salts etc., increases during their treatment with the concentrated beam of accelerated electrons of high energy (1-3 MeV). This can help to open new ways in designing high purity oxide supports and catalysts via the low-waste and energy-saving technology.
- ❑ The data on the factors affecting the phase formation in the synthesis of wide-pore high-silica zeolites of alumina composition allow the direct synthesis of wide pore zeolites of BETA and MOR structure containing considerably smaller amounts of aluminium than the well known zeolites. These systems are particularly suitable as catalysts for selective petrochemical and organic syntheses.

Design and Improvement of Catalysts and Catalytic Processes:

- ❍ Carbon-accumulating high-loaded Ni and Ni-Cu catalysts for the low-temperature decomposition of methane were developed. They helped to design a new environment-friendly technology for processing methane (natural gas) and torch gases into inexpensive carbon materials.
- ❍ Efficient catalysts, allowing to solve the urgent environmental problem related to the disarmament, i.e. the detoxication of sewage waters and washings containing the toxicants of today's propellants (nonsymmetric dimethyl hydrazine), were designed.
- ❍ The Omsk Department of the Institute designs successfully new basic technologies aiming at the improvement of hydrocarbon feedstock processing. The catalysts meant for the isomerization and reforming of hydrocarbons, alkyl phenols and production of alkyl benzenes, have been designed and studied. For the first time in Russia, a more than 60% yield of petroleum was obtained by the composition optimization of catalysts used in vacuum gasoil and heavy feedstock cracking.
- ❍ Much attention was focussed on the design of catalysts for organic synthesis and medicines production. The design of preparation technique of V-Ti catalysts, which fits the demands of commercial productions of the formic acid from formaldehyde and nicotinic acid from β-picoline, can serve as an example.
- ❍ Design of catalysts and processes for environment protection provided rather important results. Thus, a new "closed"-cycle technology purifying liquid sewages, namely cyanosulphur purification of coke gas and adsorption-catalytic reverse-process for gas purification from aromatics, were developed. Cu- and Co-substituted ZSM-5 zeolite catalysts were optimized, which allowed to increase their activity in the selective catalytic reduction of nitrogen oxides at the high concentrations of sulphur dioxide, water, carbon dioxide and oxygen. The activity of these zeolite catalysts is more superior to that of the presently known ones.

Mathematical Modeling and Optimization of Catalytic Processes and Plants:

- ⇒ New experimental kinetic data on the ethylene polymerization were obtained for a wide series of supported Ti-Mn catalysts, which vary in their particle size, composition of electron-donor modifying additives, Ti state and composition. The mathematical polymerization model suggested includes the kinetic scheme of formation and deactivation of the active sites and considers monomer diffusion in the polymer particles.
- ⇒ Basically new theoretical and experimental ways were applied in studies of the complex processing of high-temperature-solid-biomass-gasification products. The method of thermodynamic energetic calculations of chemico-technological schemes of complex processing of the biomass gasification products was suggested. Algorithms and calculation programs were developed. A new concept on the experimental performance of the high-temperature gasification of solid biomass particles in a fluidized bed catalyst reactor has been proposed.
- ⇒ A series of works aimed at the development of the theoretical basis for processing the acidic hydrogen sulphide-containing gases of coke-chemical industry has been accomplished.

THE SOURCE OF RESEARCHERS

Education of research personnel plays a great role in the Institute activities. It is a part and parcel of teaching high school and university students, and their direct participation in the 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 the Institute activities.

INTERNATIONAL COOPERATION

A high authority of the Boreskov Institute of Catalysis (BIC) allows to preserve and extend its relations with many scientific centers abroad. In 1994 according to the agreement between the Russian Academy of Sciences (RAS) and the Research Society of Germany (RSG), BIC has continued its joint investigations with the Munich University in the "Preparation and Study of Metal Catalysts Supported on Carbon Carriers" (Institute of Inorganic Chemistry) and "Vanadium Based Catalysts for NO_x Reduction" (Institute of Physical Chemistry).

According to the Agreement between RAS and the Royal Society of Great Britain, concerning the problem of "Heterogeneous Catalysis", the researchers of the Institute of Catalysis worked on probation at the Wales University, where they have studied the low-temperature adsorption forms of oxygen on the surface of carbon supported silver by the electron spectroscopy. At the Laboratory of Synchrotronous Radiation in Darsbery, they have examined the structure of supported catalysts by EXAFS. Joint research on the design and implementation of a novel method - the surface acoustic resonance spectroscopy - was carried out with the Chemical Department of the Cambridge University. Basing on the data obtained, a joint project for the development of this method during 1994-95 was suggested and approved by the Royal Society of UK.

A fruitful collaboration with the Institute of Energy Conversion and Storage (TAE-CNR, Messina) in the program "Catalysis for Solving the Energy Problem" was continued in 1994 in the framework of the agreement between RAS and the National Council on the scientific research of Italy. The joint research on the novel energy-accumulating materials based on chemical heat accumulators and their implementation in heat pumps of adsorption and desorption type was performed. In progress is the work with TAE on the project "Design of Silica Based Monolith Catalysts to Solve Environmental Problems". Joint works on the fine organic synthesis (the University of Bologna) and regiospecificity of supported catalysts during copolymerization of ethylene and propylene (the University of Salerno) ware carried out at the Institute of Catalysis.

BIC also successfully cooperated with various foreign organizations in the framework of bilateral agreements. Together with the Milan University a "Theoretical Study of Zeolites by Quantum Chemistry Methods" was performed. Surface sites of oxide catalysts were studied with IR- and UV-spectroscopies together with the Turin University in the framework of project "Partial Oxidation of Light Hydrocarbons in Fuel Cells", which was supported by INTAS.

The subjects of collaboration with the Fritz-Haber Institute (Berlin, Germany) were considerably extended. In progress are joint works in the field "Study of the Nature of Autooscillations in the Oxidation of Platinum Oxide by Electron Spectroscopy". The research on the "Effect of Adsorption on the Kinetics of Hydrogen Peroxide Oxidation over Silver Poly- and Monocrystal Electrodes" was carried out. The cooperation with the Ruhr University (Bohum, Germany) developed two trends: "Design of Catalysts for the Oxidative Condensation (Dehydrocondensation) of Methane and Light Hydrocarbons" and "Quantum-Chemical Study of Interaction between Small Particles and Oxide Metal Surface". A two-year joint research program with the Institute of Crystallography and Mineralogy of the Frankfurt University "Investigation of Structure of the Reduced Copper Chromite by Neutronography and X-Ray Analysis" was accomplished. The interplay with the Chair of Theoretical Chemistry, Technical University (Munich, Germany) on the project "Spectroscopic Characteristics, Adsorption Properties and Structure of Catalytic Systems" is still in progress. In its framework the researchers have mastered the work with working stations and new supercomputers, developed new quantum-chemical programs and began to calculate the electron structure of a MoS catalyst. A joint project with the German Airspace Institute (DLR, Cologne) "Catalytic Thermochemical Gasification of Solid Organic Feedstock (Biomass) in the Fluidized Bed Reactor, Heated with Concentrated Solar Energy" is prepared.

The cooperation with the research institutions of the Netherlands are determined primarily by the Agreement between BIC and the Leiden University in the “Study of the Mechanism of NO Reduction on Platinum Metals, including under the Autooscillation Regime". As for the Technological University in Delft, the work in "Catalysis by Heteropolyacids and Related Systems" was continued.

In 1994, the cooperation with the Dutch Technical University (Lingby, Denmark) in the field "Study of Alloys of the Active Component of Vanadium Catalysts by NMR", included into the project "Catalysis for the Environment Protection" and supported by INTAS, was in progress.

Together with the Institute of Computational Chemistry (University of Girona, Spain) a study of "Open-Shell SCF Theory for Highly Symmetric Systems" was performed.

Numerous fruitful contacts with researchers and representatives of various companies from the USA, France, Germany, Sweden, South Korea, Singapore, Egypt, etc., were performed. Many scientists from various countries participated in the seminars, conferences and negotiations held by BIC, thus providing an essential contribution to the international cooperation and the development of both fundamental and applied catalysis.

BIC SB RAS PARTICIPATION IN CONFERENCES AND EXHIBITIONS

In 1994, 70 research workers of the Institute of Catalysis took an active part in 27 international conferences, symposia and schools abroad. 12 researchers were the participants of the Russian-American Seminar "Catalysis for Environment Protection" in Wilmington, USA. 8 scientists participated in the 10th International Conference on Zeolites in Berlin, Germany, and 5 presented their reports at the 6th International Symposium "Scientific Basis for Heterogeneous Catalysts Preparation", Louven-la-Neuve, Belgium.

During this year, the Institute organized and performed several seminars and conferences, including "Reverse-Process Technologies", the seminar on Environment Protection in the framework of exhibition "Chemistry-94"; the all-Russia seminar "Actual Problems of Elemental and Molecular Chemical Analysis of Multicomponent Systems".

In April, 1994, the Institute and Association "Siberian Concord", sustained by the Administration of the Novosibirsk Region and "Environmental Planning Group, Inc." (USA), carried out the International Seminar on the Commercialization of Environment Protection Technologies. The Seminar was organized in the framework of Russian-American Agreement to choose environment-saving technologies for the 1st International Conference in Moscow (Russia), dedicated to the commercialization of such technologies.

CAMPUS AND RESIDENCE

The Boreskov Institute of Catalysis is located in Akademgorodok (Scientific Center) at 30 km from Novosibirsk, the largest city in 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 ensuring scientific activity and creativity.

RESEARCH ACTIVITY

QUANTUM-CHEMICAL STUDY OF FOUR-ELECTRON CATALYTIC OXIDATION OF WATER TO DIOXYGEN IN THE PRESENCE OF DINUCLEAR AND TETRANUCLEAR HYDROXIDE COMPLEXES OF COBALT(III) AND IRON(III): CATALYTIC CYCLE INTERMEDIATES AND THEIR RELATIVE ENERGIES

M.Yu. Filatov, G.L. Elizarova, O.V. Gerasimov, G.M. Zhidomirov, V.N. Parmon

J.Molec.Catal.,
91 (1994) 71-82.

Quantum-chemical calculations have elucidated possible intermediates and their relative energies in the closed cycle of catalytic water oxidation to dioxygen by one-electron oxidants. Di- and tetranuclear hydroxocomplexes of Co^{III} and Fe^{III} serve as the simplest prototypes of artificial catalysts for the reaction under study. The predicted intermediates of consecutive one-electron oxidation on a reaction site accompanied by its deprotonation appear to be the analogs of the well-known transition metal complexes with dioxygen ligands. Only one metal ion undergoes the redox transformation that changes its valence from IV to II during the process. Meanwhile, the second metal ion only stablizes the intermediates obtained from the oxidized water molecule. Thus, this confirms the well-known hypothesis on the dinuclear nature of the "oxygen evolving reaction centre". Dioxygen molecule releases most probably after the third oxidation of reaction site. The calculated energies of intermediates participating in the catalytic cycle are in a reasonable agreement with experimental data available.

ANION-RADICAL AND PROTONATED FORMS OF MOLECULAR OZONE. *AB INITIO* CALCULATION ACCOUNTING FOR ELECTRON CORRELATION

I.I. Zakharov, O.I. Kolbasina*, T.N. Semenyuk*, N.F. Tyupalo* (Rubezhansk Dpt. of Chem.-Techn. Inst., Ukraine), G.M. Zhidomirov

Zh.Strukt.Khim.,
34 (1993) 28-32.

The *ab initio* calculations of various electronic states ($^1A_1$, $^3B_2$, $^3A_2$, $^3B_1$) performed used a 4-31G (d, p) basis set. Electron correlation was taken into account with MP4. Geometry of O_3^- and O_3H^+ was obtained. The proton affinity of O_3 appeared to be less by 1 eV than that of H_2O.

AB INITIO CALCULATIONS OF ETHYLENE ADDITION TO METAL-HYDROGEN AND METAL-METHYL BONDS IN HYDRIDES AND ALKYL COMPLEXES OF Ti, Al AND B

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

Kinet.Katal.,
35 (1994) 74-82.

Addition of ethylene to metal-hydrogen and metal-methyl bonds in H_2MR complexes (M = Ti, Al, B, R = H, CH_3) is investigated by *ab initio* SCF MO LCAO quantum-chemical method with a split-valence basis set of the Gaussian functions. The structure of a transition state for coordinated ethylene addition and energy profile for the general reaction of ethylene addition are calculated. The role of electronic and steric factors in this reaction is analyzed using boron complexes. It is shown that the electronic mechanism of ethylene insertion into the M-R bond is determined by the electron density transfer from the σ-bonded orbital of M-R bond to π*-antibonding orbital of ethylene. A concept is suggested that attributes the chemical reactivity of M-R bond to relationship between s-, p- and d-orbital interactions contributing to the bond formation. The activation energy increases as s character increases and decreases as d character increases.

CLUSTER QUANTUM-CHEMICAL STUDY OF CARBON MONOXIDE MOLECULE INTERACTION WITH SURFACE ACID CENTERS OF HIGHLY DISPERSED MAGNESIUM CHLORIDE

N.U. Zhanpeisov, E.A. Paukshtis, G.M. Zhidomirov, V.A. Zakharov

Catal. Lett.,
29 (1994) 209-215.

A modified MINDO/3 method is used to suggest cluster models describing highly disperse magnesium chlorides, which contain all sets of acid sites, i.e. three-, four-, five-coordinated magnesium ions and surface hydroxyl groups. We have considered three types of CO adsorption complexes on magnesium chloride surface. The harmonic oscillator approach was used to calculte the C-O stretching frequencies of these adsorption complexes and the O-H stretching frequencies of hydroxyl groups on magnesium chlorides. The calculated data are in a good agreement with the appropriate experimental and theoretical results.

SCF-MS-Xα CALCULATION FOR THE CORE LEVEL COORDINATION BEHAVIOUR OF LOW-COORDINATED OXYGEN IONS ON THE SURFACE OF MAGNESIUM OXIDE

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

React.Kinet.Catal.Lett.,
51 (1993) 357-364.

The behavior of core O1s levels for low-coordinated (3, 4, 5) oxygen ions on the surface and in the bulk of magnesium oxide has been studied. $Mg_{13}O_{14}^{2-}$ and $Mg_{14}O_{13}^{2+}$ clusters have been calculated by the SCF-MX-Xα method. The binding energies of 1s oxygen states are found to decrease with the lowering coordination. Such a dependence on coordination is attributed to the larger changes in the Madelung potential as compared to those of the pure electron contributions to the binding energy of electron in the oxygen ion. The coordination dependence of ion oxygen charges and relaxation energies is also discussed.

KINETIC PHASE TRANSITION IN SIMPLE REACTIONS ON SOLID SURFACE

V.P.Zhdanov, B.Kasemo* (Department of Applied Physics, Chalmers University of Technology, Göteborg, Sweden)

Surf.Sci.Rep.,
20 (1994) 111-190.

This review is primarily focussed on the first-order kinetic phase transitions related to bistability and resulting in chemical waves. Such transitions predicted and often well described by common mean-field kinetic equations are experimentally observed in rapid surface reactions such as CO or hydrogen oxidation on transition metals under UHV conditions and at atmospheric pressure as well. Continuous kinetic phase transitions in heterogeneous reactions predicted by the Monte Carlo simulations for the systems with a high reaction rate, provided that the adsorbed species are immobile, are also discussed in detail.

HARTREE-FOCK STATES ENERGY SPECTRA FOR ICOSAHEDRAL OPEN-SHELL STRUCTURES WITH ELECTRONIC CONFIGURATIONS g^N (N=1-7)

B.N.Plakhutin

Chem.Phys.Lett.,
227 (1994) 396-400.

We derived the Hartree-Fock energy of states, arising from the molecular open-shell electronic configurations g^N (*dim* g = 4, N = 1-7) of icosahedral symmetry systems. These energies are represented in terms of the integral invariants (reduced electronic repulsion matrix elements), $H^k(g, g)$, which are close by their physical nature to the Slater-Condon parameters $F^k(l, l)$ for an atom with configuration l^N. Similar representations are derived for the electronic repulsion integrals, <mn|m'n'>, over the 4-fold degenerate g-orbitals of "standard assignment".

CLUSTER QUANTUM–CHEMICAL STUDY OF CARBON MONOXIDE MOLECULE INTERACTION WITH SURFACE ACID CENTERS OF HIGHLY DISPERSED MAGNESIUM CHLORIDE

N.U. Zhanpeisov, E.A. Paukshtis, G.M. Zhidomirov, V.A. Zakharov

Catal.Lett.,
29 (1994) 209-216.

Within the MINDO/3 method cluster models giving a description of highly dispersed magnesium chloride containing all sets of acid sites, i.e. three-, four- and five-coordinated magnesium ions, and surface hydroxyl groups have been proposed. Three types of CO adsorption complexes on the magnesium chloride surface have been considered. The C-O stretching frequencies of these adsorption complexes and the O-H stretching frequencies of hydroxyl groups on magnesium chloride calculated by a harmonic oscillator approach are in a good agreement with available experimental and theoretical data.

CLUSTER QUANTUM-CHEMICAL STUDY OF THE INTERACTION OF DIMETHYL METHYL-PHOSPHONATE WITH MAGNESIUM OXIDE

N.U.Zhanpeisov, G.M.Zhidomirov, I.V.Yudanov, K.J.Klabunde (Kansas Univ., Manhattan, Kansas, USA)

J.Phys.Chem.,
98 (1994) 10032-10035.

In the framework of a supermolecular approach using the MINDO/3 method various channels of dimethyl methylphosphonate (DMMP) adsorption on a magnesium oxide surface are considered.

One-center molecular adsorption is energetically more favourable than the two-center molecular adsorption. In the former case the DMMP adsorption occurs via a donor-acceptor interaction between a lone electron pair of oxygen in the -P=O group and a vacant orbital of magnesium cation. This corresponds to the transfer of electron density from the DMMP molecule to a five-coordinated magnesium site. The doisociative adsorption of DMMP takes place over the entire MgO surface and proceeds with a considerable gain in energy as compared to molecular adsorption. This process would be limited only by an ease of access for the fragments of dissociated DMMP molecules on a dehydroxylated magnesium oxide.

On the basis of calculation results a possible mechanism of destructive DMMP decomposition on MgO and some other problems are discussed.

ON THE ROLE OF SURFACE α-OXYGEN IN FORMATION OF CATION RADICALS AT BENZENE ADSORPTION ON ZSM-5 ZEOLITE

A.M. Volodin, V.A. Bolshov, G.I. Panov

J.Phys.Chem.,
98 (1994) 7548-7550.

The role of an atomic oxygen form (α-form) produced during N_2O decomposition on Fe-containing ZSM-5 in conversion of adsorbed benzene molecules was studied by *in situ* ESR technique. We have shown that α-oxygen does not participate in the formation of electron acceptor sites (A_s) responsible for the ionization of aromatic compounds. The ionization process proceeds both in the presence and absence of α-form. In the latter case instead of benzene cation radicals, the ESR spectra show phenol radicals resulting from the benzene oxidation by α-oxygen.

RADICAL INTERMEDIATES IN PHOTOINDUCED FORMATION OF BENZENE CATION RADICALS OVER H-ZSM-5 ZEOLITES

V.A. Bolshov, A.M. Volodin, G.M. Zhidomirov, A.A. Shubin, A.F. Bedilo

J.Phys.Chem.,
98 (1994) 7551-7554.

Radical particles are shown to appear under irradiation (hν > 2.8 eV) of HZSM-5 zeolites with adsorbed benzene. The particles are the benzene cation radical precursors on the zeolite. Heating causes the irreversible destruction of particles and the emergence of benzene cation radical spectrum. The obtained radicals have no detectable hyperfine splittings on protons, their spectrum remaining almost the same when using deuterobenzene. A possible structure of the particles is discussed.

PHOTOSTIMULATED FORMATION OF RADICALS ON OXIDE SURFACES

A.M. Volodin, V.A. Bolshov, T.A. Konovalova

Molec.Eng.,
4 (1994) 201-226.

The article presents the results of *in situ* ESR investigations of the mechanism of photostimulated processes producing radical and ion-radical particle on the surfaces of oxide dielectrics (magnesium, calcium and aluminium oxides, zeolites). Three types of reactions are discussed: (i) formation of oxygen anion-radicals on MgO and CaO surfaces; (ii) formation of benzene cation radicals on ZSM-5 zeolites; (iii) formation of radical particles from aromatic nitro compounds adsorbed on alumina.

Spectral dependences registered and surface active center properties revealed show that coordinatively unsaturated surface sites absorb light in the first system. As for the other processes in question, electron donor-acceptor (EDA) complexes between adsorbed molecules and surface active sites are supposed to be key intermediates.

Three EDA complexes are shown to incorporate the donor solvent molecules as well. In this case the energy characteristics of photoprocesses are substantially determined by the ionization potential of the solvent molecules.

For all reactions, the mechanism of photo and thermostimulated processes are compared and the possibility of their similiraty is discussed.

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

K.I. Zamaraev†

Usp.Khim,
62 (1993) 1051-1063.

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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 the development of new industrial catalysts and catalytic processes. 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.

CONTENTS

THE ACTIVE SITE STRUCTURE IN SUPPORTED PALLADIUM CATALYSTS FOR THE DEEP OXIDATION: EXAFS DATA

D.I. Kochubey, T.G. Starostina, P.G. Tsyrulnikov (Department of Institute of Catalysis, Omsk, Russia), K.I. Zamaraev†

Kinet.Katal.,
34 (1993) 716-720.

The active site structure of supported Pd catalysts for deep oxidation, containing 0.3-0.4 mass.% of Pd, was studied by EXAFS. We studied the catalysts both during the initial state and when the steady-state activity was already attained in the butane oxidation. The catalytic activity of Pd/La-Al_2O_3 catalysts appeared to correlate with the Pd-Pd distances in the oxide structure of an active site.

TETRAHYDROFURANE POLYMERIZATION CATALYZED BY HETEROPOLYACID $H_3PW_{12}O_{40}$ IN THE PRESENCE OF ALCOHOLS

G.M.Maksimov, A.V.Golovin

Vysokomol. Soed.,
36 (1994) 499-502.

^1H NMR was used for studying the products of tetrahydrofurane (THF) polymerzation catalyzed by $H_3PW_{12}O_{40}$ heteropolyacid at 60°C in the presence of mono- and polyalcohols. In the presence of polyalcohols, we have obtained THF copolymers containing polyalcohol fragments both inside the molecule and at its ends. In the presence of monoalcohols, ethers ofTHF homopolymer are formed. As for the propargyl alcohol, a polymer with a triple bond at the molecule end are formed. We tried to syntheze THF copolymers containing some other organic compounds. We think that such copolymers will be obtained if all monomers can interact with a heteropolyacid and then dissolve in the catalyst phase.

ON THE NATURE OF PARAMAGNETISM ARISING IN SiO_2-Al_2O_3-N_2-C SYSTEM AT HIGH TEMPERATURES

S.V. Vosel, A.A. Altynnikov, W.G. Thomas* (Davy Faraday Res. Lab., The Royal Inst. of GB, UK), D.V. Kalinkin, V.F. Anufrienko

Zh.Neorg.Khim.,
39 (1994) 1830-1834.

We have identified two types of EPR symmetric singlet spectra of various width for the alumosilicate system. The spectra of 14-15 G width can be attributed to the metastable phase of carbon and that of 2-6 G to the alumosilicate alloy paramagnetism. EPR signals are presumably caused by the active behavior of nitrogen in the processes. The proper paramagnetism detected in natural alumosilicates may indicate that they form under reduction conditions in the interior of the earth.

COMPLEXES OF Cr(III) AND HETEROPOLY ANIONS $|PW_{11}O_{39}|^{7-}$ OR $|P_2W_{20}O_{70}|^{10-}$: SYNTHESIS AND STATE IN CONCENTRATED SOLUTIONS

L.R. Kravchenko, M.A. Fedotov, R.I. Maksimovskaya, L.I. Kuznetsova

Zh. Neorg.Khim,
39 (1994) 629-634.

We have followed the complex formation of heteropolyanions (HPA) $PW_{11}O^{7-}$ and $P_2W_{20}O_{70}^{10-}$ with an aquanion Cr^{3+} in aqueous solutions by magnetic methods (NMR ^{31}P, ^{17}O, ^{183}W, ^1H, ^{14}N, ^{23}Na, ^{39}K, ESR, magnetic susceptibility). NMR ^{31}P, ^{17}O, ^{183}W was used for characterizing $PW_{11}O_{39}CrL$ and $CrP_2W_{20}O_{70}L_x$ HPA obtained in concentrated solutions. We have isolated tetrabutylammonia (TBA) salts of these HPA. In the acetonitrile solution, HPA $CrP_2W_{20}O_{70}$ appeared to contain Na^+ and K^+.

CATALYTIC PROPERTIES AND THE PHASE COMPOSITION OF PRODUCTS OF THE PHOSPHORUS-MOLYBDENUM HETEROPOLYACID THERMAL DECOMPOSITION. I. PHOSPHORUS - MOLYBDENUM HETEROPOLYACID THERMAL DECOMPOSITION

V.M. Bondareva, T.V. Andrushkevich,
R.I. Maksimovskaya, L.M. Plyasova, A.V. Ziborov,
G.S. Litvak, L.G. Detusheva

Kinet.Katal.,
35 (1994) 129-134.

Using *in situ* XPD, NMR ^{31}P of solid samples and solutions as well as the thermal analysis have enabled us to study the thermal decomposition of $H_3PMo_{12}O_{40} \cdot 13H_2O$. We have suggested a scheme of the heteropolyacid conversion and identified the intermediates, aqueous free $H_3PMo_{12}O_{40}$ and anhydride $H_xPMo_{12}O_{38.5+x}$ ($x \approx 0.1$), oxide form $(PMo_{12}O_{38.5})_n$ and the end products, trioxide of molybdenum promoted by phosphorus and molybdenyl pirophosphate $(MoO_2)_2P_2O_7$.

REVERSE NITRO-NITROSO CONVERSIONS IN RUTHENIUM(II) COMPLEXES: NMR ^{15}N, ^{17}O AND ^{99}Ru STUDIES

V.A.Emelyanov, M.A.Fedotov, A.V.Belyaev

Zh.Neorg.Khim.,
38 (1994) 1842-1848.

NMR ^{99}Ru, ^{15}N and ^{17}O was used for studying the conversion of $[RuNO(NO_2)_4OH]^{2-}$ and $[Ru(NO_2)_6]^{4-}$ in aqueous alkaline solutions of $NaNO_2$. We have found the dominating complex forms under these conditions and suggested a mechanism of the reverse formation of $[Ru(NO_2)_6]^{4-}$.

NMR OF VARIOUS NUCLEI FOR STUDYING THE HYDROLYTIC POLYCONDENSATION OF AQUA IONS IN MIXED SOLUTIONS OF Al(III) AND Cr(III) NITRATES

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

Zh.Neorg.Khim.,
38 (1994) 1849-1854.

Hydrolytic polycondensation of Cr(III), Al(III) was investigated in mixed solutions of nitrates by NMR ^{14}N, ^{27}Al, ^{2}D, ^{1}H and the static magnetic susceptibility method. Unlike binar systems Al(III)-Fe(III), Al(III)-Co(II) and Al(III)-Ni(II), the hydrolytic polycondensation of Al(III) and Cr(III) proceeds concurrently, irrespectively of the component correlation. Cr(III) ions prevent the formation of the hydroxy complex $[Al_{13}(OH)_{32}(H_2O)_8]^{7+}$.

THE COMPOSITION OF 12-MOLYBDOPHOSPHOROUS HETEROPOLYACID THERMOLYSIS PRODUCTS DETERMINED BY WATER LEACHING AND NMR ^{31}P

R.I. Maksimovskaya, V.M. Bondareva

Zh.Neorg.Khim.,
39 (1994) 1298-1306.

NMR ^{31}P method was used to determine Mo/P = 1/1 and 12/1 ratios in the two water-soluble phases, formed during $H_3PMo_{12}O_{40}$ heating at 400-470°C. They were identified as $(MoO_2)_2P_2O_7$ and $[PMo_{12}O_{39}^-]$ $[PMo_{12}O_{38}^+]$ respectively. Spectrum of the 12/1 phase exhibited a signal of $\delta = -24.3$ ppm, which was attributed to the "heteropolycation" $PMo_{12}O_{38}^+$. After heating at 500-700°C, the phase 1/1 alone and a lowly soluble MoO_3 preserve.

ELECTRODIALYSIS FOR THE SYNTHESIS OF HETEROPOLYACIDS

G.M. Maksimov, R.I. Maksimovskaya, I.V. Kozhevnikov

Zh.Neorg.Khim.,
39 (1994) 623-628.

We have estimated the electrodialysis potentials for the synthesis of heteropolyacid (HPA) solutions of various composition and structure: $H_{3+n}PM_{12-n}(V, Nb)_nO_{40}$, $H_6P_2M_{18}O_{62}$, $H_xPMo_{11}XO_{39}$, $H_xSiW_{11}XO_{39}$ ($X=Pd^{2+}$, Rh^{3+}, Fe^{3+}, Cu^{2+}, Cr^{3+}, Co^{3+}, Ni^{2+}), $H_xXM_6O_{24}$ ($X = Te^{6+}$, Co^{3+}, Cr^{3+}, Ga^{3+}), $H_6XM_9O_{32}$ (X^{4+}=Ni, Mn), $H_8XW_{10}O_{36}$ (X^{4+}=Ce, U, Sn), $H_{15}P_5W_{30}O_{110}$ (M^+ = W, Mo) and in the systems of $X-W^{6+}$ ($X = Te^{4+}$, S^{4+}, Se^{4+}, Sb^{3+}, As^{3+}, Bi^{3+}, P^+). The synthesis products were analysed by NMR ^{31}P, ^{183}W, ^{17}O and IR spectroscopy. The yields of α-$H_6P_2M_{18}O_{62}$, $H_3PMo_6O_{40}$, $H_8CoMo_6O_{24}$, $H_{3+n}PM_{12-n}(V,Nb)_nO_{40}$ (n=1, 2) and of $H_6As_2W_{21}O_{69}$-$H_7AsH_2W_{18}O_{60}$ mixture were close to the quantitative one. In other cases, HPA either partially or completely decomposes. We conclude that the electrodialysis method is very attractive for the synthesis of HPA, as stable concentrated aqueous solutions.

NMR ISOTROPIC SHIFT OF NITROGEN AND CARBON NUCLEI IN PARAMAGNETIC COMPLEXES OF NICKEL AND COBALT

A.V. Kessenikh (Res. Inst. Chem.&Esp. Pure Chem. Subst., Moscow, Russia), A. Atayev, B.N.Plakhutin, M.A.Fedotov

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

Using NMR ^{14}N and ^{13}C we have experimentally studied isotropic paramagnetic shifts (IPS) of NMR trialkylpyrasole in dihalogenide complexes of Ni and Co (d^8-d^7 configuration). In the present paper we compare our results to the calculated values of Fermi-contact term into the shift, which were obtained via the Hartree-Fock method unrestricted towards spin in the INDO approximation. The methods of signals assignment in the NMR ^{13}C spectra of ring pyrasole carbons base on the correlation of data for the complexes studied with the experimental results obtained for the labile paramagnetic adducts of the same ligand. The IPS value of the coordinated metal 2N consists adequately with the simplified calculation.

MONOCYCLIC COMPLEXES FORMED BY PLATINUM(II) OR PALLADIUM(II) WITH AMINOACIDS OF THE GLYCINE SERIES

L.F. Krylova, L.D. Dikanskaya, M.A. Fedotov

Koord.Khim.,
20 (1994) 57-59.

In order to synthesize monocyclic amino acid complexes $K[MLCl_2]$, we have used reaction $K_2PtCl_4 + LH$ (1:1) for M = Pt, L = Am, Ser and of $PdCl_2+LH+KHCO_3$ (1:1:1) for M = Pd, L = Gly, Am, Ser, Sar, which proceed in the aqueous solution. Here Gly, Am, Ser and Sar are anions of glycine, aminobutyric acid, serine and sarcosine respectively. All complexes were characterized by the elemental analysis. We discuss the reaction mechanism. NMR spectra on ^{195}Pt, ^{14}N, ^{17}O and ^{35}Cl nuclei of aqueous solutions of complexes were recorded. In the aqueous solution, H_2O molecule appears to substitute Cl^- in coordinates N-M-Cl.

MONOHISTIDINE COMPLEXES OF PLATINUM(II) AND PALLADIUM(II)

L.F. Krylova, L.D. Dikanskaya, M.A. Fedotov

Koord.Khim.,
20 (1994) 780-785.

The interaction between K_2MCl_4 (M = Pt, Pd) and histidine (HisH) (1:1) in an aqueous solution has been studied. $[M(His)Cl(H_2O)]$ (I, II), $[Pt(HisH)Cl_2]$ (III), $[Pt(HisH_2)Cl_3]$, $HisH_3[MCl_4]$ were obtained. NMR ^1H, ^{14}N, ^{195}Pt and IR spectra of these complexes were recorded. Complexes I and II appeared to have the same composition, with the tautomer forms of His^-. Mixture II was divided into components. We have found the coordination of HisH in III to be similar to that in the known palladium analog. In complex $[Pt(HisH_2)Cl_3]$, cation $HisH_2^+$ is as monodentate ligand coordinated through the tertiary nitrogen atom of the heterocycle.

STILBENE EPOXIDATION WITH t-BUTYL HYDROPEROXIDE AND HYDROGEN PEROXIDE CATALYZED BY TRANSITION METAL SUBSTITUTED HETEROPOLY TUNGSTATES

O.A. Kholdeeva, G.M. Maksimov, M.A. Fedotov, V.A. Grigoriev

React.Kinet.Catal.Lett.,
53 (1994) 331-338.

Tetra-n-butylammonium salts of transition metal substituted heteropolytungstates, $PW_{11}MO_{39}^{n-}$, catalyze the epoxidation of stilbenes by t-butyl hydroperoxide (M = Co^{II}, Mn^{II}, Cu^{II}, Ti^{IV}, Ru^{IV}, V^V, Nb^V) and hydrogen peroxide (M = Zr^{IV}) in acetonitrile. Epoxidation of cis-stilbene is nonstereospecific.

CHEMISTRY IN THE SECOND COORDINATION SPHERE OF METAL COMPLEXES

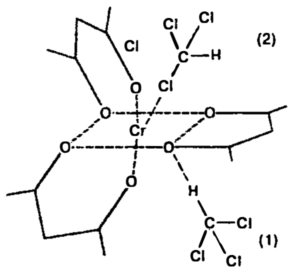
K.I. Zamaraev†

New J.Chem.,
18 (1994) 3-18.

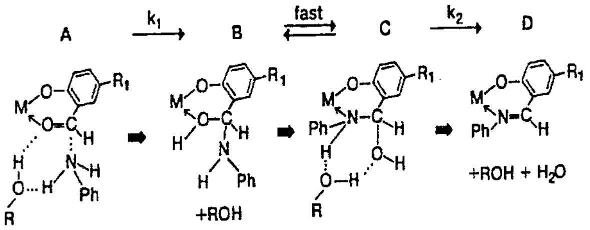
Chemistry in the second coordination sphere of electrically neutral metal complexes ML_n in organic solvents is discussed with particular emphasis on:

(1) composition and stability of the outer-sphere complexes (coordination numbers, stability constants, enthalpies and entropies of formation); (2) life times of the outer-sphere complexes; (3) structure of the outer-sphere complexes; (4) nature of the outer-sphere coordination bonds; (5) effect of the outer-sphere coordination on the structure and physico-chemical properties of ML; (6) reactions in the outer coordination sphere.

Typical examples of an outer-sphere complex (OSC) and reaction in the second coordination sphere of a metal complex are given in the figures below.



The structure of the OSCs of $CHCl_3$ with $Cr(acac)_3$. H-complex - (1); X-complex - (2).



The mechanism of the Schiff base formation in the coordination sphere of metal atoms. The reaction proceeds via the outer-sphere coordination of the NH_2Ph reagent and is catalyzed by ROH as another outer-sphere ligand. M = Cu(II), Zn(II), or Ni(II); R = CH_3, R_1 = H, Cl, Br or NO_2. The second chelate ligand and axial ligand(s) B are not shown.

PECULIARITIES OF ESR SPECTRA OF V-Ti OXIDE SYSTEMS

A.A. Altynnikov, G.A. Zenkovets, V.F. Anufrienko

React.Kinet.Catal.Lett.,
52 (1994) 59-63.

ESR analysis of 1-20 wt.% V_2O_5 samples heated at 700-950°C has revealed the formation of V^{4+} ion clusters upon V^{4+} ion stabilization in Ti^{4+} substitution points of rutile.

ESR STUDY OF ORDERED Ti(III) CLUSTERS IN FROZEN SOLUTIONS

A.A. Altynnikov, O.V. Kalinkina, V.F. Anufrienko

React.Kinet.Catal.Lett.,
52 (1994) 261-267.

The ESR spectrum of exchange-coupled Ti^{3+} ions of $g_\perp < g_\parallel \cong g_e$ has been observed in dissociation products of metallic titanium in HCl, evidencing the formation of chloride clusters of mutually ordered Ti^{3+} ions in d_z2-ground state in distorted tetrahedral coordination. The cooperative Jahn-Teller effect (CJTE) defines orbital ordering of the d^1 of Ti^{3+} ions in the cluster.

IN SITU STUDIES OF HETEROGENEOUS CATALYSIS: DIFFRACTOMETRIC AND SPECTROSCOPIC APPROACHES

J.M. Thomas (Davy Faraday Res. Lab., The Royal Inst. of GB, UK), K.I. Zamaraev†

Topics in Catalysis
1(1994) 1-8.

Lessons are drawn from the work of molecular biologists who have succeded in elecucidating the mechanisms of many enzymes from X-ray crystallographic analyses of data recorded on the catalyst-reactant system prior to and after catalytic reaction. The use of *in situ* infrared spectroscopy to clarify the processes of adsorption and catalytic reactions on uniform heterogeneous catalysts is exemplified through a series of studies of the dehydration of the four isomers of butanol over H-ZSM-5.

POSSIBLE IMPACT OF HETEROGENEOUS PHOTOCATALYSIS ON THE GLOBAL CHEMISTRY OF THE EARTH'S ATMOSPHERE

K.I. Zamaraev†, M.I. Khramov, V.N. Parmon

Catal.Rev.-Sci.Eng.,
36 (1994) 617-644.

A possible impact of heterogeneous photocatalytic processes on the Global Chemistry of the Earth Atmosphere is discussed. These processes can occur in the atmosphere near the surface of Earth on dust particles under the action of ultraviolet, visible and even near infrared solar light. Quantitative estimates suggest that these so far neglected indirect photochemical reactions are perhaps not less important for the chemistry of the atmosphere than the well-known direct photochemical reactions that proceed in the upper layers of the atmosphere under the action of far ultraviolet light.

MECHANISTIC STUDY OF *sec*-BUTYL ALCOHOL DEHYDRATION ON ZEOLITE H-ZSM-5 AND AMORPHOUS ALUMINOSILICATE

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J.Chem.Soc.Faraday Trans.,
90 (1994) 2147-2153.

The dehydration of *sec*-butyl alcohol has been studied by *in situ* FTIR and gas-chromatographic (GS) kinetic methods in the range 60-140°C on zeolite H-ZSM-5 and amorphous aluminosilicate (AAS) samples with a well characterized number and strength of Bronsted acid sites. Under flow conditions (GC kinetic studies), the reaction yields butenes [but-1-ene, (Z)- and (E)-but-2-ene] and water, with an activation energy 40±1 kcal mol^{-1} determined from steady-state data. Under non-steady-state conditions, the so-called "stop effect" is observed: namely, an increase in the rate of butene evolution (as compared with that at steady state) when the flow of alcohol into the reactor is halted. The course of dehydration on HZSM-5 in a static IR cell was followed by the appearance and growth of a peak for adsorbed water (water deformation peak at 1640 cm^{-1}). The rate constant determined from the kinetics of water formation in the FTIR experiments (1.1×10^{-3} s^{-1} at 70°C) is found to be 400 times as high as the rate constant calculated from GC steady-state kinetic data. All these anomalous phenomena observed under flow conditions (the flow rate of reaction, the high activation energy and the "stop effect") can be explained by the slowing down of dehydration under these conditions as a result of the reverse reaction, i.e. the hydration of the product butene with product water. When the zeolite pores are free from physically adsorbed reactants (in the FTIR experiments during the "stop effect"), the extent of the reverse reaction decreases and the rate of butene formation increases. On AAS, which has acid sites of similar strength, but which has a much more open surface (average pore diameter ca. 50 Å compared with 5.5 Å for ZSM-5) similar effects are observed, but they are much less pronounced. This probably arises from the lower reactant concentration in the AAS at steady-state and hence, a lower concentration of water in the vicinity of the active sites.

DEHYDRATION OF *n*-BUTANOL ON ZEOLITE H-ZSM-5 AND AMORPHOUS ALUMINOSILICATE: DETAILED MECHANISTIC STUDY AND THE EFFECT OF PORE CONFINEMENT

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J.Catal.,
149 (1994) 36-51.

This study of the catalytic dehydration of *n*-butanol on zeolite H-ZSM-5 and amorphous aluminosilicate confirms the reaction scheme proposed earlier by the authors for isobutal dehydration. The rate constant for *n*-butanol dehydration on H-ZSM-5 (determined from *in situ* FTIR kinetic studies by monitoring the growth of the water deformation peak at 1640 cm^{-1}) is shown to be the true dehydration rate constant (1.7×10^{-4}s^{-1} at 100°C). On the other hand, the rate constants determined from GC steady-state kinetic studies (temperature interval 105-185°C) are effective ones, giving activation energies 22±2 kcal/mol and 33±2 kcal/mol for complete dehydration and dehydration to butene only, respectively. By studying the dehydration reaction under different conditions (flow and static reactors, steady-state and non-steady-state regimes) and on samples with rather similar acid strengths but different porous systems (H-ZSM-5 microporous channels with diameter ~ 5.5 Å, and amorphous aluminosilicate pores of average diameter ~ 50 Å), it was shown that depending on the concentration of butanol in the immediate vicinity of the active alkoxide intermediate $\exists\text{-}OC_4H_9$, different reaction paths are utilized. High concentrations of alcohol favour ether formation, whereas low ones favour butene. This also explains the so-called "stop effect" observed in GC experiments, where an increase in the rate of butene formation occurs when the flow of alcohol is stopped and replaced with a flow of pure helium. Here, decreasing the concentration of alcohol in the micropores results in more of the alkoxide intermediate transforming to butene rather than to ether (which was the case at steady state).

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

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Magnetic Reson. Chem.,
32 (1994) 16-23.

The molecular mobility and dehydration reaction of tert-butyl alcohol, selectively deuteriated in the methyl groups ($(t\text{-BuOH})[2\text{-}^2H_9]$, dTBA), absorbed on H-ZSM-5 zeolite was studied using ^2H 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 $2.7 \pm 1.2^\circ$ compared with the same angle in solid dTBA. This is explained by location of the alcohol molecules at channel interactions of the zeolite, whose dimensions exceed those of the dTBA molecule. The lifetime of the dTBA molecule at these adsorption sites exceeds 1×10^{-5} s. The observed reaction products are deuteriated water with an unusual ^2H NMR lineshape and two types of butene oligomers: less mobile species with the lineshape typical of solid-state ^2H NMR and more mobile species with a liquid-like lineshape. The number of more mobile species increases with increase in temperature. In addition, ^2H NMR indicates the presence of *tert*-butyl groups in the reaction products. For oligomers with a liquid-like shape, the diffusion coefficient D is $3 \times 10^{-13} m^2 s^{-1}$ at 373 K, whereas for oligomers with a solid-like lineshape $D << 5 \cdot 10^{-14} m^2 s^{-1}$ at 173-373 K. The diffusion coefficient for the *t*-BuOH molecule was estimated as $D << 2 \cdot 10^{-14} m^2 s^{-1}$ within the temperature range 173-296 K.

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

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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 ^2H NMR, the proton of the acidic ≡Al-OH-Si≡ group of the zeolite is transferred into the CH_2= group of the octene-1 molecule. (2) According to ^{13}C NMR the ^{13}C label inserted into the terminal CH_2= group of the octene-1 molecule is scrambled over its hydrocarbon skeleton. Thermodynamic and kinetic parameters for carbon scrambling are measured within the temperature range 290-343 K. The zeolite framework is shown to favour the formation of the linear rather than branched carbenium ion.

REVERSE OSMOSIS FOR SEPARATION OF REACTION SOLUTIONS IN HOMOGENEOUS CATALYSIS

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J.Membrane Sci.,
86 (1994) 37-45.

The potential of reverse osmosis (RO) in separation of soluble homogeneous catalysts from reaction products were studied. Two environmentally important liquid phase processes were considered: (A) detoxication of NO and H_2S catalyzed by iron-containing phosphotungstate heteropoly anion $PW_{11}Fe^{II}(H_2O)O_{39}^{5-}$:

$$2NO + 2O_2 + H_2S \rightarrow 2HNO_3 + S$$

and (B) detoxication of the water soluble sulphides catalyzed by the sodium salt of tetra(sulphophthalocyanine)cobalt(II):

$$S^{2-} + O_2 \rightarrow (S, SO_3^{2-}, SO_4^{2-}, S_2O_3^{2-})$$

For reaction (A), the RO retention of the NO_3^- product was found to decrease with the concentration of the heteropoly anion catalyst, reaching negative values, whereas the retention of the catalyst amounted to 99%. Due to the negative retention of the nitrate ions and high positive retention of the catalyst, their efficient separation was achieved. For reaction (B), RO allowed to retain the catalyst almost completely (retention exceeded 99.9%), while the products (sulphur-containing anions) exhibited markedly lower retentions.

For both reactions, the structure and activity of the catalysts remained unchanged after the RO separation, thus enabling their multifold re-use.

SEPERATION OF ETHYLENE AND ETHANE OVER POLYPHENYLENEOXIDES MEMBRANES: TRANSIENT INCREASE OF SELECTIVITY

O.M. Ilinich, K.I. Zamaraev[†]

J.Membrane Sci.,
82 (1993) 149-155.

A transient increase of the separation factor α-C_2H_4/C_2H_6 was observed upon a rapid increase of the pressure of an ethylene-ethane mixture over homogeneous membranes made of poly-phenyleneoxides. Separation factors as high as 20-50 were achieved with the relaxation time being close to 100-200 min for 60-70 micrometer thick films. The reasons for the increased permselectivity of polyphenyleneoxides towards olefins are discussed.

FOURIER TRANSFORM ION CYCLOTRON RESONANCE STUDIES OF GAS-PHASE REACTIONS BETWEEN TUNGSTEN IONS AND HYDROCARBONS

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Organometallics,
13 (1994) 2536-2538.

Fourier Transform Ion Cyclotron Resonance Spectrometry (FT/ICRS) has been used for the gas-phase study of the interaction between singly-charged positive tungsten ions W^+ and hydrocarbons (C_2-C_9, alkenes C_2-C_6, cycloalkenes C_3-C_6). For most of the hydrocarbons, dehydrogenation without carbon skeleton destruction was almost the only reaction pathway. The number of H_2 molecules eliminated depends on the size and type of hydrocarbon and varies from 1 to 6. Significant amounts of C-C cleavage products have been found in the cases of cyclopropane and 2-methylpropane only. Reaction products distributions for these two hydrocarbons suggest that certain deviations from classical mechanisms (C-H or C-C insertion/shift of *b*-H atom/H_2 or alkane elimination) are observed.

^{51}V NMR AND EPR STUDY OF THE MECHANISTIC DETAILS OF OXIDATION WITH $VO(O_2)(Pic)(H_2O)_2$

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J.Molec.Catal.,
92 (1994) 245-255.

Using ^{51}V NMR, it was shown that peroxo complex $(VO)(O_2)(Pic)(H_2O)_2$ (Pic = picolinic acid) exists in CH_3CN, MeOH and H_2O in the form of $VO(O_2)(Pic)H_2O \cdot CH_3CN$, $VO(O_2)(Pic)H_2O \cdot MeOH$ and $VO(O_2)(Pic)(H_2O)_2$, respectively. To elucidate the nature of reactivity of vanadium peroxo complexes of $VO(O_2)(Pic)H_2O \cdot S$ family towards hydrocarbons their interactions with spin trap 3,3,5,5-tetramethyl-pyrroline-N-oxide (TMPO) were investigated by EPR. Only the peroxo complex $VO(O_2)(Pic)H_2O \cdot CH_3CN$ was reactive towards the hydrocarbons and the spin trap. This complex can abstract the β-hydrogen atom from TMPO (V^V reduces to V^{IV} by this reaction). Such hydrogen atom abstraction was not observed for the other radical species studied (free radicals $OH^\bullet$ ($HO_2^\bullet$), $RO^\bullet$ ($RO_2^\bullet$) and superoxo complex $Pd_3(OAc)_5O_2$). The latter species form with TMPO a spin adduct by addition to the double bond. The data provide evidence, that the diradical species V^{IV}-O-O are active particles of oxidation by $VO(O_2)(Pic)H_2O \cdot CH_3CN$.

Deactivation of $VO(O_2)(Pic)H_2O \cdot CH_3CN$ upon substitution of CH_3CN by stronger σ-donor ligands (e.g., H_2O, MeOH, DMF) may be caused by prevention of electron transfer from the peroxo group to the metal to give V^{IV}-O-O. Vanadium(V) superoxo complex $V^V(O_2^{\bullet-})$ detected by EPR in a solution of $VO(O_2)(Pic)(H_2O)_2$ in 30% H_2O_2 was inert towards alkenes and spin traps.

^{1}H MAS NMR STUDIES OF ALUMINA-SUPPORTED METAL OXIDE CATALYSTS

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J.Phys.Chem.,
98 (1994) 13621-13624.

The interaction of two-dimensional vanadium oxide and molybdenum oxide overlayers with the surface hydroxyls of an alumina support were examined with ^{1}H MAS NMR spectroscopy. The measurements demonstrated that these surface metal oxide overlayers are homogeneously distributed over the alumina surface and essentially titrate all the accessible surface hydroxyls at monolayer coverage. The investigation also revealed that there are a small number of protons formed near monolayer coverage, suspected of being Bronsted acid sites, which are not titrated by these metal oxide overlayers and are capable of undergoing H/D exchange. In addition, there are protons in blocked pores of the alumina support that neither are accessible to be the metal oxide overlayers nor are capable of undergoing H/D exchange. The present ^{1}H MAS NMR results are in excellent agreement with the corresponding IR spectroscopy results on the same catalysts.

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

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

The porous structure of a number of silica gels is characterized by ^{129}Xe NMR of adsorbed xenon. On the basis of expeimental data for the samples with well defined structure, an empirical correlation between the ^{129}Xe NMR chemical shift and the parameters of the porous structure is proposed. The energetic parameterts of xenon adsorption have been studied from the temperature dependence of the chemical shifts. The possibilities and limitations of ^{129}Xe NMR spectroscopy of adsorbed xenon for studying the porous structure of silica gel are discussed.

ZSM-5 ZEOLITE MODIFIED WITH VANADYL IONS

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Zeolites,
14 (1994) 629-634.

Properties of the ZSM-5 zeolite modified with VO^{2+} ions in a one-step exchange reaction in water medium have been investigated. Physico-chemical characterization (chemical analysis, XRD, MAS NMR, ESR) shows that during the preparation the ZSM-5 zeolite structure remains preserved and the vanadyl ions enter the zeolite structure. Sample acidity is of Bronsted and Lewis types and can be reduced by treatment with NaCl solution. Doping with vanadyl ions produces catalysts active in ammoxidation of *m*-xylene.

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

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J.Molec.Catal.,
87 (1994) 57-66.

^{51}V and ^{1}H solid-state NMR data show the formation of a number of surface tetrahedral and octahedral V complexes, whose types depend on the sequence of titanium deposition, in V_2O_5-TiO_2-SiO_2 catalysts. From ^{1}H NMR MAS data follows that V_2O_5 interacts both with SiO_2 and TiO_2, while in the SiO_2-TiO_2 system, large amounts of TiO_2-like species are formed. The latter interact with V species supported either before or after TiO_2 deposition. It was found from ^{51}V NMR data that the structure of surface V complexes depends on the sequence of V and Ti deposition. The formation of several surface tetrahedral and octahedral complexes as well as of two types of mixed triple V-Ti-Si complexes on SiO_2 surface has been observed. The latter are of two types: (1) formed after Ti deposition on SiO_2 surface, which already contains supported V species and can be attributed to V atoms in highly distorted tetrahedral environment. (2) belong to V in nearly regular tetrahedral environment and are formed after simultaneous deposition of V and Ti on SiO_2 surface.

The treatment of catalysts in reaction H_2S+O_2 results in the reduction of both tetrahedral and octahedral V species, with tetrahedral V being more stable in the Claus reaction, but comparison with catalytic data is necessary to reveal which types of complexes are responsible for the catalytic activity.

^{1}H and ^{51}V HIGH-RESOLUTION SOLID STATE NUCLEAR MAGNETIC RESONANCE STUDIES OF SUPPORTED V_2O_5/TiO_2 CATALYSTS

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J.Molec.Catal.,
88 (1994) 311-324.

^{1}H solid state NMR data show the existence of several types of hydroxyl groups on TiO_2 surface, depending on the surface impurities. $VOCl_3$ selectively interacts with these groups. According to ^{51}V NMR data, the structure of the surface vanadium complexes, independently of the preparation method, is determined by the type of surface hydroxyls. On clean TiO_2 surface at low vanadium concentrations, two types of surface complexes with vanadium in the distrorted tetrahedral environment of oxygen atoms are formed. One of them contains OH groups in the coordination sphere. At high V contents, the associated species with V in the octahedral coordination are formed.

LONG-TERM STABILITY OF THE V_2O_5/Al_2O_3 CATALYST FOR THE SELECTIVE REDUCTION OF NITROGEN OXIDES

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Catal.Lett.,
28 (1994) 25-31.

Changes of the V_2O_5/Al_2O_3 catalyst aged for up to 10 years under real conditions of the selective catalytic reduction of NO_x by ammonia (SCR) at the tail gases of the nitric acid plant were characterized by ^{51}V NMR spectroscopy, porosimetry, temperature programmed reduction (TPR) and catalytic activity measurements. The catalytic activity and the redox properties of the catalyst were found intact. Only small variations of the ratio of the octahedral and tetrahedral vanadia species were documented by ^{51}V NMR on aged catalyst.

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

M.Yu. Smirnov, V.V. Gorodetskii

Catal.Lett.,
19 (1993) 233-238.

The reaction between isolated carbon atoms and nitrogen oxide molecules in the adlayer on Pt(111) surface has been studied. Carbon atoms have been deposited on the surface from the special source. The reaction was found to proceed at T ca 100 K and to provide, at least, two intermediate surface species, which have been assigned to adsorbed isocyanate NCO_{ads} and fulminate CNO_{ads} particles. Both intermediate dissociated into on-top state of CO_{ads} and N_{ads} under heating to $T < 300$ K.

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

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J.Chem.Phys.,
100 (1994) 6907-6914.

Elementary steps of the CO oxidation - which are important for understanding the oscillatory behavior of this catalytic reaction - are investigated simultaneously on different Pt-single crystal surfaces by field ion microscopy. Due to preferential ionization probabilities of oxygen as imaging gas on those surface sites, which are adsorbed with oxygen, these sites can be imaged in a lateral resolution on the atomic scale. In the titration reaction a Co_{ads}-precovered field emitter surface reacts with gaseous oxygen adsorbed from the gas phase or, vice versa, the O_{ads}-precovered surface with carbon monoxide adsorbed from the gas phase. The competition of the manifold of single crystal planes exposed to the titration reaction at the field emitter tip is studied. The surface specificity can be documented in the specific reaction delay times of the different planes and in the propagation rates of the reaction-diffusion wave fronts measured on these individual planes during the titration reaction with a time resolution of 40 ms. At 300 K the CO_{ads}-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 fronts move with a velocity of 8 Å/s at {012}, with ca. 0.8 Å/s at {111}, and have a very fast "switch-on" reaction at the (001) plane with 500 Å/s. At higher temperature, T = 350 K, an acceleration of reaction rates is combined with shorter delay times. The titration reaction of a precovered O_{ads} surface with CO_{gas} at T = 373 K shows the formation of CO islands starting in the {011} regions with a quickly moving reaction front into the other surface areas without showing particular delay times for different surface symmetries. The two reverse titration reactions have a largely different character. The titration of CO_{ads} with oxygen adsorbed from the gas phase consists of three different steps, (i) the induction times, (ii) the highly surface specific reaction, and (iii) different rates of wave front propagation. The reaction of CO_{gas} with a precovered O_{ads} layer on the other hand starts with nucleating islands around the {001} planes from where the whole emitter surface is populated with CO_{ads} without pronounced surface specificity.

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

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J.Chem.Phys.,
100 (1994) 6915-6922.

The oscillating CO oxidation is investigated on a Pt-field emitter tip by using the field ion mode of surface imaging of O_{ad} sites with O_2 as imaging gas. Based on data of the titration reactions (V.Gorodetskii et al., J.Chem.Phys., 100 (1994) 6907), external control parameters for the regions of bistability and of self-sustained isothermal oscillations could be found. On a field emitter tip, oscillations can be generated in a rather large parameter space. The anticlockwise hysteresis of O_2^+ ion currents in temperature cycles occurs in agreement with results on single crystal planes. Unexpected regular oscillation sequences could occasionally be obtained on the small surface areas of a field emitter tip and measured as function of the CO partial pressure and of the temperature. Different stages within oscillating cycles were documented by field ion images. Oscillations of total ion currents are correlated with variations in the spatial brightness of field ion images. In the manifold of single crystal planes of a field emitter {331} planes around the {011} regions are starting points for oscillations which mainly proceed along [100] vecinals. This excludes the {111} regions from autonomous oscillations. With slightly increased CO partial pressures fast local oscillations at a few hundred surface sites of the Pt(001) plane display short-living CO islands of 40 and 50 Å diameter. Temporal oscillations of the total O_2^+ ion current are mainly caused by surface plane specific spatial oscillations. The synchronization is achieved by diffusion reaction fronts rather than by gas phase synchronization.

HYDROGENATION OF ISOLATED ATOMS AND SMALL CLUSTERS OF CARBON ON Pt(111) SURFACE: HREELS/TDS STUDIES

M.Yu. Smirnov, V.V. Gorodetskii, A.R. Cholach, D.Yu. Zemlyanov

Surface Sci.,
311 (1994) 308-321.

The reaction of hydrogen with isolated atoms and small clusters of carbon adsorbed on Pt(111) surface was investigated by HREELS and TDS. The carbon adsorption layers were prepared by evaporation of carbon atoms onto the metal surface cooled down to 100 K. The surface carbon produced by this method reveals a high activity towards hydrogen: the reaction occurs at T≥170 K. The initial carbon concentration is found to determine the chemical content of products in the adlayer. At $n_C < 2\times10^{14}$ at/cm^2, when isolated atoms C_{ads} prevail in the initial adlayer, methine CH_{ads} formation is chiefly observed revealing two bands in HREELS: δ(CH) at 800 and ν(CH) at 2960 cm^{-1}. The CH_{ads} particles dissociate at 510 K leading to hydrogen evolution and formation of carbon islands with a graphite-like structure. At higher concentration, the carbon adlayer contains small clusters $C_{x_{ads}}$ in addition to the isolated atoms leading to more complex reaction products. An ethylidyne species $\geqslant$C-CH_3, is detected among the products with characteristic bands $\delta_s(CH_3)$ at 1360 and ν(CC) at 1130 cm^{-1}. It is assumed that ethylidyne molecules are produced in the course of a consecutive hydrogenation of the $C_{2_{ads}}$ cluster. Dehydrogenation of hydrocarbon surface species causes hydrogen evolution at T = 350, 410, 450, 510 and 600-700 K. Ethylidyne dissociation is associated with the desorption peak at T = 450 K: and ethynyl CCH_{ads} being the product. It is shown that the highest temperature stage of the dehydrogenation in the adlayer occurring at T > 600 K is accompanied by an increase of the carbon content in the C_xCH_{ads} molecules, finally resulting in the formation of islands with a graphite-like structure.

IMAGING THE OSCILLATING CO OXIDATION ON Pt-SURFACES WITH FIELD ION MICROSCOPY

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Catal.Lett.,
19 (1993) 223-231.

The oxidation of carbon monoxide on platinum surfaces is investigated by field microscopy (FIM) and compared to earlier work by field electron microscopy (FEM). The reaction gas is used as the field ion imaging gas at pressures of $< 10^{-4}$ mbar and at temperatures of the catalytic reaction. In FIM the surface is imaged by O_2^+ ions which are preferentially ionized at oxygen-covered surface areas. During temperature variations regions of bistability could be detected by FEM and FIM. Finally self-sustained isothermal oscillations of the catalytic CO oxidation could be measured from the periodic fluctuations of the O_2^+ field ion current. Atomic resulution shows that the Pt(331) planes are the pace makers of the oscillation.

NO ADSORPTION ON UNRECONSTRUCTED AND RECONSTRUCTED Pt(100) SURFACE AT 300 K: HREELS STUDIES

D.Yu. Zemlyanov, M.Yu. Smirnov

React.Kinet.Catal.Lett.,
53 (1994) 97-105.

Dissociative adsorption at 300 K is shown to proceed only on unreconstructed Pt(100)-(1x1) surface. When heated, NO(ad) layers behave in a similar way on both surfaces. Dissociation products are N_2 and O(ad). Adsorption on the (hex) surface is supported to occur in islands. The islands size in the saturation layer appears to be ~40 Å.

HREELS/TDS IDENTIFICATION OF INTERMEDIATES IN THE LOW-TEMPERATURE H_2+O_2, NO+H_2, NH_3+O_2 REACTIONS ON Pt(111) SURFACE

V.V.Gorodetskii, M.Yu.Smirnov, A.R.Cholach

Proc. 10th Int. Congr. on Catalysis, Budapest. 1993,
Elsevier Sc. Publ., Pt B, p. 1587-1590.

The aim of the present study of the scantily-investigated field of low-temperature oxidative catalysis is to establish the mechanism of the reactions proceeding with the participation of the reactants in the molecularly adsorbed states. High Resolution Energy Loss Spectroscopy (HREELS) and Thermal Desorption Spectroscopy (TDS) have been used for the study of the low-temperature adsorption of N_2, O_2, NO, NH_3 and H_2+O_2, NO+H_2, NH_3+O_2 reactions on the Pt(111) surface. Coordination, stability, and reactivity of adsorbed states of reactants have been determined, reaction intermediates have been detected. Experiments have been carried out by VG ADES-400 spectrometer. The monochromatic electron beam with a kinetic energy of 2.5 eV and resolution of 10 meV (80 cm^{-1}) have been used.

ORIGIN OF THE SPATIOTEMPORAL OSCILLATIONS OBSERVED DURING THE NO+H_2 REACTION ON A Rh FIELD EMITTER

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Surface Sci.,
320 (1994) 281-294.

The main purpose of the study described in the present paper was to obtain more detailed information on the mechanism of the spatiotemporal oscillations found recently by field emission microscopy for the NO+H_2 reaction on a Rh tip. These oscillations are related to the kinetics of the reaction over a Rh wire. There are two kinetic regions of the steady-state reaction. The oscillations are attributed to the reversible transition between these kinetic regions. The observed sharp moving wave can be ascribed to the hydrogenation of a nitrogen layer, followed by fast combination and/or decomposition of the adsorbed intermediate NH and restoring of its surface coverage by the NO+H_2 interaction. Surface defects and, probably, grain boundaries are responsible for the initiation of the chemical waves in the course of the sustained oscillations.

OSCILLATORY BEHAVIOUR OF THE NO-H_2 REACTION OVER Rh(533)

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Surf.Sci.,
319 (1994) L29-L33.

Waves moving over the surface of a Rh field emitter tip in an oscillatory way during the NO-H_2 reaction have been visualized earlier by field electron microscopy (FEM). An autocatalysis model has been proposed to describe the oscillatory behaviour of the reduction of NO by H_2. To study the oscillatory behaviour and the effect of the surface structure in more detail a large Rh(100) surface and a large stepped Rh(533) surface, Rh[4(111)*(100)], have been selected. The first results show that, in correspondence with the FEM experiments, rate oscillations could be observed over the Rh(533) surface in the 10^{-6} mbar pressure regime around 470 K. No oscillatory behaviour was obtained on the Rh(100) surface under these conditions. The structure-sensitivity of the process is related to the large dependence of the Rh-N bond strength on the surface structure. Nitrogen desorbs at a much higher temperature from Rh(100) than from Rh(533).

DYNAMIC STUDIES OF SURFACE REACTIONS WITH MICROSCOPIC TECHNIQUES

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Progress in Surface Science,
42 (1993) 143-169.

Work function changes which are combined with surface processes can be investigated and used to characterize adsorption states during heterogeneous catalytic reactions. The oscillatory behaviour of the CO oxidation was studied on palladium and platinum single crystal surfaces as well as on platinum field emitter tips. On macroscopic crystals the reaction was simultaneously characterized by mass spectrometric analysis and by work function measurements via a Kelvin probe with an area of ≈ 30 mm^2 being probed. In a second series of experiments photoelectron emission microscopy (PEEM) was applied to follow surface processes with a spatial resolution of ≈ 1 µm. Finally, Pt surfaces were investigated with a lateral resolution of ≈ 20 Å by using the field emission microscopy (FEM).

Gas phase coupling of oscillations as demonstrated by the simultaneous oscillations of two separated macroscopic crystals, was missing at small areas of a field emitter. The PEEM registers local oscillations under conditions where the Kelvin probe fails to register dynamic processes. FEM data showed that critical radii for nucleation could be as small as few Å.

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

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Appl.Surf.Sci.,
67 (1993) 198-205.

Platinum field emitter tips ((111)-, (001)- and (012)-oriented) are used to investigate local surface properties during the oscillatory regime of the CO oxidation at T = 430-480 K and partial pressure $P_{O_2} = 5 \times 10^{-4}$ mbar and $P_{CO} = 5 \times 10^{-5}$ mbar. Changes in surface coverage and catalytic activity are indicated by variations of the local work function and field emission current. Self-sustaining isothermal oscillations could be observed on different crystal planes. (i) A fast "switching on" of emission currents is initially noticed when the oxygen adsorption layer is transferred into a CO-layer. Starting - after a certain induction period - from the (011) region the oxygen side is quickly switched into the CO side, which slowly returns back to the catalytically active oxygen side. (ii) The formation of reactive wave fronts starts in the (011) region and propagates in the direction of (111) and (100) planes. The CO wavefront and the O wavefront move alternatively in opposite directions and display different propagation velocities, which could be measured. The frequencies and amplitudes of oscillations critically depends on temperatures and partial pressures. Compared to single crystal planes a broadening and shift of oscillatory regimes in parameter space is noted. In certain cases period doubling could be measured.

COUPLING BETWEEN ADJACENT CRYSTAL PLANES IN HETEROGENEOUS CATALYSIS BY PROPAGATING REACTION-DIFFUSION WAVES

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Nature,
370 (1994) 276-279.

Understanding of the mechanisms and kinetics of heterogeneous catalytic reactions has come largely from the study of gas-solid interactions on well defined single-crystal surfaces. But real catalysts usually consist of nanometre-sized particles on which several different crystal planes are exposed. In general, it has been assumed that their properties can be regarded as a superposition of the contributions from each individual structural element. Here we show that this assumption may be invalid, even qualitatively, in certain cases. We have studied the oxidation of hydrogen on platinum faces at low pressure and room temperature. On a macroscopic Pt(100) single crystal the reaction reaches a steady state with a uniform distribution of adsorbates. But on the platinum tip of a field ion microscope, on which several different crystal planes are exposed, the reaction has a very different character. The tip contains a region of the (100) plain just 40 nm in diameter, on which the reaction rate displays sustained temporal oscillations. This effect is associated with continuously changing distributions of the adsorbed species in the form of propagating waves, which are generated by coupling of reactions occurring on adjacent crystal planes. This kind of interaction between different crystal planes may exert a profound influence on the kinetics of heterogeneous catalysis.

ANGLE RESOLVED PHOTOEMISSION STUDY AND CALCULATION OF THE ELECTRONIC STRUCTURE OF THE Pt(111) SURFACE

V.M. Tapilin, D.Yu. Zemlyanov, M.Yu. Smirnov, V.V. Gorodetskii

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

Angle resolved photoemission spectra of Pt(111) were measured along the $\overline{\Gamma}\,\overline{K}$ and $\overline{\Gamma}\,\overline{M}$ direction of the surface Brillouin zone (SBZ). The electronic structure of a semi-infinite Pt(111) crystal was calculated applying the LMTO-TB approximation aid interpretation of the spectra. The experimental spectra are well described by the calculated bulk band structure. Both the experiment and calculation reveal a surface state near the Fermi level in the neighborhood of the $\overline{K}$ point of the SBZ.

OSCILLATING HYDROGEN-WATER REACTIONS ON A PLATINUM FIELD EMITTER

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Surf.Sci.,
318 (1994) L1211-L1218.

The spatial and temporal behaviour of surface reaction-diffusion fronts has been examined during oscillating H_2/H_2O reactions on a Pt field ion emitter. Mass and energy resolved measurements, discriminating between different reaction pathways, have been made of local yields of ions such as H_3O^+ and $H_3O^+ \cdot H_2O$. Periodic out-burst of ion yields correlate with the passage of wave across the emitter apex imaged by field ion microscopy. The experimental observations together with the predictions of a kinetic lattice gas model suggest that the supply of hydrogen, primarily by surface diffusion from the emitter shank plays a vital role.

DIRECT IMAGING OF CATALYTIC SURFACE REACTIONS IN THE FIELD ION MICROSCOPE: THE OXIDATION OF HYDROGEN ON PLATINUM

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Recl.Trav.Chim.Pays-Bas,
113 (1994) 444-447.

A field-ion microscope (FIM) was used in the investigation of hydrogen oxidation at temperatures between 300-430 K and pressures of $p(O_2) = 5 \times 10^{-4}$ mbar, $p(H_2) = 3 \times 10^{-4}$ to 7×10^{-4} mbar. The H_2O molecules produced act as an imaging gas and display the catalytically active surface area. The structure-sensitive H_2O formation was studied under steady-state conditions or in the oscillatory regime or in form of chemical waves. The displacement of Pt lattice atoms is spectacular in the Pt(100) plane, where the transformation from (1x1)Pt(100) to hex Pt(100) can be directly imaged.

MASS SEPARATION OF IMAGE GAS FIELD IONS IN THE FIELD ION MICROSCOPE

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Appl.Surf.Scie.,
76/77 (1994) 70-72.

A simple magnetic mass separator is described which can be inserted in a conventional field ion microscope in order to identify the mass of the imaging-gas ions. The mini-mass spectrometer has been designed to allow a mass separation of $\Delta m/m \sim 0.1$ from small surface areas of as few as ~ 100 surface sites. An application to a FIM study of hydrogen oxidation on Pt will be given.

ISOTHERMAL OSCILLATIONS OF THE HYDROGEN OXIDATION REACTION ON PLATINUM: INVESTIGATIONS IN THE FIELD ELECTRON AND FIELD ION MICROSCOPY

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Appl.Surf.Sci.,
76/77 (1994) 129-135.

During the reaction of $H_2 + 1/2\ O_2 \rightarrow H_2O$ on a platinum field emitter at $300 < T < 400$ K, $P_{H_2} = 5 \times 10^{-7}$ to 5×10^{-4} mbar and $P_{O_2} = 3 \times 10^{-5}$ to 6×10^{-4} mbar, three different adsorption phases can be distinguished *in situ* via FEM and FIM. In FEM the different local work functions lead to areas of differing brightness, i.e. an O_{ads} covered surface with high work function appears black and a H_{ads} covered surface with lower work function bright. In FIM, oxygen acts as the imaging gas (O_2^+ ions) of the O_{ads} covered surface areas and even brighter images are formed by the product water, thus identifying active sites of the reaction. At steady-state conditions the adsorption of hydrogen appears in the form of islands with 30 to 50 Å diameter black areas. The oscillating H_2/O_2 reaction follows a Langmuir-Hinshelwood mechanism. The O_{ads} covered surface starts at the (111) planes ({331} terraces) and proceeds in an anisotropic reaction sequence of planes until finally the (001) plane is covered by hydrogen. This H_{ads} layer at the Pt(001) surface is transferred into the O_{ads} layer by a reaction front travelling in the reverse direction, starting from the central Pt(001) and propagating to the peripheral {111} planes.

THE SURFACE SPECIFICITY OF THE OSCILLATING CO OXIDATION ON PLATINUM INVESTIGATED BY FIELD ION MICROSCOPY

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Appl.Surf.Sci.,
76/77 (1994) 122-128.

The *in situ* observation of the CO oxidation in the field ion microscope is possible due to the preferential field ionization of molecular oxygen which acts as imaging and displays O_{ads} sites with atomic resolution. A dynamic bistability of the oxidation reaction is caused by catalytically inactive CO_{ads} covered Pt surfaces and active O_{ads} covered ones. Self-sustained long-lasting oscillations of the $CO + 1/2\ O_2 \rightarrow CO_2$ reaction are investigated at $P_{CO} \sim 10^{-6}$ to 10^{-5} mbar, $P_{O_2} \sim 1 \times 10^{-4}$ to 5×10^{-4} mbar, and temperatures from 330 K to 550 K. Oscillation frequencies increase from 10^{-3} s^{-1} at 330 K to 1 s^{-1} at 550 K. A pronounced surface selectivity is found, surface regions near the {110} planes, i.e. {331} terraces, acts as pacemakers. The Pt{111} planes are always CO_{ads} covered and do not participate in oscillations. Some general conclusions are drawn on the surface specificity of catalytic surface reactions and on still open questions of oscillating surface reactions.

THE NO TITRATION BY DEUTERIUM ON THE Pt(100) SURFACE. THE EVIDENCE FOR THE PRESENCE OF THE REACTION ZONE

D.Yu. Zemlyanov, M.Yu. Smirnov, V.V. Gorodetskii

Phys.Low-Dim.Struct.
4/5 (1994) 89-94

The reaction between deuterium and adlayers prepared by NO adsorption on a reconstructed Pt(100)-(hex) surface has been studied by HREELS, TDS and LEED. NO adsorbs molecularly with the molecules forming islands. The reconstructed surface restores to the (1×1) phase within the boundaries of the islands. It was found that at the first stage the reaction of NO_{ad} with deuterium the reaction zone is formed along the island boundaries.

NO ADSORPTION ON RECONSTRUCTED AND UNRECONSTRUCTED Pt(100) SURFACE AT 300 K: TDS STUDIES

D.Yu. Zemlyanov, M.Yu. Smirnov, V.V. Gorodetskii

React. Kinet.Catal.Lett.,
53 (1994) 87-95.

The consequence of filling NO and N_2 thermodesorption states and the adsorption rate are found to depend on the initial surface structure. The initial sticking coefficients for (1x1) and (hex) structures are 1 and 0.35 respectively. If $\theta_{NO} < 0.3$ ML, the dissociation probability of NO is shown to be higher when adsorption occurs on the unreconstructed surface.

HREELS/TDS STUDY OF NO REACTION WITH HYDROGEN ON Pt(100) SURFACE

D.Yu. Zemlyanov, M.Yu. Smirnov, V.V. Gorodetskii

Catal.Lett.,
28 (1994) 153-160.

NO adsorption on a Pt(100)-(*hex*) surface and NO_{ads} reaction with hydrogen at 300 K have been studied by HREELS, LEED, TDS and isothermal desorption. NO adsorbs in molecular form, its molecules gathering in islands with a high local coverage. Surface reconstruction into a (1x1) phase proceeds within the boundaries of islands. Reaction NO + H_2 performed via NO_{ads} previous heating in vacuum at T_h = 375-425 K. Kinetics of NO_{ads} titration appears to be autocatalytic. Nitrogen is the major reaction product.

DIRECT OBSERVATION OF SURFACE MOBILITY WITH MICROSCOPIC TECHNIQUES: PHOTOEMISSION ELECTRON- AND FIELD ELECTRON MICROSCOPY

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New Aspects of Spillover Effect in Catalysis, 1993,
T.Inui et al. (Eds.), Elsevier Sci.Publ. B.V., p. 189-194.

Two new technical developments have been applied in order to investigate surface mobility in real time on the microscopic scale. The PEEM technique registers the local work function as induced by adsorption structures during catalytic reactions. The FEM technique was also applied *in situ* during surface reactions. Both techniques are operated at low gas pressures, low emission currents and high detector amplification. Thus, gas phase ionization is omitted and still bright emission patterns are obtained.

Systems with bistable adsorption structures as well as those with oscillating reactions have been investigated. On Pt- and Pd-single crystal planes as well as on Pt-field emitter surfaces fundamental processes such as phase nucleation, reaction wave propagation and synchronization in surface reactions, could be studied during oscillatory behaviour of carbon monoxide oxidation. In a new attempt of spillover research the mobility and transfer of adsorbed particles across different surface structures (including subsurface oxides) has been investigated.

PECULIARITIES OF OXYGEN AND ARGON MOLECULES ADSORPTION ON A SUPERCONDUCTING ADSORBENT

D.V. Andreev, L.L. Makarshin, V.N. Parmon

Sverkhprovod.:Fiz.Khim.Tekhn.,
7, 5 (1994) 884-888.

A low-temperature adsorption of argon and oxygen molecules on superconducting and nonsuperconducting $YBa_2Cu_3O_{7-x}$ ceramics in a temperature range of 77.4-98 K has been studied. As the adsorbent transfers to its superconducting state, oxygen molecules loose their adsorption capacity, whereas argon molecules continue to adsorb in the same manner. Such a peculiar behaviour of oxygen seems to relate to magnetic interaction between the electron spin of the oxygen triplet molecule and a completely diamagnetic surface of the superconducting adsorbent.

USE OF FUELS, CAPABLE OF REVERSIBLE EXOTHERMAL CONVERSIONS WITH DECREASE IN THE MOLE NUMBER, FOR GENERATION OF MECHANICAL WORK IN GAS-TURBINE

S.I. Prokopiev, Yu.I. Aristov, V.N. Parmon

Izv.Akad.Nauk,
ser. Energ., 3 (1994) 70-78.

Efficiency of mechanical energy generation by gas turbines has been calculated for fuels, whose transformation at the stage of chemical energy release leads to the decreasing of moles number. Several fuel mixtures are discussed that participate in the following reversible reactions:

$2H_2 + O_2 \rightleftarrows 2H_2O$ (ΔH^0_{298} = -484 kJ/mol);

$3H_2 + CO_2 \rightleftarrows CH_4 + H_2O$ (ΔH^0_{298} = -206 kJ/mol);

$3H_2 + N_2 \rightleftarrows 2NH_3$ (ΔH^0_{298} = -92 kJ/mol);

$2SO_2 + O_2 \rightleftarrows 2SO_3$ (ΔH^0_{298} = -284 kJ/mol);

$C_6H_6 + 3H_2 \rightleftarrows C_6H_{12}$ (ΔH^0_{298} = -207 kJ/mol).

The thermodynamic efficiency of chemical-to-mechenical energy conversion can exceed 50%. Moreover, the spent fuel can be reused in the production cycle. The methanation of syngas appears to be the most promising for practice.

CATALYSTS FOR WATER OXIDATION ON THE BASE OF STARCH STABILIZED COLLOID OF Co(III) - HYDROXIDES

G.L. Elizarova, L.G. Matvienko, O.P. Pestunova, V.N. Parmon

Kinet.Katal.,
35 (1994) 326-367.

Colloidal catalysts containing Co(III) hydroxo-complexes and synthesized by starch stabilization serve for water oxidation. The polymerization degree of starch in the solutions and its effect on the size of the colloidal catalyst particles were studied. The catalytic properties of colloids depend on starch concentration and synthesis temperature. Two forms of the catalyst particles are distinguished in the colloid. One of them consists of hydroxo-compounds of a low molecular weight and has a high activity. The other form is highly polymerized and less active. The nature of buffer, where catalytic reactions proceeds, is also of importance, because a partial colloid dissolving is possible. Factors affecting the composition, activity and stability of colloid catalyst are discussed.

A NEW LOW-WASTE TECHNOLOGY OF SUPPORT AND CATALYST PRODUCTION VIA ELECTRON BEAM ACTIVATION OF OXYGEN- CONTAINING SOLID SUBSTANCES

O.P. Krivoruchko, Yu.Yu. Tanashev, Yu.I. Aristov, V.N. Parmon

2nd Intern. Exhibition-Seminar "Catalysis-94",
St.Petersburg, Proc. of Seminar "Urgent Problems of
Catalysts Manufacturing and Large-Scale Application of
Catalysis", Novosibirsk, 1994 p. 48-53.

A new method serves to activate the crystal hydroxides of transition and non transition metals that are a feedstock for many catalysts. The method uses the concentrated beam of accelerated electrons to perform a thermal decomposition of oxygen-containing compounds under severe non equilibrium conditions. In order to illustrate the potentialities of elaborated electron-beam assisted radiation-thermal activation (RTA) method gibbsite, bayerite and kaolinite were treated by U-12M and ILU-6 accelerators with 3.0 and 2.5 MeV electron energies were used . As the absorbed radiation power exceeds 1 W/g, Al(III) hydroxides completely and rapidly convert to either an oxide or a multiphase system, containing amorphous hydroxide. The latter system appears to be thermodynamically unstable and thus is more reactive. The activated state is a long-living one. The radiation energy consumed in the course of formation of the amorphous product is close to 1-2 kJ/mol. The RTA of gibbsite gives the products capable to undergo hydration under mild temperatures and to form plastic masses. Hydration leads the crystallization processes producing pseudoboehmite. The RTA product of kaolinite even farther from equilibrium state than metakaolinite, obtained via the conventional calcination. ^{27}Al NMR spectra, obtained after kaolinite activation, exhibit the lines typical for Al(III) cations in the AlO_4, AlO_5 and AlO_6 coordination.

The suggested RTA method produces no toxic sewages and effluents. It contains few stages and does not pollute environment at feedstock activation. Power consumption is quite admissible. At present using the RTA method the Institute of Catalysis together with the Institute of Nuclear Physics develop a new waste-less technology to produce alumina supports, catalysts, adsorbents, drying agents and fillers.

SYNTHESIS OF ULTRAFINE PARTICLES OF TRANSITION METAL SULPHIDES IN THE CAVITIES OF LIPID VESICLES AND THE LIGHT-STIMULATED TRANSMEMBRANE ELECTRON TRANSFER CATALYZED BY THESE PARTICLES

M.I. Khramov, V.N. Parmon

J.Photochem.Photobiol.A: Chem.
71 (1993) 279-284.

A new method for synthesis of ultrafine (ca.40Å) transition metal sulphide particles (CdS and CuS) in the cavities of lipid vesicles has been developed. Sulphide precursor species are incapsulated in the vesicle cavities, then sulphide anions are added to the water phase outside the cavities (the outer solution). The rate V of the transition metal sulphide particles formation is regulated by adjusting pH of the outer solution. At the initial stages this rate is proportional to the concentration of molecular form of H_2S in the outer solution: $V = k{\cdot}[H_2S]$, $k = 9\,s^{-1}$. The particles growth can be stopped at any stage by adding an alkali to the outer solution. The rate and quantum yield of the visible light-stimulated transmembrane electron transfer in the lipid vesicles, containing CdS particles in the cavities, and electron carrier cetylviologen in the membrane, has been studied.

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. Gordeyeva, V.N. Parmon.

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

A new thermocatalytic method, ICAR, for nuclear-to-chemical energy conversion is suggested. The 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. Two variations of the suggested method are studied, based on the endothermic catalytic reactions of methane and methanol steam reforming as well as on ammonia decomposition. The conditions of intensive heat release immediately inside the catalyst bed were simulated by means of an electron accelerator. A new type of uranium-containing catalyst for steam reforming of methane was synthesized and studied. These special catalysts, as well as conventional commercial catalysts being used in the ICAR method were shown to be capable of ensuring a considerable intensification of the energy-accumulating chemical reaction and of increasing the specific power loading of the energy conversion up 100-150 kW dm^{-3}. The results of mathematical simulation of direct thermochemical conversion of radiation (nuclear) energy are also presented. Some advantages of the ICAR method and expected difficulties of its practical application are discussed here in order to point out some problems that should be solved in the near future.

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

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Int.J. Hydrogen.Energy,
18 (8), 637-680 (1993).

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

PHOTO-OXIDATION OF TRIS(2,2′-BIPYRIDINE) IRON(II) COMPLEX BY PERIODATE IN AQUEOUS SOLUTION

O.V. Gerasimov, V.N. Parmon and S.V. Lymar

J.Photochemical. Photobiol.A:Chem,
74 (1993) 21-29.

Thermal and photochemical oxidations of Fe(bpy)$_3^{2+}$ (bpy≡2,2′-bipyridine) by the periodate anion IO$_4^-$ in acidic aqueous solution were studied. For the thermal process, the rate-limiting step is a monomolecular dissociation of the iron(II) complex preceding the fast oxidation by IO$_4^-$. Photo-oxidation of Fe(bpy)$_3^{2+}$ by IO$_4^-$ is reported for the first time. The dependence of apparent quantum yield IO$_4^-$ concentration favours a static mechanism, that includes the outer-sphere complex [Fe(bpy)$_3^{2+}$IO$_4^-$] formation. The complex formation has an equilibrium constant 38±11 mol^{-1}dm^3 and is accompanied by an approximate 1 nm bathochromic shift of the metal-to-ligand charge transfer band of Fe(bpy)$_3^{2+}$. The complex [Fe(bpy)$_3^{2+}$ IO$_4^-$] is believed to undergo irreversible intramolecular electron transfer excitation with the efficiency (0.45±0.1)%. In contrast to IO$_4^-$, the persulphate anion (S$_2$O$_8^{2-}$) does not show any activity in the photo-oxidation of Fe(bpy)$_3^{2+}$. This surprising specificity is explained in terms of the difference between the sizes and geometries of the oxidizing anions; the small IO$_4^-$ penetrates between bipyridine ligands and reaches the internal d-orbitals of Fe(bpy)$_3^{2+}$ from where the electron is transferred, but the bulkier S$_2$O$_8^{2-}$ has no access to the Fe d-shell.

GAS-PHASE ELECTROCATALYTIC REDUCTION OF CO_2 PROMOTED BY COBALT POLYPHTHALOCYANINE

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

5th Intern. Symp. Macromolecule,
Metal complexes, Bremen, Germany. Proc., 1993, p.290.

Reduction of CO_2 to CO and organic products under mild conditions is of great interest in the search for alternative trends in energetics.

It was found that CO_2 was readily reduced to CO on a carbon gas-diffusion cathode impregnated with cobalt polyphthalocyanine ($CoPc_i$) in a gas-liquid electrochemical cell at room temperature and atmospheric pressure. The current efficiency of the reaction reached 97% at current densities of up to 80 mA/cm^2, the experimental conditions being optimum. The selectivity of the electroreduction of CO_2 to CO was close to 100%.

The catalytic action of $CoPc_i$ was proved by the fact that in its absence the main product of the electrode reaction was H_2 formed due to water reduction, the current efficiency of CO formation not exceeding 4%.

The effects of the electrode potential, $CoPc_i$ content, reaction temperature and reactants concentration on the current density and CO and H_2 yields were examined.

A reaction scheme including two competing electrode reactions of CO_2 reduction to CO promoted by $CoPc_i$ and dihydrogen evolution from water proceeding mainly on the bare spots of carbon electrode fits well the experimental data.

The Faradaic efficiency of CO qeneration is independent of $CoPc_i$ content with $CoPc_i$ more than 3% (mass) and decreases sharply with decreasing the catalyst content. An increase of the temperature of the solution and acidity in the liquid part of the cell caused a decrease of the CO current efficiency.

The catalyst was found to be rather stable, the turnover number exceeding 10^4 mole CO to the mole of $CoPc_i$.

KINETIC FEATURES OF INTERFACIAL ELECTRON TRANSFER SENSITIZED BY COLLOIDAL CdS. I. A PULSE PHOTOLYSIS STUDY

E.N. Savinov, V.E. Nagornyj, V.N. Parmon

Khim.Fiz.,
13 (10), 56-65 (1994).

A photobleaching relaxation of $2\cdot10^{-4}$M CdS colloids with the average radius of particles r≈50Å was studied with pulse photolysis in systems containing L-cysteine (10^{-2} M) as a sacrificial donor of electrons and O_2 (in natural concentration) as an acceptor of electrons. The photobleaching reflects the kinetics of interfacial electron transfer. Under the experimental conditions, the concentration of the excess electrons **n** trapped by CdS colloids appeared to be proportional to ΔD^z, where ΔD is a light-generated change in the optical absorbance, **z** = 0.8. At a high initial concentration of excess electrons $\mathbf{n_o}$, the rate of interfacial electron transfer was proportional to exp(γ′n), while at low n_o - to n·exp(γn), where γ′ and γ are constants. The “switching” of these dependences takes place when the average surface concentration of the excess electrons in the CdS particles attains 10^{13} cm^{-2}. The explanation of this kinetic features suggests the influence of CdS particles “charging” by trapped electrons on their double layer potential, i.e. on the activation energy of the interfacial electron transfer.

ADSORPTION OF ALIPHATIC ALCOHOLS, ALKANOIC ACIDS AND ACETONE ON THE SILICA GEL SURFACE: CHEMICAL AND STERIC FACTORS OF MONOLAYER FORMATION; APPARENT FRACTAL DIMENSION

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Molec.Cryst.Liquid Crystals,
248 (1994) 159-171.

A detailed and critical analysis of factors which may lead to mistakes in measuring the number of molecules in a monolayer on the surface of different silica gels, when using aliphatic alcohols, alcanoic acids and acetone as adsorbates is made. The chemical factors is due to the complex interactions of alcohol (acid) molecules with the surface hydroxy groups of different reactivity. This results in a two-steped form of adsorption isotherms studied by IR techique. The steric factors is connected with pecularities of packing adsorbates molecules on the surface of micropores, if one takes into consideration the intrinsic volume of the molecules. As a result, the apparent fractal dimension (D_a >2) of the surface can be introduced, if the adsorbent surface has no irregularities of the atomic scale size. This effect was shown by simulation of adsorption on the surface of the Menger sponge. Based on the analyses mentioned above, an accurate method for measuring a monolayer adsorption and surface fractal dimension was suggested.

1,4-BIS(1,2,5-TRIPHENYL-4-PYRIDIL) BENZENE AS A NOVEL HYDROPHOBIC ELECTRON RELAY FOR DIHYDROGEN EVOLUTION IN PHOTOCATALYTIC SYSTEMS ON THE BASE OF LIPID VESICLES

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J.Photochem.Photobiol. A: Chem.,
83 (1994) 153-159.

1,4-bis(1,2,5-triphenyl-4-pyridil) benzene ("benzoviologen") is efficient lipofilic reversible electron relay, which can be used to build structurally organized molecular systems based on lipid vesicles for photocatalytic water cleavage. Benzoviologen has an advantage over the widely used conventional lipofilic viologens, since its reduced forms possess more negative reduction potentials. This promotes photostimulated transmembrane electron transfer and catalytic water reduction at neutral or even slightly basic pH. The kinetic properties of benzoviologen and its capacity to produce one- and two-electron-reduced forms were studied. The ability to couple vectorial transmembrane electron phototransfer with dihydrogen evolution from water over a dispersed Pd catalyst was proven experimentally.

PARTIAL OXIDATION OF ETHANE BY *IN SITU* GENERATED H_2O_2

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Catalysis Lett.
27 (1994) 355-360.

Selective partial oxidation of ethane to ethanol and acetaldehyde by *in situ* generated H_2O_2 has been achieved under cathodic current passing through a carbon supported Nafion-H catalytic membrane. A correlation between H_2O_2 generation rate and reaction rate been found.

QUANTUM-CHEMICAL STUDY OF THE FOUR-ELECTRON CATALYTIC OXIDATION OF WATER TO DIOXYGEN IN THE PRESENCE OF DINUCLEAR AND TETRANUCLEAR HYDROXIDE COMPLEXES OF COBALT(III) AND IRON(III): INTERMEDIATES OF THE CATALYTIC CYCLE AND THEIR RELATIVE ENERGIES

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J. Molec. Cat.,
91 (1994) 71-82.

The quantum-chemical calculations have been performed to elucidate possible intermediates and their relative energies in the closed cycle of catalytic oxidation of water to dioxygen by one-electron oxidants. Di- and tetranuclear hydroxocomplexes of Co(III) and Fe(III) served as the simplest prototypes of artificial catalysts for the reaction under study. The predicted intermediates of the consecutive one-electron oxidation of the reaction site accompanied by its deprotonation appear to be analogs of well-known chemical structures of the type of transition metal complexes with dioxygen ligands. It is found that during the process only one metal ion experiences the redox transformations changing its valence state from IV to II, while the second metal ion serves mostly to stabilize the intermediates resulting from the oxidized water molecule. Thus, it confirms the well-known hypothesis on the at least dinuclear nature of the "oxygen evolving reaction centre". Release of dioxygen molecule occurs most probably after the third oxidation of the initial form of the reaction site. The calculated energies of intermediates participating in the catalytic cycle are in a reasonable agreement with available experimental data.

POLYHEDRAL SILSESQUIOXANES AS PRECURSORS OF TAILOR-MADE HETEROGENEOUS CATALYST CENTRES. I. WATER OXIDATION

V.L. Kuznetsov, G.L. Elizarova, L.G. Matvienko, I.G. Lantyukhova, V.N. Kolomiichuk, A.A. Zhdanov, O.I. Shchegolikhina

J.Organometallic Chemistry,
475 (1994) 65-72.

Fe-, Ni-, Cu- and Mn-polyhedral oligometallasilsesquioxanes 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 associated in the solution and on the supports surface. It was found that the complex distribution on the carbon support (soot) is close to monomolecular. The highest O_2 yield at the oxidation of water with $Ru(bpy)_3^{3+}$ complexes has been obtained when Fe_6/C was used as the catalyst. It has been found that supports have a strong influence on the catalytic properties of supported complexes. The catalysts prepared based on the Fe_6 complexes were 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 it is necessary for the formation of O_2 to have at least two metal ions associated with each other in active centre.

REVERSE OSMOSIS FOR SEPARATION OF REACTION SOLUTIONS IN HOMOGENEOUS CATALYSIS

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J.Membrane Sci.,
86 (1994) 37-45.

The possibilities of reverse osmosis in the separation of soluble homogeneous catalysts from the reaction mixture were investigated. Two environmentally important reactions were tested: (i) Nitric oxide detoxication with sulphur hydride in the presence of iron-containing phosphotungstate and (ii) Sulphide and polysulphide oxidation with oxygen in the presence of cobalt(III) tetrasulphophthalocyanine. For both reactions the reverse osmosis membranes were found to separate efficiently the catalysts from other reaction mixture components keeping the catalyst structure and activity unchanged, and thus allowing their manifold reuse in the catalytic processes.

IN SITU ELECTROCHEMICAL PROMOTION OF CATALYTIC ACTIVITY: THE CASE OF CH_4 AND CO OXIDATION ON METALLIC ELECTRODES

V.A.Sobyanin

US-Russia Workshop of Environmental Catalysis,
Wilmington, Delaware, USA. Proc., 1994, p. 51.

In this report we review our current research activities on the nature of Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA) phenomenon of the oxidation of methane and carbon monoxide over metal electrodes deposited on solid oxide electrolyte. In particular, the chain-like mechanism of catalytic reaction under the NEMCA condition as well as the prospect of applying the electro-chemical cells with solid electrolyte to exhaust emission control has been discussed.

STAGES IN THE MODIFICATION OF A SILVER SURFACE FOR CATALYSIS OF THE PARTIAL OXIDATION OF ETHYLENE. I. ACTION OF OXYGEN

V.I. Bukhtiyarov, A.I. Boronin, V.I. Savchenko

J.Catal.,
150 (1994) 262.

The interaction of silver foil with oxygen within a wide range of temperatures and O_2 pressures has been studied by XPS, TPD and TPR. It has been shown that depending on the treatment conditions two adsorbed oxygen states with a different ionicity of the Ag-O bond can be formed, as well as oxygen dissolved in the silver bulk.

"Ionic" oxygen (E_b(01s) = 528.4 eV) forms at the initial step of O_2 adsorption; its incorporation into the uppermost silver layer proceeding at T > 420 K. This state is responsible for ethylene adsorption, followed by its destruction and complete oxidation to CO_2 and H_2O. Dissolving of oxygen atoms in the silver bulk starts at T>470 K. No effect of the dissolved oxygen on the electronic and catalytic properties of the "ionic" oxygen has been revealed. The "covalent" oxygen (E_b(01s) = 530.5 eV) starts to accumulate at higher temperatures and pressures. A possible mechanism for its formation, wich includes the creation of specific defective sites on silver surface, is discussed. Though varying widely pressures and temperatures to modify clean silver foil by O_2, we failed to produce a surface active in ethylene epoxidation.

STAGES AT THE MODIFICATION OF A SILVER SURFACE FOR CATALYSIS OF THE PARTIAL OXIDATION OF ETHYLENE. II. THE REACTION ACTION OF MEDIUM

V.I. Bukhtiyarov, A.I. Boronin, I.P. Prosvirin, V.I. Savchenko

J.Catal.,
150 (1994) 268.

The modification of clean silver foil by C_2H_4+ O_2 and CO+O_2 reaction mixtures has been studied by XPS, TPD and TPR. The C_2H_4+O_2 treatment was found to activate the clean silver surface for ethylene oxide formation. This is accompanied by the formation of some surface species (carbonates, elementary carbon and adsorbed oxygen) and by dissolving of oxygen and carbon atoms in the silver bulk. Displacing ethylene in the reaction mixture by CO and comparing the silver surface composition after the action of both mixtures we see that a surface active center contains two adsorbed oxygen species with a different ionicity of the Ag-O bond. The "ionic" oxygen ($E_b(01s) = 528.5$ eV) produces Ag^+ ions as sites for ethylene adsorption, while the "covalent" one ($E_b(01s) = 530.5$ eV) seems to react with the adsorbed ethylene to produce ethylene oxide. A possible mechanism of the "covalent" oxygen formation and the influence of various factors (surface composition, morphology, etc.) on this process are discussed.

STUDY OF REACTIVITY OF OXYGEN STATES ADSORBED AT SILVER SURFACE TOWARDS C_2H_4 BY XPS, TPD AND TPR

V.I. Bukhtiyarov, I.P. Prosvirin, R.I. Kvon

Surface Sci.,
320 (1994) L47.

The reactivity of oxygen states adsorbed at surface of silver foil towards ethylene has been studied by XPS, TPD and TPR. Isotope experiments, when the "ionic" oxygen (BE(01s) = 528.4 eV) is labelled by ^{18}O and the "covalent" oxygen (BE(01s) = 530.5 eV) - by ^{16}O, have been carried out. Both the oxygen species were found to desorb separately. Experiment with ethylene has indicated that the "ionic" oxygen is active in a total oxidation only, while the "covalent" oxygen participates in the ethylene epoxidation.

ARXPS-BASED ANALYSIS OF DIFFERENT OXYGEN STATES ADSORBED AT SILVER FOIL

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Surf. Rev.&Lett.,
1 (1994) 577.

Atomic oxygen states adsorbed on silver surface have been studied by the angle-resolved XPS. All species were found to have a different structure of the adsorbed layers. Oxygen with BE(01s) = 528.4 eV ("ionic" state) incorporates into the second layer, while the layers below and above consist of practically pure silver. Oxygen atoms with BE(01s) = 530.5 eV ("covalent" state) occupy only uppermost layer with a coverage close to half a monolayer. As the oxygen coverage exceeds a monolayer for O_{ads} with BE(01s) = 529.5 eV, oxygen atoms start to incorporate into the deeper silver layers, i.e. bulk silver oxide is formed. These data indicate that ARXPS followed by a restoration of the depth concentration profile is a useful technique to analyze the adsorbate location with respect to the upper substrate layers.

FEATURES OF THE INTERACTION OF A $CO+O_2$ MIXTURE WITH SILVER UNDER HIGH PRESSURE

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Surface Sci.Lett.,
293 (1993) L826-L830.

The interaction of $CO+O_2$ reaction mixtures with polycrystalline silver has been studied by XPS and TPD. When the clean surface is exposed to $CO+O_2$ mixture, CO dissociates producing carbon atoms. This process proceeds through the decomposition of surface carbonate formed during the interaction of CO_2 as a product of CO oxidation with the transient surface oxygen. The appearance of carbon atoms is accompanied by the accumulation of so-called "covalent" oxygen taking an active part in ethylene epoxidation.

SURFACE ACOUSTIC WAVE RESONANCE SPECTROSCOPY (SAWRS) AS A NOVEL TECHNIQUE TO STUDY SURFACE PHENOMENA

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Surface & Interface Analysis,
22 (1994) 585-589.

A new method is proposed for investigating surface phenomena. It monitors the acoustic vibration modes of surface structures with a high resolution. Experimental SAWR spectra can be obtained under a narrow frequency band excitation ($\Delta\omega/\omega = 10^{-5}$) within a wide range (100 kHz - 10 MHz). The method application to study Ag(111) and Pt(100) single crystals has revealed the existence of very narrow resonance acoustic vibration modes with $\Delta\omega/\omega = 10^{-3}$-$10^{-4}$. The behaviour of these anomalous peaks is very sensitive to the surface structure and to the presence of adsorbates. SAWRS will likely develop into the potentially powerful method to study the surface processes.

HIGH–TEMPERATURE STATES OF ADSORBED OXYGEN ON Pt(100): STUDY BY XPS AND TDS

A.I. Boronin, R.I. Kvon, I.P. Prosvirin

14th Europ.Conf. on Surface Sci.- "ECOSS-14", Leipzig, Germany. Abstract, 1994, WeA054, p. 120.

Various states of oxygen adsorbed on Pt(100) have been studied with the XPS and TDS methods. Reaction mixture $CO+O_2$ was found to affect significantly the state of chemisorbed reactive oxygen and the formation of inactive oxygen states. The latter are characterized by a high desorption temperature (T>1000 K). The high temperature oxygen states (HTOS) formation appears to be accompanied by the surface disordering and by the penetration of oxygen atoms into the subsurface layers. We have registered the diffusion-segregation phenomena for two HTOS with 01s binding energy BE(01s) = 529.8 eV and 531.4 eV. These states seem to be the subsurface oxygen atoms localized below the Pt(100) islands and along their boundaries respectively. The third HTOS that is characterized by BE(01s) = 532.0 eV and high thermal stability is interpreted as Pt oxide like PtO_2.

COMPARISON OF COMPOSITION OF IRIDIUM THIN FILMS OBTAINED BY CVD ON DIFFERENT SUBSTRATES

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Int. Conf. on Thin Films, Taiwan. Proc., 1994, p.117.

Thin iridium films were prepared by CVD via thermolysis of tris(2,4-pentanedionato)iridium(III). Deposition was performed under atmospheric pressure with hydrogen or oxygen as gas reactants. Alumina, silica, silicon and copper were used as substrates. The film composition was studied by the X-ray photoelectron spectroscopy. The investigation of iridium films deposited on alumina and silica has shown that iridium exists as a metal phase and as $IrAl_xO_y$, $IrSi_xO_y$ surface compounds in the interface region. We have observed the effect of deposition temperature on the ratio of both metal and mixed phases. For silicon substrates, the interface depth increases as compared to that of iridium films deposited on the oxide substrates. We have found copper to diffuse through iridium films and to segregate. The present study shows that the composition of iridium films strongly depends on the nature of substrates and deposition temperature.

STATE OF IRIDIUM IN Ir/Al_2O_3 CATALYSTS STUDIED BY X-RAY PHOTOELECTRON SPECTROSCOPY, SMALL-ANGLE X-RAY SCATTERING AND ELECTRON MICROSCOPY

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Zh.Prikl.Khim., 67 (1994) 14-20.

Supported Ir/Al_2O_3 catalysts have been studied by a complex of physical methods allowing to determine the electron state, particles size and morphology of support. The binding energies $BE(Ir4f_{7/2})$ of Ir particles were found to be usually higher than that for iridium in the bulk. This effect depends on the size of particles and preparation procedure as well as on the following treatments of catalysts. The correlation of XPS results with the data of other methods allows to make a conclusion about a strong interaction of metal support in these catalysts. The supports role in the formation of iridium states is also discussed.

MECHANISM OF THE LOW-TEMPERATURE OXIDATION OF RHODIUM

A.N. Salanov, V.I. Savchenko

Kinet.Katal., 35(5), 780 (1994).

TDS and AES were used to study the interaction of O_2 with Rh(100) and polycrystalline Rh at $P_{O_2} = 10^{-5}$-10^{3} Pa and T = 400-600 K. The surface oxide of Rh forms at 10^{-5}-10^{-1} Pa, while Rh_2O_3 forms at $P_{O_2} > 10^{-1}$ Pa. The film of the latter grows via the K-M mechanism of the low-temperature metal oxidation. The film growth is a function of the oxygen pressure and sample temperature as well.

Oxygen adsorbs on the Rh surface to form a saturated adsorption layer. The latter rearranges and yields a thin oxide film. Oxygen particles adsorbed on this film catch electrons tunnelling through the oxide layer and produce Rh^+ and O^- particles on the metal-oxide and oxide-gas interfaces, respectively. The rate of the oxide film growth is determined by the stage of O^- penetration into the oxide layer. Within this layer, the particles move rapidly, reach the oxide-metal boundary and rearrange the oxide film. Rh^+ and O^- particles form an electric field F, which decreases the energy barrier for the O^- particle penetration into the oxide. As P_{O_2} increases, the concentration of O^- particles on the oxide surface rises. The samples temperature increase accelerates their penetration into the oxide layer.

OXYGEN INTERACTION WITH RHODIUM AT LOW PRESSURES

A.N. Salanov, V.I. Savchenko

Surface Sci.,
296 (1993) 393-399.

Oxygen adsorption and desorption on polycrystalline Rh and Rh(100) at $P_{O_2} < 10^{-5}$ Pa and 400-1600 K have been studied using TDS and AES methods. Adsorption kinetics for both samples is described by the King model taking account of the effect of both precursor state and lateral interaction on O_2 adsorption. Under desorption at low surface coverages ($\theta < 0.3$) the adsorbed oxygen particles penetrate into metal and then diffuse back to the surface. At $\theta > 0.3$ the processes of formation/decomposition of surface oxide Rh_2O_3 take place. Adsorption and desorption data for both samples are similar. Thus the rhodium surface structure has a weak effect on these processes.

^{1}H AND ^{51}V HIGH RESOLUTION SOLID STATE NUCLEAR MAGNETIC RESONANCE STUDIES OF SUPPORTED V_2O_5/TiO_2 CATALYSTS

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Journal of Molecular Catalysis
88(1994) 311-324.

^{1}H solid state NMR data show the existence of several types of hydroxyl groups on TiO_2 surface, depending on the surface impurities. $VOCl_3$ selectively interacts with these groups. According to the ^{51}V NMR data, the structure of vanadium complexes is determined by the type of surface hydroxyls independently of preparation method. On a clear TiO_2 surface at a low vanadium concentration two types of surface complexes with vanadium in the distorted tetrahedral environment of oxygen atoms are formed, one of them containing OH groups in the coordination sphere. At a high V content associated species with V in octahedral coordination are formed.

DYNAMIC MODEL OF SELF-OSCILLATORY EVOLUTION IN CARBON MONOXIDE OXIDATION OVER Pt(110)

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React. Kinet. Catal. Lett.,
51 (1), 211-217 (1993).

According to the proposed reaction mechanism of catalytic CO oxidation on a Pt(110) surface, which has been well supported by experimental data, a kinetic model (six ODE's) was constructed accounting for the dynamics of adsorbates on the surface. This model completely reproduces the qualitative features of reaction dynamics under fixed parameters (temperature and partial pressures of reagents), i.e. induction period before the beginning of self-oscillations and further time evolution of shape, period and amplitude of self-oscillations up to the achievement of a stable limit cycle (or steady state). In addition, the model predicts the possibility of "bursting" regimes (intermittancy) of self-oscillations.

TRIGGER MECHANISM OF SELF-OSCILLATIONS AND EFFECT OF MOLECULE SELF-ORGANIZATION IN THE COURSE OF THE MONTE CARLO MODELING OF BIMOLECULAR CATALYTIC REACTION

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J. Catal.,
142 (1), 198-205 (1993).

The dynamics of processes on metal surfaces and conditions for rate oscillations taking into account the reconstruction of catalyst are investigated using the Monte Carlo technique for catalytic reaction:

$$2A + B_2 = 2AB$$

following the Langmuir-Hinshelwood mechanism. We have studied the oscillatory kinetics and spatio-temporal self-organization caused by jumpwise variations in the catalytic properties of the surface. The following conditions were used. The adsorbed B_2 particles did not dissociate and did not react until A-coverage was less than the critical coverage Θ_A^{cr}. When, however, A-coverage reached their critical value, the adsorbed B_2 particles dissociated instantly into B-particles and reacted with the adjacent A-particles. It has been found that in a certain region of Y_A (a ratio of partial pressures of A and B_2 in the gas phase) the oscillatory kinetics is controlled mainly by one compact cluster of A-particles. We have established the specific mechanism of A-clusterization. We have also found that in a certain region of Y_A our stochastic system demonstrates a route to chaos which is very similar to intermittancy.

INFLUENCE OF INTERACTION $PdCl_2$ WITH CARBON SUPPORT ON STATE AND CATALYTIC PROPERTIES OF Pd/C CATALYSTS

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V.N. Kolomiichuk, A.I. Boronin, V.A. Likholobov

6th Intern.Symp. on Sci. Bases for the Prep.
of Heterog. Catalysts, Louvain-la-Neuve, Belgium.
Prepr., 1994, p. 201-210.

The influence of a substructure, texture and chemical properties of carbon supports on the proceeding of each stage of Pd/C catalyst formation was studied for one of conventional methods for the catalysts manufacturing involving H_2PdCl_4 adsorption on the support followed by drying and reduction procedures. The adsorption was found to be accompanied by the formation of mononuclear π-complexes of $PdCl_2$ with >C=C< fragments of the support surface. Drying step gives rise to $PdCl_2$ clusters that conserve coordination with these fragments. The consequence of this strong interaction and carbon matrix imperfection is that the surface of metallic particles formed at the reduction stage appears to be partially or completely blocked by carbon networks.

The dispersion and catalytic behaviour of Pd/C catalysts was found to depend on the interaction of both mono- and polynuclear catalyst precursors with the support.

EXPLOSION METHOD: SUBSTRUCTURAL PROPERTIES OF HIGHLY-DISPERSE DIAMONDS

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16th Conf. on Appl. Crystallography, Cieszyn,
Poland, Abstracts, 1994, p. 64.

In order to obtain diamonds, trinitrotoluene, RDX or octogen explosives decomposing to release free carbon are commonly used as starting materials. Gases, liquid and solid coolants, foams serve for cooling. The conditions of detonation products cooling are responsible for the phase composition, structure and substructure of the materials synthesized.

We have determined the substructural properties of the high-disperse diamond phase obtained using the explosion energy and water as a coolant. The diamond phase composition and substructural properties were varied at drying.

Moist samples appear to have a bidisperse distribution of crystalite size: a fine fraction (m=10 Å) and a larger (m=35 Å) one. The crystallite distribution becomes monodisperse at drying. Kinetic studies have shown the diamond phase amount to increase. The crystallization of this phase follows the first order equation. The diffraction pattern shows that halo associated with the X-ray amorphous phase decreases. So, we can suggest that the X-ray amorphous phase comprises a number of carbon clusters stabilized by the solvation shell. The cluster structure contains the diamond-structure fragments. The shell removal at drying causes an oriented (accretion) growth of diamond crystallites. The diamond crystallites, having almost no microdefects, sinter to produce 25 Å crystallites. With highly active diamond clusters, the room temperature is apparently sufficient for their sintering.

STRUCTURE OF METAL-METAL OXIDE $Pd\text{-}V_2O_5/Al_2O_3$ CATALYST FOR COMPLETE OXIDATION OF HYDROCARBONS

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Appl.Catal.A: General,
112 (1994) 141-148.

$Pd\text{-}V_2O_5/Al_2O_3$ catalyst system was studied by X-ray diffraction methods, chemical analysis and electron-spin resonance spectroscopy. Under the complete benzene oxidation conditions, the following phases were observed: $\beta\text{-}Na_xV_2O_5$, $\theta\text{-}Al_{0.33}V_2O_5$ and $Al_{0.07}{}^{+3}V_{0.07}{}^{+5}V_{1.86}{}^{+4}O_4$. An efficient delocalization of electrons between the clustered V^{+4} ions in these phases facilitates the electron transfer in the redox steps of catalytic oxidation.

PECULIARITIES OF NICKEL OXIDE STRUCTURE TRANSFORMATION UPON CO HYDROGENATION

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J.Catal.,
144 (1993) 50-59.

A study has been made of the effect of nickel oxide morphology on the mechanisms of structural transformation during activation in a CO/H_2 environment using *in situ* X-ray powder diffraction and transmission electron microscopy. It was found that in the initial reaction stage nickel oxide structure transforms in two ways: (i) reduction of NiO to Ni with the formation of Ni/NiO system; and (ii) carbidization of NiO with the development of Ni_3C/NiO catalyst. The specific phase transition has been shown to depend on the structural similarity between the crystal lattices of the parent oxide and resulting product. The obtained data revealed that interaction of NiO with CO/H_2 reaction mixture is a structure sensitive reaction. The role of carbon monoxide in both topochemical processes is also discussed.

GAS CHROMATOGRAPHY TO CONTROL PURIFICATION OF INDUSTRIAL EFFLUENTS CONTAINING NITROGEN OXIDES

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M.V. Zarodysheva, L.I. Panina, M.E. Shalayeva

Intern. Sci.-Tech. Conf. on Ecology of Chemical Productions, Severodonetsk, Ukraine. Abstracts, 1994, p. 137-138.

A gas-chromatography analysis has been designed to detect the small quantities of NO and NH_3 in the presence of large oxygen amounts. Analysis scheme is suggested.

ANTHRAQUINONES FORMATION ON ZEOLITES WITH BEA STRUCTURE

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Zeolites & Related Microporous Materials: State of the Art, 1994. Studies in Surface Science & Catalysis (Eds.J.Weitkamp, H.G.Karge, H.Pfeifer, W. Holdrich), Elsevier Science B.V., 84 (1994) 1905-1912.

Until recently zeolites with BEA structure attracted an attention mainly in the field of conversion of hydrocarbons. However, their unique physico-chemical properties let to suppose that these systems can be successfully used in reactions of organic synthesis. It is known that zeolites with BEA structure represent high-silica materials which pore structure consists of 3-D connected channels system formed with 12-membered rings with diameter of ca. 7Å. Obviously that such zeolites can be used as catalysts for synthesis of large organic molecules.

Interaction of phthalic anhydride (PhA) with aromatic hydrocarbons is an interesting object for investigation, both for science purposes and for industrial applications. Use of zeolites in this reaction is an example of acylation of aromatics on solid acid catalysts; on the other hand such a study creates possibilities for developing of more appropriate technology for production of anthraquinone compounds.

There are few references in literature concerning use of zeolites with FAU structure in this reaction. However, a detailed study on interaction of phthalic anhydride with aromatics on zeolites is not known until now. The present work contains experimental material on investigation of catalytic properties of zeolites with BEA structure in anthraquinones formation. Study of interaction of both initial reagents and reaction products with acid sites of zeolite was performed using IR technique. On the base of obtained data a mechanism of formation of reaction products is proposed.

Taking into account obtained experimental data a mechanism of an interaction of phthalic anhydride with benzene on zeolite surface can be proposed:

1. At reaction temperatures less that 250°C a solution of PhA in benzene can exist inside zeolite channels, at increased temperatures benzene in zeolite channels in the form of liquid film does not exist.
2. On zeolite surface PhA forms of H-complexes with acid OH-groups which are characterized by wide bands at 2450 and 2950 cm^{-1}.
3. Starting with 200°C formation of benzoylbenzoic acid (BBA) in its adsorbed state as H-complexes (bands at 1610 and 1710 cm^{-1}) is observed. Above 250°C BBA is seen to be decarboxylated, bonds at 1610, 1710 cm^{-1} disappear.
4. On the base of fact of easier conversion of PhA in the presence of benzene to condensed products it should be supposed anthraquinone (An) formation at 200°C.
5. Reaction products, namely, An and BBA, are decarboxylated and decarbonylated easier than PhA.

OXIDATIVE DEHYDROGENATION OF LIGHT PARAFFINS IN THE PRESENCE OF SULPHUR DIOXIDE. INFLUENCE OF CATALYST TEXTURE

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2nd Tokyo Conf. on Advanced Catal.
Science & Technology, Tokyo, Japan.
Abstracts, (1994), p. 209.

We have studied how the origin and texture of some supports affect the active component formation, oxidative condensation products (OCP), during the oxidative dehydrogenation of propane by sulphur dioxide. The porous structure was found to play a key role in the paraffin conversion to olefin. The *in situ* formed optimum structure alters with time. Micropores are generated, causing catalyst deactivation. A comparative conversion of light paraffins to olefin by sulphur dioxide has been provided. OCP was studied by the XPS techniques.

SURFACE PROCESSES IN THE CATALYTIC OXIDATIVE COUPLING OF METHANE TO ETHANE

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Recl. Trav. Chim. Pays-Bas,
113 (1994) 459-464.

Recent results on surface reaction steps in the oxidative coupling of methane (OCM) obtained from (1) transient experiments and (2) a microkinetic analysis are summarized. The interaction of methane and oxygen with MgO and Sm_2O_3 surfaces was investigated by applying H/D- and oxygen-isotope-exchange reactions. The role of short-lived adsorbed oxygen species in methane activation and product formation over MgO and Sm_2O_3 catalysts is discussed. Furthermore, elementary reaction steps and their rate constants are derived for the oxidative conversion of methane to CO_x and ethane from kinetic data for different $(CaO)_x(CeO_2)_{1-x}$ catalysts; the rate constants are related to the solid's properties, i.e. electron and O^{2-} conductivity.

TRANSIENT STUDIES ON REACTION STEPS IN THE OXIDATIVE COUPLING OF METHANE OVER CATALYTIC SURFACES OF MgO AND Sm_2O_3

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J. Catal.,
146 (1994) 346-357.

Adsorption of CH_4 and O_2 as well as surface reactions of CH_4, CD_4 and CH_4-CD_4 mixtures in the absence and presence of gas-phase oxygen were studied over MgO and Sm_2O_3 in the temperature range from 373 to 1073 K applying the temporal analysis of products (TAP) reactor. Formation of $CH^{\bullet}_3$ radicals was observed during surface reaction of methane in the Knudsen-diffusion regime while ethane and ethylene were detected only at increasing pulse intensity, i.e., in the molecular-diffusion regime. The reactivity of surface-lattice oxygen of MgO and Sm_2O_3 was studied in the Knudsen regime with respect to the H-D exchange in methane. Surface hydroxyl groups were found to participate in this reaction, but no direct interaction of methane molecules on the catalyst surface occured. H-D exchange proceeds via a multistep mechanism involving methane-surface interaction leading to dissociative adsorption of methane. The pathways of surface-oxygen species of short lifetimes were monitored using sequential pulses of oxygen and methane having various time intervals between 0.02 and 20 s. On MgO, surface-lattice oxygen is responsible for methyl radical formation resulting in C_2-hydrocarbons, while adsorbed oxygen species have very short lifetimes (< 0.1 s) on the surface and take part in the reactions of total oxidation. On Sm_2O_3, active oxygen species formed by the interaction of gaseous O_2 with the catalyst surface have lifetimes up to 20 s and are mainly responsible for methane conversion and product formation. Based on the response analysis it was assumed that direct intertaction of gas-phase methane with active oxygen surface species is the first step in the oxidative coupling of methane (OCM) over Sm_2O_3. It was found that the type of methane activation which takes place in H-D exchange was not involved in the OCM reaction over Sm_2O_3. The interaction of C_2H_6, CO, and CO_2 with the surface of Sm_2O_3 was also studied. C_2H_6 was converted to C_2H_4 and CO_x; CO was efficiently oxidized to CO_2, which was strongly adsorbed on Sm_2O_3 up to T = 1073 K.

TRANSIENT STUDIES ON OXYGEN ACTIVATION ON A Sm_2O_3 SURFACE IN THE OXIDATIVE COUPLING OF METHANE

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Catalysis Today,
21 (1994) 301-308.

The interaction of N_2O with a Sm_2O_3 surface and the reaction of methane with surface oxygen species from N_2O decomposition were studied applying the temporal-analysis-of-product (TAP) reactor. Formation of C_2 hydrocarbons depended on the concentration of adsorbed oxygen but the overall reaction was limited by the rate of N_2O decomposition which was lower than that of the dissociative adsorption of molecular oxygen under the conditions applied. It might be assumed that the fast transformation of O or O^- initially produced by dissociative adsorption of N_2O resulted in the formation of adsorbed oxygen species similar to those formed by interaction of gas-phase oxygen with the samaria surface at low temperature (908 K). Different surface processes are suggested to be responsible for the activation of these two oxidants.

TRANSIENT STADIES ON THE ROLE OF OXYGEN ACTIVATION IN THE OXIDATIVE COUPLING OF METHANE OVER Sm_2O_3, Sm_2O_3/MgO, AND MgO CATALYTIC SURFACES

O.V. Buyevskaya, R.M. Rothaemel*, H.W. Zanthoff*, M. Baerns* (Lehrstuhl für Technische. Chemie., Ruhr-Univer.Bochum, Bochum, Germany)

J.Catal.,
150 (1994) 71-80.

The interaction of oxygen with catalytic surfaces of MgO, Sm_2O_3 and Sm_2O_3 (5 mol.%)/MgO and the reaction of methane with short-lived surface oxygen species over Sm_2O_3 were studied by transient experiments. The oxygen exchange between gas-phase $^{18}O_2$ and surface oxygen $^{16}O_2$ was investigated in the temperature range from 539 to 1035 K. The oxygen-exchange activity decreased from Sm_2O_3 (E_a = 81 kJ/mol) via Sm_2O_3/MgO (E_a = 96 kJ/mol) to MgO (E_a = 261 kJ/mol). The presence of methane did not influence the exchange rate of $^{18}O_2$ with the surface. This indicates (a) that oxygen activation on the surface is faster than activation of methane and (b) that neither gas-phase oxygen nor nondissociated surface oxygen is involved in the reaction with methane under the reaction conditions applied. It was shown that the surface reaction of methane with oxygen intermediates formed from gas-phase O_2 is faster than the desorption of any diatomic oxygen species. Over Sm_2O_3, the degree of oxidative conversion of methane and the resulting product distribution are determined by the amount of surface-oxygen species formed by dissociation of gaseous O_2 on the catalyst surface. It is suggested that these active oxygen sites consist of highly reactive short-lived species (below 200 ms) and also species having longer lifetimes.

RHODIUM-CATALYZED PARTIAL OXIDATION OF METHANE TO CO AND H_2. TRANSIENT STUDIES ON ITS MECHANISM

O.V. Buyevskaya, D. Wolf*, M. Baerns* (Lehrstuhl für Techniche. Chemie, Ruhr-Univer. Bochum, Bochum, Germany)

Catal.Lett.,
29 (1994) 249-260.

The reaction of methane with surface oxygen as well as the interaction of methane/oxygen mixtures with a Rh (1 wt %)/γ-Al_2O_3 catalyst was studied by applying the temporal-analysis-of-product (TAP) reactor. The product distribution was strongly affected by the degree of surface reduction. CO_2 is formed as a primary product via a redox mechanism with the participation of surface oxygen. The dehydrogenation of methane yielding carbon deposits on the surface occurs on reduced surface sites. The formation of CO proceeds with high selectivity (up to 96%) at 1013 K via fast reaction of surface carbon species with CO_2.

RHODIUM-CATALYZED PARTIAL OXIDATION OF METHANE TO CO AND H_2. *IN SITU* DRIFTS STUDIES ON SURFACE INTERMEDIATES

K. Walter*, O.V. Buyevskaya, D. Wolf*, M. Baerns* (Lehrstuhl für Technische. Chemie, Ruhr-Univer. Bochum, Bochum, Germany)

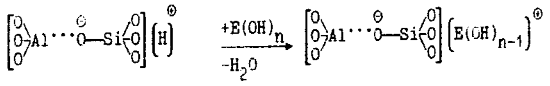
Catal.Lett.,
29 (1994) 261-270.

Reaction steps in the oxidation of CH_4 to CO and H_2 over a Rh(1 wt %)/γ-Al_2O_3 catalyst were studied using *in situ* DRIFTS at 973 K and 0.1 MPa. Product distribution and the resulting absorption band intensities of the respective adsorbates were strongly influenced by oxygen coverage and carbon deposits on the surface. CH_4 is dehydrogenated to carbon deposits and H_2 and is simultaneously oxidized to CO_2 and H_2O. OH surface groups in the support are involved in the CH_x conversion to CO via reforming reaction. The reaction of surface carbon with CO_2 was assumed to contribute to CO formation. Formate is a by-product of the reaction.

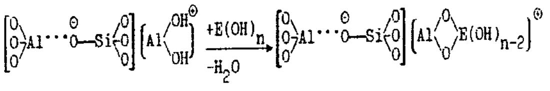
AROMATIC ALKYLATION WITH LOWER OLEFINS ON CHEMICALLY MODIFIED ZEOLITES

V.N. Romannikov

Tendencies in the acidic properties of medium-pore ZSM-5 and wide-pore BETA and ZSM-12 zeolites modified with magnesium, boron and phosphorus compounds have been systematically studied using ^{15}N NMR of adsorbed N_2O, ^1H NMR MAS and IR spectroscopy of OH-groups and adsorbed CO [1-5]. The modification of H-form of the zeolites may be described by schemes 1 and 2 for the two types of strong acid centers respectively:



(1)



(2)

On one hand, this modification can decrease the concentration of both types of highly acidic centers, and on the other hand, it produces the secondary low-acidic centers.

The activity and position selectivity of the modified zeolites were studied in the alkylation of monoaromatics by ethylene [1-4]. As found, when the concentration of strong centres decreases, the conversion of aromatics also decreases, and the distribution of aromatic isomers turns from the equilibrium to primary one. Unlike ZSM-5, where para-isomer is the dominating product, whose formation is determined by steric restrictions on the bimolecular alkylation intermediate, the position selectivity of ethylation on the wide-pore BETA zeolites is kinetically controlled, and the primary product contains all three isomers (para, meta and ortho). As a consequence, the ratio of isomers depends on the ratio of factors of partial substitution rates (i.e. on the activity of o-, m- and p-positions of the aromatic ring). When the size of the substituent increases (e.g., in di-iso-propylation reaction), para-isomer becomes the primary alkylation product on BETA and on some other wide-porous zeolites [5]. The reason is that steric restrictions hindering the formation of di-iso-propylation intermediate (like in ethylation reaction on medium pore ZSM-5 zeolite) appear.

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METAL PHTHALOCYANINES FIXED ONTO POLYORGANOSILOXANE MATRICES AS OXIDATION CATALYSTS FOR HS GROUPS

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Catal. Today,
17 (1993) 31-40.

New samples were prepared by supporting the sulfo-derivatives of cobalt phthalocyanine on the surface of poly(amino,methyl)siloxane matrices as well as by their insertion into the matrix framework during the synthesis. A comparison of the catalytic activity of resulting samples in the oxidation of a sulphide solution was carried out. A study of the structure of encapsulated and fixed CoPc as well as their state after the catalytic reaction were studied by the reflectance electron spectroscopy.

THE METHOD OF SO_2 AND NO_X REMOVAL FROM WASTE GASES

Z.Pai

1st Intern. Environ. Technology Business Action
Conference, Moscow, Russia. Proc., (1994), p.384.

We suggest a new method for the SO_2 and NO_x removal from flue gases via their absorption by aqueous solutions containing phosphates and homogeneous catalyst IC-27-1. Then the solution is treated by H_2S under mild conditions.

The SLP process scheme is a closed circuit containing some contact solution. The scheme also involves the extraction of solid impurities from a gas on a filter as solid reaction products, and a liquid flow to compensate the loss.

The efficiency of SO_2 and SO_3 removal is 98-100%, while that of NO and NO_2 removal - 80-93%, despite a rather large fluctuation of SO_2 and NO_x concentration in the gas. The process produces no harmful wastes. It transforms sulphur and nitrogen containing exhausts to elemental sulphur and valuable fertilizers (ammophoska), which can be used as commercial products.

MATHEMATIC SIMULATION OF SLP-COKE PROCESS. II. STEADY-STATE REGIMES OF HYDROGEN SULPHIDE AND SULPHUR DIOXIDE CHEMISORPTION BY AMMONIUM-PHOSPHATE SOLUTIONS

A. Yermakova, Z.P. Pai, Ye.A. Ivanov, S.I. Fadeev* (Institute of Mathematics SB RAS, Novosibirsk, Russia)

Koks i Khim.,
4 (1994) 19-26.

The chemistry of SO_2 and H_2S coabsorption by ammonium-phosphate buffer has been examined. A set of chemical reactions, modeling buffer interactions with gas acid components, is proposed. Kinetics, describing these reactions, are suggested. Effective constants of reaction rates are determined via the inverse problem solution with regard to both lab and pilot experimental results. Pilot experiments were performed at the Norilsk Integrated Mining-Metallurgy Plant.

Basing on a chemical model of absorbing solution, we have represented an unsteady-state model of the liquid-phase desulfurization (LCONTUR model) as a system of conventional differential equations under certain initial conditions.

We have also solved the problem on the equilibrium in a buffer (serving as initial condition for the LCONTUR model) taking into account the phosphoric acid dissociation in ammonia medium.

We studied the steady-state absorption solution under acid gas effect, basing on unsteady-state model. The steady state was found as a function of the initial buffer equilibrium composition, concentration of acid component in a gas and the time of gas and absorbent contact. A single steady-state solution was proved to exist. We have also designed efficient algorithm and software for the steady state calculation.

We have studied the influence of various technology parameters on the solution of steady state composition and recommend some optimum parameters.

We have analyzed the pilot plant (Norilsk Integrated Minin-Metallurgy Works) operation and compared experimental and calculated values of steady-state modes.

SULPHUR PRODUCTION IN THE PROCESS OF PURIFICATION AND CONVERSION OF HYDROCARBON RAW MATERIALS

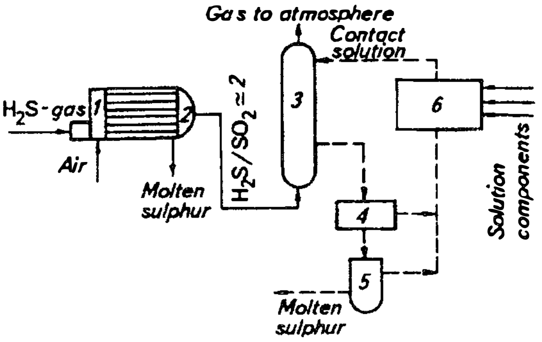
Z.P. Pai, A. Yermakova, N.N. Kundo, V.A. Kirillov

Chemistry for Sustainable Development,
2 (1), 423-425(1994)
1st Russia-Japan Joint Symp. on Petroleum, Natural Gas
and Petrochemistry, Yuzhno-Sakhalinsk, Russia.
Proc., (1993) p. 142-143.

The liquid-phase purification methods accompanied by sulphur recovery appear to be feasible for the processing of the low-concentrated sulphurous exhaust gases or small volumes of concentrated sulphides.

Thus, the liquid-phase Claus process seems to be rather promising.

Chemical and technological peculiarities of SLP method (liquid-phase sulphur removal) are considered. Fig. 1 presents a general scheme for the processing of gases containing more than 20 vol.% of hydrogen sulphide and CO_2, H_2O admixtures. The scheme comprises such important stages as heating, catalysis and sulphur separation.



CHEMICAL PROPERTIES OF LIQUID-PHASE CATALYTIC PROCESS FOR SULPHUR REMOVAL

Z.P. Pai, N.N. Kundo, V.A. Kirillov

11th Intern. Congr. on Chemical Engineering, Chemical
Equipment Design and Automation, Praha, Czech
Republic. Proc., B (1993) 37.

Purification of gases from SO_2 and H_2S assisted by homogeneous catalysts IC-27-1, IC-27-2, IC-27-3 and based on the liquid phase Claus reaction has been performed at 50°C and pH = 4.6:

$$SO_2 + H_2S \rightarrow 3S + 2H_2O$$

Mechanism and kinetics of the reactions proceeding during reduction of SO_2 absorption products by hydrogen sulphide were elucidated. Analysis with marked molecules applied for the studying of Na_2SO_3 reduction in a phosphate buffer medium (pH = 5) has revealed two reactions:

$$Na_2SO_3 + 2H_2S \xrightarrow{k_1} 3S + 2NaOH + H_2O$$

$$Na_2SO_3 + S \xrightarrow{k_2} Na_2S_2O_3$$

where $k_2/k_1 = 3$.

Thiosulphate reduction assisted by IC-27-1 catalyst limits the whole process. It can be described by the following kinetic equation:

$$W = K[S_2O_3^{2-}]^{1.5}\ [H_2S]^n\ [H^+]^m$$

here K is the reaction rate constant: n = 1 at $P_{H_2S} < 2\cdot 10^4$ Pa; m = 1 at pH > 5.

REDUCTION OF NITRIC OXIDE IN AQUEOUS SOLUTIONS CONTAINING SO_3^{2-} AND $S_2O_3^{2-}$ IONS

Z.P. Pai, S.V. Kapterev, A. Yermakova, N.N. Kundo

11th Intern. Congr. on Chemical Engineering, Chem. Equipment Design and Automation, Praha, Czeck Republic. Proc., **B** (1993) 38.

The mechanism of NO interaction with oxygen-containing sulphur compounds in a weakly acidic medium was investigated. The rates of NO absorption by contact solutions based on phosphate buffer and containing 0.15 M of SO_3^{2-} or $S_2O_3^{2-}$-ions differ by two orders of magnitude.

If formaldehyde is added into reaction mixture, the forming SO_3^{2-} ion is combined in a solid complex and NO is not reduced. Thus, $S_2O_3^{2-}$ ion is not involved directly into this reaction, since it serves as a donor of SO_3^{2-} ions at pH = 5.

INFLUENCE OF NITRIC ION IN NITRIC OXIDE REDUCTION BY AMMONIUM SULPHITE IN AQUEOUS SOLUTIONS

S.V. Kapterev, Z.P. Pai, N.N. Kundo

11th Intern.Congr. on Chemical Engineering, Chemical Equipment Design and Automation. Praha, Czeck Republic. Proc., **B** (1993) 39.

We have shown that N_2O is a product of NO reduction by oxygen-containing sulphur compounds. The presence of induction period indicates N_2O generation to proceed through the formation of intermediates. Nitrosylsulfonates could be such intermediates. At pH = 5, they decompose with time

$$ON(SO_3^-)NO^- \rightarrow N_2O + SO_4^{2-}$$

The addition of NO_2^- ions at $[NO_2^-]/[SO_3^{2-}] = 0.8$ decreases significantly NO absorption, and at $[NO_2^-]/[SO_3^{2-}] \geq 1$ N_2 and NO are produced. This phenomenon is most probably caused by the direct oxidation of SO_3^{2-} by NO_2^- ion present in the solution.

The later fact should be taken into account when new liquid phase processes of gas purification from SO_x and NO_x are designed.

KINETIC STUDY OF DIMETHYLSULPHIDE AND METHANETHIOL SYNTHESES

V.Yu. Mashkin[†]

Appl.Catal. A:General, 109 (1994) 45-61.

Kinetics of methanethiol and dimethylsulphide decomposition as well as of interaction of methanol with methanetiol and hydrogen sulphide on aluminumoxide catalysts have been studied. Some general regularities in the reaction mechanism have been revealed. This study reveals the similarites of dimethylsulphide and methanethiol synthesis. All studied reactions proceed through the methoxylation of the catalyst surface affected by methanethiol, dimethylsulphide and methanol.

In the subsequent steps CH_3O groups interact with the methanethiol or H_2S molecules activated on the basic centers producing desired products. Kinetic models for the reactions on a non-uniform catalyst surface have been proposed.

As for the majority of heterogeneous catalytic reactions proceeding on the non-uniform surfaces, the non-uniformity parameter α (the coefficient in the Bronsted-Polyani relation) attains 0.5 for the synthesis of dimethylsulphide and methanethiol. The kinetic models describe the experiment sufficiently well. They can be used to model and optimize the processes.

CONTROL OF UNSTEADY STATE OF CATALYST IN NONISOTHERMAL FLUIDIZED BED

A.A. Ivanov, S.I. Reshetnikov, E.A. Ivanov, E.M. Sadovskaya, V.P. Gaevoi

In a fluidized bed reactor catalyst particles move continuously in the field of varying composition of reagents and temperature. Under the influence of reaction mixture each particle permanently changes its properties being in unsteady state with respect to the surrounding reagents. If the characteristic time of particle diffusion along the bed is lower/comparable to the relaxation time of chemical steps of catalysis, even under steady state condition of a reactor operation, the catalyst state will be unsteady with respect to the surrounding reagents [1].

Process efficiency can be considerably increased if the reaction is performed with unsteady state of the catalyst [2,3]. Experimental study of the influence of the unsteady state of catalyst was carried out for the process of the o-xylene oxidation to phthalic anhydride [4]. It was shown that due to this phenomenon the selectivity of the process can be increased by 10-12% in a fluidized bed reactor in comparison to a fixed bed reactor.

Mathematical model taking into account the catalyst unsteady state is developed. It has been shown that selectivity of the processes of hydrocarbons partial oxidation in the fluidized bed reactor can be increased by forming the optimal temperature profile [5,6].

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MECHANISMS OF CATALYTIC ACTIVATION OF METHANE AND ETHYLENE ON MAGNESIA SURFACE ELUCIDATED BY ISOTOPIC KINETICS

V.S. Muzykantov, A.A. Shestov, H. Ehwald* (*Inst. Appl. Chem., Berlin, Germany)

2nd Workshop Meeting on C_1-C_3 Hydrocarbons Conversion, Krasnoyarsk, Russia. Abstracts (1994).

The use of rigorous kinetic equations of redistribution of isotope molecules [1-3] allows to discriminate types of dissociation of molecules on the surface on the basis of kinetic parameters obtained from experimental data. It was shown that dissociation proceeds with formation of single atomic surface hydrogen:

1. $CH_4 + 2Z = ZCH_3 + ZH$
2. $C_2H_4 + 2Z = ZC_2H_3 + ZH$
3. $H_2 + 2Z = 2ZH$

The reversible performance of these reactions realizes the homoexchange (variants 1-3 in the table). Addition of hydrogen leads to decreasing homoexchange rates of methane and ethylene.

The surface forms ZH in these reactions are identical. This conclusion follows from the experimental results of investigation of the heteroexchange between different chemical partners (variants 4-8); CH_4-H_2 (the result of a simultaneous performance of reactions 1 and 3), C_2H_4-H_2 (reactions 2 and 3) and CH_4-C_2H_4 (reactions 1 and 2). The heteroexchange rate in each of these cases is nearly equal to a quarter of the homoexchange rate (R_A/K_A in the table) of the less active partner. It means that one of four atoms of the molecule C_nH_4 is involved in an heteroexchange act (in accordance to reactions 1 and 2).

Table

Rates of homoexchange (K) and heteroexchange (R) of methane, ethylene and dihydrogen on magnesium oxide
($P_A = P_b = 33.3$ Pa, T = 295 and 688 K)

No	Isotopic variant		$K_a \cdot 10^{10}$ $\frac{\text{molec}}{\text{sec}\cdot\text{cm}^2}$		R_a/K_a	n_A	E_A (kJ)
	Exchanging gas	Exchange partner					
	A	B	295K	688K			
1	H_2+D_2	-	13	>100	-	1	-
2	CH_4+CD_4	-	<<0.1	1.8	-	1	85
3	$C_2H_4+C_2D_4$	-	1.5	>100	-	1	17
4	H_2+D_2	C_2H_4	9	>100	<<1	1	-
5	CH_4+CD_4	D_2	<<0.1	1.7	0.24	1	~90
6	$C_2H_4+C_2D_4$	D_2	0.5	>100	0.23	1	19
7	CH_4+CD_4	C_2D_4	<<0.1	1.4	0.27	-	-
8	$C_2D_4+C_2D_4$	CD_4	~1	>100	<<1	-	-

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DEEP OXIDATION OF HYDROGEN AND HYDROCARBON GASES ON CATALYTIC HEAT RELEASING ELEMENTS

V.A. Kirillov, N.A. Kuzin, V.A. Kuzmin, A.V. Kulikov, A.B. Shigarov

Zh. Khim. Prom.,
5 (1994) 56-60.

We suggest a mathematical model and procedure for calculating the oxidation of hydrogen and hydrocarbon containing gases on catalytic heat-generating elements. Using numerical calculations, we have analyzed various schemes of heat recuperation in order to increase its efficiency. The effect of supported catalyst layer thickness on the temperature profile along the element length was studied. We also compare our calculations with experimental data.

LIQUID DISTRIBUTION IN THE TRICKLE BED REACTOR

V.A. Kirillov, V.M. Khanayev

European Symp. on Catal. in Multiphase Reactors, Lyon,
France. Proceed., (1994) 121-125.

We present our experimental data on the effect of phase flow rates, bed loading, start-up conditions, particle wettability and distributor type on the liquid distribution in the gas and liquid downflow through the trickle bed.

EXPERIMENTAL STUDY AND MATHEMATICAL MODELING OF KINETICS OF ETHYLENE POLYMERIZATION ON SUPPORTED Ti-Mg CATALYSTS

V.B. Skomorokhov, V.A. Zakharov, V.A. Kirillov, S.A. Sergeev

Kinet. Katal.,
35 (1994) 464-471.

We present kinetic data on ethylene polymerization over highly active supported Ti-Mg catalysts of various particle size doped by electron-donor modifiers that provide kinetic curves of different shape.

We suggest a mathematical model of polymerization process and a kinetic scheme of active sites formation and deactivation. The scheme accounts for the monomer diffusion in a polymer particle.

A correlation of experimental and modeling data have enabled us to obtain the parameters and constants of individual polymerization stages.

DECOMPOSITION OF LIQUID HYDRAZINE IN REACTOR WITH FIXED CATALYST BED: MODELING

V.M. Khanayev, N.A. Kuzin, V.A. Kuzmin

Europ. Symp. on Catalysis in Multiphase Reactors,
Lyon, France. Proceed., (1994) p. 131-132.

In order to build physical and mathematical models, hydrazine was decomposed on catalyst short layers. The catalyst temperature, reaction stoichiometry, and hydrazine transformation degree were measured regarding the layer length. Experimental data were described using a three-temperature mathematical model of hydrazine decomposition in the reactor.

Numerical calculations with the model and experimental data have shown that at first diffusion transfer from the gas phase to the catalyst surface is the limiting factor, then the rate of liquid hydrazine evaporation starts to limit the process over reactor length. The difference in the temperatures of gas and liquid phases in the reactor makes reactor part, where the two-phase flow occurs, longer than that calculated with regard to equilibrium between vapour-gas and liquid phase. The liquid phase temperature does not exceed the diffusion temperature, which depends on the pressure and cannot be lower than the self-heating point of the gas-liquid mixture in the exothermal reaction.

WETTING EFFICIENCY OF THE CATALYST PARTICLE

V.A. Kirillov, D.A. Akimov

Europ. Symp. on Catalysis in Multiphase Reactors, Lyon,
France. Proceed., (1994) p. 51-52.

It is possible to determine three main groups of parameters controlling the wetting efficiency, f_w.

First, f_w is mainly controlled by hydrodynamic factors. Among them are the hydrodynamic regimes of phase flow, mass flow rate on each phase, physical properties of liquids, conditions of liquid spread over the surface and pores impregnation with a liquid.

Second, the catalyst particles are sufficiently overheated. In this case only thermodynamic factors are important. The physical process maturing is similar to phenomenon when the liquid drops interact with a heated surface. Therefore, the wetted surface fraction is a mean value and is determined by the ratio of time spent by the liquid on the heated surface t_2 and sum t_1+t_2, where t_1 is the time spent by the particle in the non-wetted regime.

Third, f_w is controlled by chemical factors. This occurs if phase transformations accompany reaction process.

Here we suggest some theoretical approaches and present experimental data on f_w determining.

ORIGIN OF AGGLOMERATES OBSERVED IN HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY (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 and V.A. Likholobov

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

Computer simulation has been applied to interprete "spots on stem" images observed in the HRTEM micrographs of a catalyst containing $PdCl_2$ complexes anchored on phosphinated silica. Molecular models of isolated molecules $\mathbf{P_2}$ or $\mathbf{P_2}\cdot PtCl_2$ ($\mathbf{P_2}$=diphosphine ligand covalently attached to the amorphous SiO_2 layer), aggregates ("islands") of anchored Pt(II) complexes, $[\mathbf{P_2}\cdot PtCl_2]_n$ (n=2-5), and metal clusters Pt_n (n=1-20) attached to the SiO_2 surface via a graphite "stem" were constructed. Multislice programs were used to simulate the HRTEM images of these models. The comparison of real images obtained using a 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 $[\mathbf{P_2}\cdot PtCl_2]_n$ "islands" under the electron beam. The results emphasize the necessity of computer simulation for a correct interpreting of HRTEM images, especially when the objects are sensitive to the heating effects of the electron beam.

INFLUENCE OF AN INTERACTION OF $PdCl_2$ WITH CARBON SUPPORT ON STATE AND CATALYTIC PROPERTIES OF PD/C CATALYSTS

P.A. Simonov, E.M. Moroz, A.L. Chuvilin, V.N. Kolomiichuk, A.I. Boronin and V.A. Likholobov

8th International Symposium on Scientific Bases for the Preparation of Heterogeneous Catalysts, Louvain-la-Neuve, Belgium. Prepr., (1994) 3.

We have studied how the structure, texture and chemical properties of carbon supports affect each stage of Pd/C catalyst formation in a conventional procedure of catalyst production involving the H_2PdCl_4 supporting followed by drying and reduction. Adsorption was found to be accompanied by the formation of mononuclear π-complexes of $PdCl_2$ with the >C=C< fragments of support surface. Drying gives rise to $PdCl_2$ clusters that retain in the coordination with these fragments. The consequence of this strong interaction and carbon matrix imperfection is that the surface of metal particles formed during the reduction stage appears to be partially or completely blocked by the carbon networks.

The dispersion and catalytic behaviour of Pd/C catalysts was found to depend on the interaction of both mono- and polynuclear catalyst precursors with the support.

STUDY OF SURFACE STRUCTURE OF CATALYTIC CARBON FILAMENTS BY SECONDARY ION MASS SPECTROSCOPY

V.P. Ivanov, V.B. Fenelonov, L.B. Avdeeva, O.V. Goncharova

React.Kinet.Catal.Lett., 53 (1994) 197-203.

Catalytic carbon filaments (CCF) produced by decomposition of methane on nickel catalysts consist of graphite basal planes packed in files with an interplanar spacing of d_{002} = 0.340-0.34 nm. Separate layers of a pack differ slightly in size and so the external (accessible) surface of a filament has microdefects with the width equal to d_{002} or its multiples. The structure of accessible filament surface determines the special adsorption properties of CCF.

The structure of surface layers of CCF was studied using surface etching with argon ions and registration of displaced secondary ions by a mass-spectrometer (SIMS method). It was determined qualitatively the thickness of defect surface layers accessible for adsorption. The defect layer of sample CCF-1 (with the graphite layers inclined towards the filament axis) is 3-4 nm and thicker by a factor of 1.5 than that of CCF-2 (with the graphite layers perpendicular towards filament axis). Perhaps, CCF-1 has more surface defects.

STRUCTURE AND TEXTURE OF A CATALYTIC FILAMENTOUS CARBON: A NEW CARBON SORBENT

L.B. Avdeeva, O.V. Goncharova, E.M. Moroz, V.B. Fenelonov

4th Intern. Symp. on Adsorption and Liquid
Chromatography of Macromolecules. Omsk, Russia.
Procced., (1994) p. 34.

Catalytic filamentous carbon (CFC) is produced via decomposition of saturated hydrocarbons C_1-C_4 over high loaded nickel catalysts at 475-575°C. CFC is a graphite-like carbon, whose graphite layers are formed due to the epitaxial growth of carbon on a metal particle.

We have studied the porosity, surface value and the degree of graphitization (disordering) of two CFC modifications as the functions of the composition and structure of nickel particles, the sites of the CFC filament formation, as well as of the decomposed feedstock nature and conditions of its decomposition.

We have found that various CFC have a monosize porous texture, pore diameter varies from 11 to 19 nm, regardless the catalyst or hydrocarbon type, conditions of CFC preparation. Meanwhile, the average pore volume varies within 0.3-0,7 cm^3/g. The surface is 100-300 m^2/g. However, the position and density of carbon layer packed files (packs) of different CFC are not the same. An interplanar spacing (d_{002}) varies within 0.341-0.347 nm; while the turning angle of graphite layers to the filament axis varies from 10 to 90°.

Defects in the graphite layers files along the width and length of a fibre were detected by XPS, SIMS, EM methods. Such defects provide an inhomogeneous surface of fibres on the atomic level. We suggest that micropores (1 nm long) exist on the surface of CFC. We think that the adsorption of organic molecules followes the intercalation model, since during hydrocarbons adsorption, the interplanar spacing of CFC increases and the degree of a three-dimensional ordering decreases.

ALUMINA SUPPORTED SULPHIDE CATALYSTS. I. HYDROGENOLYSIS OF THIOPHENE

A.N. Startsev, S.A. Shkuropat, E.N. Bogdanets

Kinet. Katal.,
35 (1994) 282-287.

A series of γ-Al_2O_3-supported sulphide (Ni-Mo) and (Co-Mo) catalysts were prepared via 2 methods: 1) by successive anchoring of metal complexes of molybdenum and then of nickel or cobalt; 2) by the traditional method of impregnation by the incipient wetness technique with the aqueous solution of molybdenum and nickel (cobalt) salts. The catalysts of the metal-complex origin are more active in the thiophene hydrogenolysis than the impregnated ones, though in both cases identical kinetic regularities of this reaction were observed. The difference in the activity is supposed to be caused by the heterogeneous composition of the surface species in the impregnated catalysts.

ALUMINA SUPPORTED SULPHIDE CATALYSTS. II. HIGH RESOLUTION ELECTRON MICRSCOPY DATA

A.N. Startsev, V.I. Zaikovskii

Kinet. Katal.,
35 (1994) 288-291.

The surface morphology of the γ-alumina supported sulphide (Ni, Mo) and (Co, Mo) catalysts are studied by the high resolution transmission electron microscopy (HRTEM). The catalysts were prepared by metal complexes anchoring or by traditional impregnation method. The active component of these catalysts appears to crystallize in the structures that are typical for the sulphide particles in the Mo/Al_2O_3 catalysts. The single slabs of active component join to the support surface through the edge or basal plane. Reasons of stabilization of high dispersion of sulphide species are discussed in terms of the lack upon of their epitaxial interaction with a support. A higher activity of catalysts, derived from the metal complexes, against that of impregnated catalysts, is supposed to be due to a higher dispersion and a more homogeneous composition of the surface species.

ALUMINA SUPPORTED SULPHIDE CATALYSTS. III. XPS DATA.

A.N. Startsev, A.V. Kalinkin

Kinet. Katal.,
35 (1994) 292-295.

Electron state of metals, included into the composition of the active component of sulphide (Ni, Mo)/Al_2O_3 and (Co, Mo)/Al_2O_3 catalysts prepared both with use of metal complexes and by the traditional method of impregnation, has been studied. The binding energy (BE) of electrons on the Ni2$p_{3/2}$ and Co2$p_{3/2}$ levels in bimetal catalysts appears to be higher in comparison to highly dispersed Ni or Co sulphides. This BE increase is ascribed to the decrease of electron density on Ni and Co ions as a new chemical compound forms, i.e., a sulphide bimetallic species (SBMS). In the sulphide catalysts prepared by impregnation, a portion of Ni and Co atoms stays in the oxygen environment.

ALUMINA SUPPORTED SULPHIDE CATALYSTS. IV. Mo K-EDGE EXAFS OF MOLYBDENUM CATALYSTS

A.N. Startsev, D.I. Kochubey

Kinet. Katal.,
35 (1994) 591-600.

Models mimicking the structure of a MoS single slab up to 25 Å in size are presented. The models base on the principle of electroneutrality of $(MoS_2)x$ macromolecule provided for that all the valence bonds on the edges of the single slab are saturated, and the MoS stoichiometry does not change. The coordination numbers of Mo to Mo and of Mo to S depending on the form and size of MoS single slab and on its orientation to alumina surface (parallel or perpendicular) are analyzed. The EXAFS data can be explained, if we assume that peripheral (terminal) Mo or S atoms do not show in the EXAFS spectra due to essential Debye-Waller factor.

ALUMINA SUPPORTED SULPHIDE CATALYSTS. V. INFLUENCE OF P AND F ON ATOMIC CATALYTIC ACTIVITY OF SULPHIDE HDS CATALYSTS

A.N. Startsev, O.V. Klimov, V.A. Kalinkin, V.M. Mastichin†

Kinet. Katal.,
35 (1994) 601-607.

The effect of P and F additives on the properties of sulphide hydrodesulfurization catalysts was studied. The catalysts were prepared via the "surface assembly" of the direct active component precursor. F and P do not hinder the surface assembly of Ni-Mo surface species. The activity of promoted sulphide catalysts (both mono- and bimetal) is only slightly higher than that of non-promoted ones, but this is true only at 300 °C. The MAS NMR spectra of P and the XPS data show that additives chemically interact with the active component thus decreasing the activation energy of thiophene hydrogenolysis. This phenomenon is explained in the frame of concerted mechanism.

SYNTHESIS, PROPERTIES AND STRUCTURE OF BINUCLEAR ANION "Mo(V) HYDROXIDE", $[Mo_2O_4(OH)_4(H_2O)_2]^{2-}$

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Polyhedron,
13 (1994) 505-512.

The structure of "molybdenum(V) hydroxide" has been determined. The complex was obtained via the MoO_4^{2-} molybdate anion reduction with hydrazine-hydrate in aqueous solution. This compound is assumed to have formula $(N_2H_5)_2[Mo_2(\mu\text{-}O)_2O_2(OH)_4(H_2O)_2]$, dihydrazonium [di-μ-oxo-bis-(aquadihydroxooxomolybdate(V)]. The product structure is similar to that obtained at MoO_4^{2-} reduction with $NaBH_4$ and at $(NH_4)_2MoOCl_5$ hydrolysis. At Mo(V) hydroxide dissolving in oxalic or tartaric acid solutions the diamagnetic complexes are produced and characterized by means of IR, NMR and EXAFS spectroscopy.

FTIR STUDIES OF CO CHEMISORPTION AND REACTIVITY ON Ph/SiO_2 CATALYSTS PROMOTED BY NIOBIUM OXIDE

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J.Molec.Catal.,
92 (1994) 217-233.

The aim of the present work is to study the influence of Nb^{n+} ions on the chemisorption of CO on Rh/SiO_2 catalysts by means of FTIR spectroscopy. Attempts have been made to produce catalysts with maximum possible dispersion of the rhodium particles and to achieve an intimate contact with niobium ions. For this purpose, the $(Rh+Nb)/SiO_2$ catalysts were prepared by the so-called "surface assembling" method using organometallic precursors.

$(Rh+Nb)/SiO_2$ catalysts were obtained by anchoring the nanometer Rh particles on surface low-valent Nb^{n+} ions. These materials exhibit the following specific features compared to Rh/SiO_2: low coverage of Rh surface by chemisorbed hydrogen and carbon oxide; high-frequency shift of linear CO absorption band and appearance of two absorption bands of a C and O bonded CO at 1704 and 1652 cm^{-1}. On exposure to H_2, the stability of surface carbonyls increases in the sequence: $Rh\text{-}CO\text{-}Nb^{n+} < Rh\text{-}CO < Rh_2(CO) < Rh+(CO)_2$.

C- and O-bonded CO on $(Rh+Nb)/SiO_2$ catalysts appears to be the least stable when exposed to hydrogen. For the possible function of C- and O-bonded CO in syngas conversion on promoted Rh, it was suggested:

(1) to decrease the activation energy of CO dissociation with subsequent formation of CH_x fragments inserting in the growing hydrocarbon chains;

(2) to facilitate CO insertion into the CH_3-Rh bond yielding the acetyl intermediate CH_3CO for the production of acetaldehyde and ethanol;

(3) to increase the rate of hydrogen atom addition to chemisorbed CO, resulting in generation of formyl species which are the precursors for methanol synthesis.

OXIDATION OF 2-METHYL-1-NAPHTHOL TO 2-METHYL-1,4-NAPHTHOQUINONE (VITAMIN K_3) VIA PHASE TRANSFER CATALYSIS IN PRESENCE OF V-Mo-P HETEROPOLYACIDS

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

Izv. Akad.Nauk, ser.Khim.,
7 (1994) 1208-1211.

$H_{3+n}HV_nMo_{12-n}O_{40}$ heteropoly acids (HPA-n) and their acid salts are efficient catalysts for the 2-methyl-1-naphthol (I) oxidation to 2-methyl-1,4-naphthoquinone (MN). HPA-n are reversible oxidizers and oxidize I with the help of the water molecule oxygen. The reduced forms of HPA-n are regenerated by dioxygen to produce initial oxidized forms of HPA-n-s used repeatedly to oxidize I. A two-phase system allows to achieve the highest selectivity of oxidation of I. In this system the catalyst is in the aqueous phase while the substrate and reaction products are in the organic phase. This provides easier catalyst separation from reaction products.

The rate and selectivity of oxidation of I depends on the HPA-n oxidation potential. The latter depends on the number of V atoms in a HPA-n molecule. As n increases, the rate of I oxidation increases, while the selectivity decreases.

Considering the composition of reaction products and the oxidation kinetics peculiarities we suggest a new mechanism for oxidation of I in the presence of HPA-n. For the best HPA-n samples, the yield of vitamin K_3 is 85%.

BINDING ENERGY OF OXYGEN IN P-Mo HETEROPOLYACID AND POTASSIUM SALT

V.M. Bondareva, T.V. Andrushkevich, Yu.D. Pankratiev

React.Kinet.Catal.Lett.,
49 (1), 103-110 (1993)

Calorimetric measurements of oxygen binding energy in of P-Mo heteropolyacid the Keggin structure and its potassium salts have been carried out. The behaviour of acid and its salts appear to behave differently in reduction and further reoxidation processes

REDOX MECHANISM OF ACROLEIN OXIDATION OVER THE PRODUCT OF MOLYBDOPHOSPHORIC HETEROPOLYACID THERMOLYSIS: $PMo_{12}O_{38.5}$

T.V. Andrushkevich, V.M. Bondareva, G.Ya. Popova, Yu.D. Pankratiev

React.Kinet.Catal.Lett.,
52 (1), 73-80 (1994).

Redox mechanism of oxygen insertion into acrolein during its oxidation by molecular oxygen on $PMo_{12}O_{38.5}$ catalyst has been studied. The latter is the product of thermolysis of the series 12 molybdophosphoric heteropolyacid. The heat of oxygen adsorption on the catalyst surface was measured by calorimetry as a function of catalyst reduction by carbon oxide. The value amounted to 72.5±2.5 kcal/mol O_2 and did not depend on the reduction degree, which was about 3.5 oxygen monolayers.

MECHANISM OF OXYGEN INSERTION INTO THE PRODUCTS OF ACROLEIN OXIDATION ON $H_3PMo_{12}O_{40}$ and $K_3PMo_{12}O_{40}$

G.Ya. Popova, T.V. Andrushkevich, V.M. Bondareva, I.I. Zakharov

Kinet.Katal.,
35 (1), 91-95 (1994).

Mechanism of oxygen insertion into the products of acrolein oxidation on $H_3PMo_{12}O_{40}$ and $K_3PMo_{12}O_{40}$ has been studied. Acrylic acid and carbon oxides appear to form via the redox mechanism. Higher rates of acrylic acid formation on the reduced heteropoly compounds are determined by the different mechanisms of acrolein activation on the oxidized and reduced surfaces.

HETEROGENEOUS OXIDATION OF ACROLEIN TO ACRYLIC ACID: FROM MECHANISM TO PROCESS

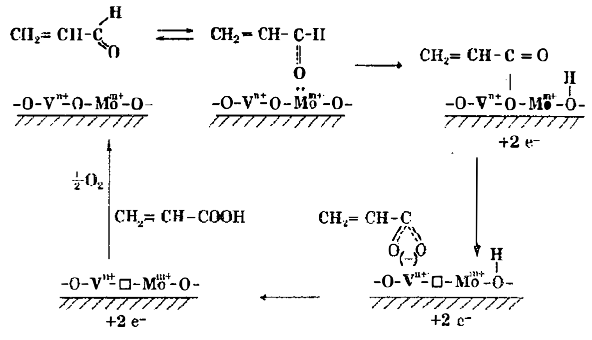
T.V. Andrushkevich

Khim. Prom-st,
4 (1994) 9-21,
Russian Chem. Industry,
26 (1994) 9-21.

We have described the design process for acrolein oxidation stage of a two-step oxidation of propylene to acrylic acid. Our work involved catalyst matching, active component studies, research on reaction mechanism and kinetics, mathematical process modeling for the fluidized- and fixed catalyst bed reactors, and at least, pilot process tests of the reaction.

According to the study of acrolein oxidation by Co-Mo-, P-Mo-, V-Sb- and V-Mo oxide systems, the latter is the most efficient in the acrylic acid formation. VMo_3O_{11+x} compound, produced under mild reduction conditions, is the active component of this system [1]. The key features of the system are: > 98% of vanadium are reduced to the four-valent state, a loose-layered structure allowing an easy introduction of admixutres in various concentrations, phase composition being preserved. Basing on this compound, we have obtained the modified catalysts of various chemical compound [2,3].

Acrylic acid forms on such catalysts via the redox mechanism [4] involving lattice oxygen (adsorption heat q_{O2} = 60-62 kcal/mol^{-1}) [5], and step-wise transformation of weakly bonded (q=18-20 kcal/mol) intermediate complexes [6,7]:



The products of deep oxidation yield from the strongly bonded surface complexes via the associative mechanism.

Kinetic equations corresponding to the mechanism [8] are:

$$r_{aa} = \frac{k_1P_a(1+k_2P_{H_2O})}{1+k_3P_a+k_2P_{H_2O}+k_4P_aP_{H_2O}+k_5P_a/P_{O_2}+k_6P_aP_{H_2O}/P_{O_2}}$$

$$r_{deep} = \frac{k_1P_a+k_8P_{aa}}{1+k_9P_a/P_{O_2}+k_{10}P_{aa}/P_{O_2}}$$

where r_{aa} is the rate of acrylic acid formation; r_{deep} is the rate of formation of deep oxidation products (CO, CO_2); P_a, P_{aa}, P_{H_2O}, P_{O_2} are the partial pressures of acrolein, acrolein acid, steam vapor and oxygen.

Two process versions were tested in pilot installations equipped either with fluidized- or fixed catalyst bed reactors. The following Table comprises the catalysts, calculated and experimental yields of acrylic acid:

Reactor type	catalyst features			Acrylic aicd yield, %	
	granule shape	size, mm	surface, m^2/g	calcu-lated	experi-mental
fluidized bed, d=100 mm, h= 3.8 m	sphere	0.2-0.5	120	93	92-94
fixed bed: tube d=32mm, h= 4.0 m	cylinder	4x4	70	95	94.5

Our experimental data indicate that the yields of acrylic acid in the fixed- and fluidized catalyst beds are very close, if the reaction proceeds in each layer under the optimum regime.

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OXIDATIVE HYDROXYLATION USING DINITROGEN MONOXIDE: A POSSIBLE ROUTE FOR ORGANIC SYNTHESIS OVER ZEOLITES

G.I. Panov, A.S. Kharitonov, V.I. Sobolev

Appl.Catal. A: General,
98 (1993) 1-20.

The use of zeolites as catalysts for selective oxidation reactions has been reviewed. Particular attention has been paid to recent studies of a gas-phase oxidative hydroxylation of aromatics by dinitrogen monoxide (N_2O). The best results were obtained for the oxidation of benzene to phenol over Fe-containing ZSM-5 zeolites. It proceeds with nearly 100% selectivity at 25-30% benzene conversion. Further progress in this promising direction, i.e. direct hydroxylation of aromatics, can provide new efficient technologies in organic synthesis. Peculiarities of dinitrogen monoxide as an oxidant and the reaction mechanism are discussed.

ON THE ORIGIN OF HIGH EFFICIENCY OF ZSM-5 ZEOLITES IN OXIDATIVE HYDROXYLATION OF AROMATICS WITH N_2O

G.I. Panov, V.I. Sobolev, A.S. Kharitonov, E.A. Paukshtis

Catalysis in Organic Reactions,
Marcel Dekker,
Inc., N.-Y., (1994) 525-530.

Oxidation of benzene with α-oxygen form produced by N_2O decomposition over FeZSM-5 zeolite surface has been studied using IR spectroscopy and chromatography. The reaction has been shown to proceed at room temperature producing phenol with a nearly stoichiometric yield. This explains the unique catalytic properties of pentasil-type zeolites in a one-step hydroxylation of aromatics by N_2O.

SILYLATION EFFECT ON THE CATALYTIC PROPERTIES OF FeZSM-11 IN BENZENE OXIDATION TO PHENOL

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React.Kinet.Catal.Lett.,
52(2), 275-283(1994).

The outer surface of the FeZSM-11 zeolite was selectively silylated without affecting the inner system of its channels. SiO_2 deposition suppressed both the acidity and catalytic activity of the outer surface in mesitylene isomerization. Neither zeolite activity, nor its stability in benzene oxidation to phenol by N_2O have changed upon silylation. This fact gives evidence that the latter reaction proceeds primarily within the zeolite channels.

FORMATION OF Zn-Co CATALYSTS OF A SPINEL STRUCTURE

G.G. Volkova, T.M. Yurieva, G.N. Kustova, L.M. Plyasova, G.V. Kharlamov, G.S. Litvak, V.F. Anufrienko

Zh.Prikl.Khim.,
67 (1994) 779-784.

Genesis of Zn-Co oxide catalysts has been studied using XRD, TA, IR and UV-VIS-DR methods. If Co : Zn = 2:1, a defect spinel, consisting of OH^- and $(H_3O)^+$ groups at 100-650°C, is formed. This spinel is a solid solution of two valent zinc cations in cobalt-zinc cobaltite. At 700°C, impurity groups are removed, Zn-Co spinel decomposes to ZnO and a spinel containing less zinc cations. We failed to obtain the stochiometric spinel $ZnCo_2O_4$ of a "normal" cation distribution over crystallographic positions by a coprecipitation and subsequent calcination.

THE CHARACTER OF THE INTERACTION BETWEEN HYDROGEN AND COPPER-CONTAINING OXIDE CATALYSTS. II. REACTIONS OF COPPER CHROMITE, REDUCED BY HYDROGEN, AND COPPER-ZINC OXIDE WITH ACETONE AND CARBON MONOXIDE

O.V. Makarova, T.M.Yurieva, L.M. Plyasova, T.A. Krieger, V.I. Zaikovskii

Kinet.Katal.,
35 (3), 371-375 (1994).

In situ high-temperature X-ray diffraction and electron microscope studies are used to show that acetone and CO are hydrogenated by adsorbed hydrogen in the absence of hydrogen in the gas phase. The process is accompanied by copper ions ionization and relaxation to regular positions in the oxide structure. We discuss the mechanisms of catalytic methanol synthesis and catalytic hydrogenation of acetone to isopropanol.

THE STATE OF COPPER-CONTAINING CATALYSTS FOR METHANOL SYNTHESIS IN THE REACTION MEDIUM

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React.Kinet.Catal.Lett.,
51 (2), 495-500 (1993).

Hydrogen interaction with solid solutions of the composition $Cu_{0.08}Zn_{0.02}O^*$ and $Cu_{0.15}Al_{0.10}Zn_{0.75}O^*$ was studied. It is shown that at catalytic temperatures, the surface of anion-modified zinc oxide contains epitaxially bonded metal copper particles. The reversibility of this phenomenon during the hydrogen removal indicates the formation of a complex system consisting of the oxide stabilized by protons and epitaxially bonded with oxide metal copper particles during the hydrogen removal.

NANOMETER SIZE COPPER PARTICLES IN COPPER CHROMITE CATALYSTS

T.M.Yurieva, L.M.Plyasova, O.V.Makarova, T.A.Krieger, V.I.Zaikovskii

6th Intern. Symp. on Scientific Bases for the Preparation of Heterogeneous Catalysts, Louvain-la-Neuve, Belgium.
Proceed., 2 (1994) 127-131.

It is hardly possible to obtain copper in the atomic state on the surface of an oxide catalyst. So, a challenging task to obtain a metallic copper with large surface area becomes of crucial importance.

It is known that high dispersed copper can be formed on the surface via reduction of copper-containing oxides. We have shown by *in situ* investigation that the nature of hydrogen interaction with copper chromite essentially depends on the method of reduction. The treatment of the sample, preheated to 450-500°C, by H_2 produces cupprous chromite, which decomposes to Cu^o and α-Cr_2O_3 at higher temperatures. If the temperature of hydrogen medium is elevated slowly, there is a change in the nature of hydrogen interaction with copper chromite. Reduction at 450°C results in copper and chromia, in this case $CuCrO_2$ is not observed.

We have observed that at 150-350°C in hydrogen copper chromite contains nanometer size metallic copper particles epitaxially bonded to the spinel surface. This state of catalyst exhibits high activity in hydrogenation reactions [1]. These copper particles were studied in this work in detail.

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DIPOLE COUPLING OF CO (NO) ADSORBED ON IRON OXIDE SURFACE CENTERS: A TYPICAL FEATURE OF SURFACE ACTIVE SITES

S.F. Tikhov, V.A. Sadykov, G.N. Kryukova, V.A. Razdobarov

Mendeleev Commun..
2 (1994) 69-71.

FTIR spectroscopy together with TEM and kinetic measurements were used to demonstrate that Fe^{2+} cluster defect centers exhibiting dipole coupling of adsorbed CO (NO) determine the iron oxide activity in CO oxidation.

CATALYTIC AND PHYSICO-CHEMICAL PROPERTIES OF $La_{1-x}Sr_xCoO_3$ PEROVSKITES

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React.Kinet.Catal.Lett.,
53 (1994) 223-229.

Catalytic properties of strontium-substituted lanthanum cobaltites in the reaction of CO catalytic oxidation were compared with the data on the chemical composition of the surface and bulk defect structure. It was found that (i) the initial catalytic activity correlates with the cobalt concentration on the surface; (ii) surface composition differs from the bulk one; (iii) the steady state activity is proportional to the density of bulk extended defects. Under our experimental conditions, no role of point defects was noted.

MONOLITH PEROVSKITE CATALYSTS OF HONEYCOMB STRUCTURE FOR FUEL COMBUSTION

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6th Intern. Symp. on Scientific Bases
for the Preparation of Heterogeneous Catalysts,
Louvain-la-Neuve, Belgium. Prepr., 2 (1994) 231-239.

We have developed a new method to synthsize disperse perovskites, using the mechanochemical activation of the solid starting compounds. The influence of defect structure of these compounds as well as the surface segregation on their catalytic properties is discussed. The basic stages of the monolith perovskite catalyst preparation are optimized. We have obtained monolith catalysts of various shape possessing high activity, thermal stability and resistance to catalytic poisons.

PEROVSKITE CATALYSTS: HIGH-SURFACE-AREA POWDER SYNTHESIS, MONOLITH SHAPING AND HIGH-TEMPERATURE APPLICATIONS

V.A. Sadykov, L.A. Isupova, S.F. Tikhov, O.N. Kimkhai

MRS Fall Meeting, Boston, USA. Proceed., (1994) 386.

Monolith perovskite catalysts of the honeycomb structure were designed for diverse high-temperature applications. The problems of powdered perovskite synthesis via efficient plasmochemical and mechanochemical methods as related to the real structure and reactivity of these compounds are discussed. Pilot testing in the reactions of fuel combustion, ammonia oxidation, methane conversion and sulphur dioxide reduction proved a high activity and stability of these catalysts.

THE STRUCTURAL FEATURES OF COBALT OXIDES: ^{57}Fe MOSSBAUER SPECTROSCOPY, TEM AND STATIC MAGNETIC SUSCEPTIBILITY MEASUREMENTS

V.L. Kuznetsov, V.A. Sadykov, V.A. Razdobarov, A.G. Klimenko

J.Solid State Chem.,
104 (1993) 412-421.

^{57}Fe Mossbauer spectroscopy data obtained at 4.2-298 K, as well as TEM and magnetic measurements were used to study in details the real structure of cobalt oxides, CoO and Co_3O_4. In the Co_3O_4 samples synthesized at low temperatures the tracer is nonuniformly distributed. It exists in the form of Fe_2O_3 inclusions generating stacking faults as well as in the form of Fe^{3+} ions in the octahedral positions of the spinel matrix. An excess of oxygen in Co_3O_4 was found to generate cation vacancies in the octahedra. A two-phase CoO-Co_3O_4 system displays a dislocation network broadening the resonance lines and increasing the quadrupole splitting. For the monophase CoO an excess of oxygen produces the microclusters of Co_3O_4. A periodic array of shear type extended defects found in modified CoO was proposed to be generated by ordering of Fe impurities in some planes of the cubic structure.

ON THE NATURE OF THE ACTIVE COMPONENT IN SUPPORTED COPPER OXIDE CATALYSTS IN REACTIONS OF COMPLETE OXIDATION

L.P. Davydova, V.B. Fenelonov, V.A. Sadykov, L.M. Plyasova, V.F. Anufrienko

Kinet.Katal.,
34 (1993) 99-103.

The catalytic properties of Cu-Al-O catalysts in the catalytic hydrogen oxidation by molecular oxygen are studied and compared with the data of XPD, ESR and CO chemisorption. The specific catalytic activity of samples was found to be close to that of bulk copper aluminate and by two orders of magnitude lower than that of copper oxide. The results analysis shows that the activity of supported catalysts correlates with the density of centers rather weakly retaining CO at room temperature and is assigned to three-dimensional clusters of copper ions on the support.

OXIDE ZIRCONIUM CONTAINING COMPOSITES. PREPARATION AND PHYSICO-CHEMICAL PROPERTIES

A.S. Ivanova, G.M. Alikina, L.P. Solovieva, V.P. Ivanov, G.N. Kustova, V.A. Sadykov

4th Europ. East-West Conf. and Exhibition on Materials and Processes, St.Petersb., Russia. Book of Abstracts, I
(1993) A-8P, p.23.

The developement of such processes as conversion of natural gases, oxidative conversion of methane and reduction of nitrogen oxides makes us study and design new oxide systems that will retain their physical structure at high temperatures. Therefore, we have studied the relationships between phase composition, structural-strength characteristics, nature and content of initial components, fraction composition, and thermal treatment conditions in binary and triple oxide Zr containing systems at 700-1000°C.

Accounting for the peculiarities of diffusion during the solid-phase synthesis and sintering within the above temperature region, we established the optimal conditions for preparing composites with a definite phase composition. The specific surface area of these composites was by two orders of magnitude larger than that of individual Zr dioxide synthesized under the same conditions.

EFFECT OF PREPARATION PROCEDURE, NATURE AND CONTENT OF R_2O_3 (R=Y, La, Ce) ON PHYSICO-CHEMICAL PROPERTIES OF R_2O_3-Al_2O_3 COMPOSITIONS

A.S. Ivanova, E.M. Moroz, G.A. Polyakova

Kinet.Katal.,
35 (1994) 786-790.

We have studied the physicochemical properties of R_2O_3-Al_2O_3 compositions (R=Y, La, Ce) prepared by the precipitation or mixing of the corresponding components. Interaction between the components appear to decrease in a series Y_2O_3-Al_2O_3 > La_2O_3-Al_2O_3 > Ce_2O_3-Al_2O_3 (in the latter case there is no interaction at all). In going from precipitation to mixing, all other factors remain the same. Precipitated R_2O_3-Al_2O_3 samples are highly disperse and thermally stable; the total specific surface of binary samples thus obtained is somewhat higher than that of the samples prepared by mixing. The R_2O_3 nature governs the porous structure of the samples under study. Yttrium- and lanthanum-aluminium samples are characterized by the polydisperse distribution of pore volumes. Cerium-aluminium compositions have fine pores.

EFFECT OF PREPARATION PROCEDURE ON THE PROPERTIES OF NICKEL-MAGNESIUM CATALYSTS FOR METHANE STEAM REFORMING

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

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

We have studied the physicochemical and catalytic properties of Ni-Mg catalysts for the methane steam reforming with regard to their preparation procedure. The solid solutions of MgO and NiO form independently of preparation procedure. Meanwhile, relationship between the solutions and their elemental cell parameters depends on the active component content and synthesis procedure. The samples obtained by mixing have a higher reduction degree than those obtained by coprecipitation. Metal nickel has the largest surface at 20-30 mass. % of Ni. Specific activity of Ni-Mg catalysts in methane steam reforming remains practically constant, $0.1 \pm 0.03\ sm^3\ m^{-2}\ s^{-1}$, regardless the synthesis procedure.

VANADIUM CATALYSTS AND DESULPHURIZATION OF SULPHUR COMPOUND-CONTAINING GASES THEREWITH

R.A. Buyanov, A.M. Tsybulevskii*, B.P. Zolotovskii, D.P. Klevtsov, V.I. Mourin* (VNIIGAS, Moscow, Russia)

US Patent,
№ 5.396.076 (1994).

A novel polyfuctional catalyst for the Claus process has been developed. It is resistant to carbonization and sulphatation thus providing a high degree of COS and CS_2 hydrolysis. The catalyst has a unique protection, it converts oxygen with very high rates. The catalyst is covered by the patents of 18 countries. We also suggest how to use this polyfunctional catalyst.

REGULARITIES OF Pt PRECURSORS AND MODIFYING DOPES SORPTION DURING PREPARATION OF BIMETAL CATALYSTS SUPPORTED ON SPINELS

N.A. Pakhomov, R.A. Buyanov

6th Intern. Symp. on Scientific Bases for Preparation of Heterogeneous Catalysts, Louvain-la-Neuve, Belgium.
Preprints, 3 (1994) 323-332.

We have studied how Pt precursors and modifying dopes in various ion sates sorb on spinels ($ZnAl_2O_4$ and $MgAl_2O_4$) and γ-Al_2O_3.

Chlorplatinate anion and additive cations are found to adsorb on support surface when deposited from single component or binary solutions, whose pH is considerably lower than that of support in its isoelectric point.

If the Pt anchoring proceeds via the ion exchange with support hydroxyls, cations deposit in the following ways:

1) via cation exchange of Cu^{2+}, Cd^{2+} and Sn^{2+} with Mg^{2+} or Zn^{2+} subsurface cations from the spinel structure, and that of In^{3+} with Al^{3+} subsurface cations.

2) via "surface precipitation". In this case, anion exchange of support OH-groups with a dissolved salt anion occurs. Then, as solution pH increases in the support pores, a modifying cation precipitates on the support surface as a hydroxide or a basic salt.

These data allow to predict experimentally a complex relationship between the components during their deposition from binary solutions and to choose purposefully the procedure of Pt and modifying additives deposition and to obtain bimetal catalysts of desired dispersity, active metal concentration and components ratio.

So, sorption from binary solutions appears to differ considerably for the elements that form (Pt-Sn system) or do not form complexes with Pt in the impregnating solution.

For the Pt-Sn complex anions, the sorption intensity is lower by an order of magnitude than for $[PtCl_6]^{2-}$. This factor restricts the use of competitive Pt and Sn deposition from the solution of their complexes to produce highly dispersed catalysts on spinel supports.

If there is no interaction in the $[PtCl_6]^{2-}$ impregnating solution, anion competes with sorption decreasing the Cu^{2+}, In^{3+} and Cd^{2+} sorption rate and / degree. Depending on the mechanism of anchoring to support surface, cations can either accelerate (Cu^{2+}) Pt sorption from diluted solutions or leave it unaffected (In^{3+}, Cd^{2+}). When Pt is deposited from the concentrated solutions, its sorption decreases as the additive content in solution increases.

LOW-WASTE PRODUCTION OF ALUMINA CATALYSTS FOR GAS SULPHUR RECOVERY

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2nd Intern. Exhibition-Seminar "Catalysis-94", St.Petersburg, Russia. Proc. of Seminar "Urgent Problems of the Catalysts Manufacturing and Large-Scale Application of Catalysis", Novosibirsk, Russia, (1994) 74-87.

A new technology for the Claus process alumina catalyst production has been developed, which unlike the traditional methods is low-waste. This technology bases on the technical alumina hydrate thermochemical activation (TCA) and its subsequent hydration. The conditions of alumina hydrate thermochemical activation that give a product with the elements of initial compound layered structure with 4-, 5- and 6-coordinated aluminium cations have been revealed. The TCA product is in a non-equilibrium metastable state and possesses extra energy and reactivity. We have considered the key points of formation of pseudoboehmite, which is one of the most important semi-products for alumina support and catalyst production. The low-waste technology has been introduced at "Agrokhim" Ltd (Shchelkovo). The catalytic activity of the Claus alumina catalyst (IC-27-22) produced by this technology is comparable to that of the best foreign samples (CR, S-100).

NEW CATALYSTS AND PROCESSES FOR ENVIRONMENTAL PROTECTION

Z.R. Ismagilov, R.A. Shkrabina, G.B. Barannik, M.A. Kerzhentsev

2nd Intern. Exhibition-Seminar "Catalysis-94", St.Petersburg, Russia. Proc. of Seminar "Urgent Problems of the Catalyst Manufacturing and Large-Scale Application of Catalysis", Novosibirsk, Russia, (1994) 54-64.

The present report reviews a seris of studies on the design of new catalysts and catalytic processes to purify gas effluents and process liquid and solid wastes.

These are the main trends of our studies: design of catalysts, supports and processes for fluidized and moving catalyst bed reactors; design of catalysts and processes for the catalytic combustion of fuels and wastes; gas purification from hydrogen sulphide via the direct catalytic H_2S oxidation to sulphur; development of honeycomb monolith ceramic catalysts for gas purification.

Spherical Alumina Supports

We have studied what conditions of the hydrocarbon-ammonia formation of supports, amount and strength of acid-peptizer; pseudoboehmite hydroxide properties allow to produce a highly strong spherical γ-Al_2O_3. For alumina spheres 1-3 mm in diameter, the average mechanical strength is 20-25 MPa. Supports and catalysts of such mechanical strength work very efficiently in the fluidized and moving catalyst bed reactors. However, if we use γ-Al_2O_3 as a support, we must find some environmentally safe technology for its production. We have designed an ingenious process for gibbsite amorphization in the fludized catalyst bed in a catalytic heat generator (CHG). The product of thermal decomposition (PTD) exhibits unique properties (primarily a very high reactivity), that provide its efficient processing to pseudoboehmite aluminium hydroxide.

The hydrocarbon-ammonia formation of pseudoboehmite hydroxide with its subsequent thermal treatment allows to obtain alumina carriers for catalysts operation in the moving and fluidized catalyst beds.

Modifying chemically alumina systems, we created a new generation of supports with a high thermal and mechanical stability. Thus, a specially designed method of Mg cations (2-4%) introduction increases the mechanical strength of Al_2O_3 spheres by 1.5-2 times at 550°C and by 4-5 times at 1200°C.

La, Ce and SiO_2 cation dopes hamper the phase transitions of the low-temperature forms of Al_2O_3 to corundum, and so stabilize the specific surface of supports.

New supports serve for the catalyst preparation when local heatings (up to 1100°C) at the intensive mechanical effects can happen.

Catalysts for Fuel Combustion in Fluidized Catalyst Bed

A number of deep oxidation catalysts recommended for the catalytic combustion were studied during the fuel combustion in common reactors. Their catalytic performance as well as structural and mechanical properties change significantly under the influence of high temperatures and reaction medium, thus causing catalysts deactivation and decomposition. Therefore, we have stated the main principles how to select the catalyst for fuel combustion in the fluidized catalyst bed. These principles take into account how the catalyst components interact during the thermal treatment.

Using these principles and the data reflecting the interaction between the oxide complexes of transition metals and various alumina supports, we have designed a series of new catalysts for fuel combustion. These catalysts exhibit high thermal and mechanical stability, but differ in their catalytic performance. We used spherical active alumina of 0.4-1.0 mm, 1.0-1.6 mm, 1.4-2.0 mm and 2.0-3.0 mm fractions as supports for catalyst preparation.

Processes Based on the Catalytic Heat Generators

The CHG are very promising for neutralizing industrial wastes and sewages containing various organic admixtures.

The process is based on the complete oxidation of organic components in the fluidized catalyst bed at 650-750°C to produce environmentally harmless products, such as water, carbon dioxide and molecular nitrogen. This method is very promising for neutralizing wastes, containing organic admixtures, liquid organic wastes, including sulphur, nitrogen, chlorine containing compounds and for neutralizing concentrated gas effluents and sewage sediments.

Direct Selective Oxidation of Hydrogen Sulphide to Sulphur

It is very important to utilize hydrogen sulphide efficiently to make power production, oil&gas production and processing friendly to environment.

A direct selective catalytic oxidation (DSCO) of H_2S by oxygen seems to be very promising for the purpose.

Highly exothermal oxidative processes, performed in a fluidized bed of strong spherical catalysts (CHG), allow to expand the use of DSCO, since there are no restrictions towards H_2S concentration, and to solve the problems related to environmental protection against H_2S.

Honeycomb Monolith Supports and Catalysts

Honeycomb monolith catalysts of various shape are widely used for synthesis, purification of gas mixtures and incineration of effluent gases. These catalysts have a low pressure drop, provide a good heat and mass transfer and a high factor of the active mass utilization.

A series of syntheses and studies of honeycomb monolith supports and catalysts were performed at the Boreskov Institute of Catalysis. Oxide ceramic supports based on cordierite ($2Al_2O_3 \cdot 2MgO \cdot 5SiO_2$), alumosilicates ($Al_2O_3$; SiO_2), alumina and titania have been studied in detail. We have also studied morphology and genesis of the phase composition of monolith supports, their structural and mechanical properties as well as their thermal stability.

Basing on our results, we have formulated the main principles for the synthesis of monolith supports of various geometry with desired structure and mechanical properties.

PREPARATION OF $LA_{1-x}Sr_xMnO_3$ PEROVSKITE CATALYSTS SUPPORTED ON CERAMIC FOAM MATERIALS

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Fall Meeting, Nov.27-Dec.2, 1994, Boston, USA.
Material Research Society, v.386 (1994).

At present, a new way to treat the exaust gas of diesel engines is required for catalytic converters in cars. Mixed oxides such as perovskites are very promising catalysts for high temperatures. To operate such catalysts at high temperatures, it is necessary to deposit these oxide catalysts as an active layer on a top of a suitable support material of high thermal stability. Both ceramic and metal substrates can be suitable for this purpose. The supported perovskite oxides are also very promising catalysts for environmentally clean energy production.

The present work concerns the preparation of $La_{1-x}Sr_xMnO_3$ catalysts supported on ceramic foam materials. Mullite foams were used as supports.

In order to prepare the perovskite catalysts supported on ceramic foams a "polymer coating" technique was designed. This technique uses synthesized non-porous perovskite powders and a polymer as a binder. The non-porous perovskite catalysts are prepared via the co-precipitation of La, Sr and Mn acetylacetonates. The catalysts were analyzed with XRD, SEM and BET methods, the reducibility of supported and massive perovskite catalysts was studied by the TPR method. The activity of $La_{1-x}Sr_xMnO_3$/(mullite foam) was measured in methane oxidation.

TiO_2 PHOTOCATALYTIC DESTRUCTION IN WATER OF VARIOUS AROMATIC POLLUTANTS CONTAINING N, P OR S HETEROATOMS

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1st European Congr. on Catal.- "EUROPACAT-1",
Montpellier, France. Abstacts, 2 (1993) 709.

The photocatalytic degradation of four nitrogen-containing compounds (benzamide, N-phenylethanamide, nitrobenzene and pyridine) and of two organophosphorous insecticides (tetrachlorvinphos and phenitrothion) has been studied. The destruction of aromatic pollutants proceeds via the ring hydroxylation at positions determined by both usual orientation rules and adsorption modes. The aromatic and aliphatic intermediates of degradation were detected and identified. Nitrogen, sulphur or phosphorus are mineralised to form nitrate or ammonium (depending on the starting oxidation state of N) sulphate and phosphate ions.

OXIDATIVE COUPLING OF METHANE OVER Si-Mo-V OXIDE HONEYCOMB CATALYSTS

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2-nd Workshop Meeting on C_1-C_2 Hydrocarbon
Converison, Krasnoyarsk, Russia.
Abstracts, (1994) 65-67.

Honeycomb monolith catalysts possess a number of unique properties that are very attractive for the oxidative coupling of methane (OCM) allowing both fundamental studies of heterogeneous-homogeneous reactions and industrial process design.

Honeycomb catalysts were produced as extrudates (monolith diameter 9.8-9.9 mm, square channel size 1.05 mm, walls thichness 0.30 mm, length 1.05 mm). Catalysts comprise mainly SiO_2 modified by V_2O_5, MoO_3 and binders. A continuous flow apparatus with a quartz tube reactor (ID=10 mm) was used. Gas was analyzed by

HP 5890 Å gas-chromatograph. The effects of reaction temperature, gas flow rate, honeycomb length, honeycomb position in the reactor, post-catalyst reaction volume, pore structure of monolith and CH_4:O_2 ratio on the catalysts activity and products distribution have been studied. The activity of honeycomb and crushed honeycomb catalysts have been compared with those of "bare" cordierite honeycomb and crushed honeycomb catalysts.

The present study shows that the conversion-selectivity patterns of such Si-Mo-V oxide catalyst in OCM reaction might be considered very promising according to the reactivity index recently proposed by Maitra.

THERMOSTABILITY OF COPPER-CHROMIUM OXIDE CATALYSTS ON ALUMINA SUPPORT PROMOTED BY LANTHANUM AND CERIUM

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6th Intern. Symp. on Scientific bases for the preparation of heterogeneous catalysts, Louvain-la-Neuve, Belgium.
Proceed., (1994) 367-374.

The thermal stability of copper and chromium oxide catalytic system on Al_2O_3 promoted by lanthanium and cerium, calcined at 1273K, has been studied by X-Ray, SBET and mechanical strength measurements. Both lanthanium and cerium are found to suppress the mineralizing effect of active components. Lanthanium appears to be a more efficient inhibitor than cerium. The content of α-Al_2O_3 phase in non-promoted catalysts is twice higher than that in promoted ones. SBET of promoted catalysts is 2-10 time higher than that of pure catalysts, while the mechanical strength of catalysts grains is almost the same (20-40 MPa).

Basing on results obtained we have stated some requirements towards the stabilizing ion to be introduced into alumina:

i) the stabilizing ion should restrict the solubility of catalyst components possessing a pronounced mineralizing effect;

ii) the stabilizing ion should at high temperatures form a stable compound with alumina (thus inhibiting the α-Al_2O_3 formation).

NEW POSSIBILITIES OF CATALYSIS FOR TREATMENT OF HAZARDOUS WASTE FROM NUCLEAR MATERIAL PROCESSING PLANTS

Z.R. Ismagilov, A.C. Heywood*, M.G. Adamson* (Lawrence Livermore National Laboratory, Livermore, USA), M.A. Kerzhentsev.

US-Russia Workshop on Environmental Catalysis,
Wilmington, Delaware, the USA.
Proceed., (1994) 51.

At nuclear material processing plants there are large quantities of accumulated mixed organic wastes of complex composition containing industrial oils, vacuum grease, used extractants and their solvents, and various hazardous organic compounds contaminated with U, Pu and their fission products.

At present the problem of environmentally safe destruction of these wastes is not yet solved satisfactorily. Ussually the wastes are kept in tanks which represent a threat to the environment because of their imflammability explosiveness, toxicity and radioactivity. The method of waste thermal incineration used in some cases can not be considered sufficiently safe because it produces toxic nitrogen oxides and other pollutants and generates sub-micron radioactive particles that may emit into the atmosphere with combustion off-gases.

We propose the environmentally safe technology to incineration organic wastes on catalysts and purify tail gases from acid components (oxides of phosphorus and sulphur and HCl) and radioactive dust. The key feature of the method is that it allows a complete oxidation of organic compounds in stochiometric mixtures with air at sufficiently low temperature (600-700°C) to prevent the thermal formation of NO_x. Special mechanically strong catalysts in a fluidized bed provide the efficient removal of reaction heat. The catalytic combustion of various wastes: organic liquid solvents, chemical industry wastes, nitrogen-containing compounds, used liquid scintillators, etc., was tested in bench and pilot-scale installations. The tests revealed that the waste incineration technology has the following advantages:

- it incinerates the wastes with high efficiency (over 99.9%);
- it suppresses pollutants formation (NO_x, CO, HC);
- does not need refractories (constituting secondary waste stream) and thus allows maintenance costs reduction.

X-RAY STUDY OF Ce DOPED Al_2O_3

V.A. Ushakov, E.M. Moroz, N.A. Koryabkina, R.A. Shkrabina

XVI Conference on Applied Crystallography, Gieszyn, Poland. Abstracts, (1994) 46.

At 1123-1323 K the low temperature forms (γ, η, χ) are known to transform to the high-temperature ones (δ, θ, æ) in alumina supports for catalysts. At higher temperatures the forms transform to α-Al_2O_3. Usually, support modification by various compounds decelerates the phase transitions and thus makes the transition forms more stable themally.

Here we report on the X-ray study of the phase composition of alumina modified by cerium ions under thermal treatment at 373-1573K. The thermal stability of alumina was shown to increase only at the low contents of cerium when their concentration attains 5 wt.% of CeO_2. The method of cerium introduction has no influence on the thermal stability of Al_2O_3. Thus, cerium appears to be less efficient in stabilizing Al_2O_3 structure due to the different and not pronounced nature of its interaction with Al_2O_3 support.

PREPARATION OF CATION-SUBSTITUTED HEXAALUMINATES WITH LARGE SURFACE AREA USING MECHANICAL ACTIVATION METHODS

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6th Intern. Symp. on Scientific bases for the preparation of heterogeneous catalysts, Louvain-la-Neuve, Belgium. Preprints, 3 (1994) 77-84.

In the present work cation-substituted barium hexaaluminates has been prepared using mechanical activation methods. The effect of precursors, milling regimes and calcination temperature on the synthesis has been investigated. A new method to prepare cation-substituted hexaaluminates with large surface area has been developed and optimum conditions for the mechanochemical synthesis of Mn and Fe loaded Ba hexaaluminates are viewed.

STRUCTURE OF METAL-METAL OXIDE Pd-V_2O_5/Al_2O_3 CATALYST FOR COMPLETE OXIDATION OF HYDROCARBONS

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Appl. Catal. A, 112 (2), 141-148 (1994).

A Pd-V_2O_5/Al_2O_3 catalyst system was studied by means of X-ray diffraction, ESR methods and chemical analysis. Under the operation conditions of complete benzene oxidation, the following phases were registered:

β-$Na_2V_2O_5$, θ-$Al_{0.33}V_2O_5$ and $Al^{3+}_{0.07}V^{5+}_{0.07}V^{4+}_{1.86}O_4$. The efficient electrons delocalization between the cluster V^{4+} ions in these phases facilitates the electron transitions at the redox step of catalytic oxidation.

INVESTIGATION OF La AND Mg DOPED Al_2O_3

V.A. Ushakov, N.A. Koryabkina, R.A. Shkrabina

Intern. Conf. on Powder Diffraction and Crystal Chemistry, St. Petersburg, Russia. Abstracts, (1994) 127.

At 1123-1323K the low temperature forms (γ, η, χ) are known to transform to the high-temperature ones (δ, θ, æ) in alumina support for catalysts. At higher temperatures the forms transform to α-Al_2O_3. Usually, support modification by various compounds decelerates the phase transitions and thus makes the transition forms more stable thermally.

Here we report on the X-ray study of the phase composition of alumina modified by the mixture of lanthanium and magnesium ions under thermal treatment at 373-1573K.

OZONE-CATALYTIC PURIFICATION OF VENTILLATION AND EXHAUST GASES FROM VOLATILE ORGANIC COMPOUNDS

V.A. Sazonov

1st Intern. Environm.Technology Business Action Conf., Moscow, Russia. Proc., (1994).

The method is based on complete oxidation of organics by ozone over a special catalyst designed at the Boreskov Institute of Catalysis. The method is especially suitable for the purification of low-concentrated gas streams containing aromatic hydrocarbons (concentration of volatile organic compounds < 150 mg/m^3). The purification degree >94% is obtained at 40-60°C (compare to conventional catalytic incineration at 300-400°C). The prototype apparatus for this process (OKA-3000) of 3000 m^3/h capacity was designed and tested.

THE TYPE OF COKE DISTRIBUTION ON OXIDE AND METAL OXIDE CATALYSTS

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2nd Workshop Meeting on C_1-C_3 Hydrocarbon
Conversion, Krasnoyarsk, Russia.
Abstracts, (1994) 99.

Carbonized catalysts are very promising as supports and adsorbents.

Catalytic decomposition of C_1-C_4 alkanes or other hydrocarbons over metals and oxides is used to produce carbon-mineral composites.

Adsorption methods were used to get some idea on the distribution and morphology of carboneous deposits. Calculation techniques for analysis of changes of surface area, pore volume, density, etc. are suggested according to the coke specific quantity distribution.

EFFECT OF PARENT TITANIUM OXIDE ON THE PHYSICO-CHEMICAL PROPERTIES OF Cu-Ti OXIDE CATALYSTS

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React.Kinet.Catal.Lett.,
52 (1994) 129-137.

The physico-chemical properties of Cu-Ti oxide catalysts have been studied. The effect of parent titanium dioxide properties (specific surface, preparation procedure) on the state of Cu ions over the anatase surfaces has been revealed.

Cu on TiO_2 surface in the analyzed system was shown to exist in two principal forms, CuO and the surface complex of Cu ions with titanium dioxide. Both the decrease of support specific surface and the increase of copper concentration in samples make the concentration of crystalline CuO phases grow. CuO provides a drastic decrease of the catalyst specific surface. However, the state of copper ions on TiO_2 surface as well as the correlation between the CuO phase amount and the surface complexes formed between the copper ions and titanium dioxide appear to be specified not only by the surface area of parent anatase, but also by its chemical nature and amount of admixtures.

RELATIONSHIP BETWEEN THE SULPHUR DIOXIDE OXIDATION AND SELECTIVE CATALYTIC NO REDUCTION BY AMMONIA ON V_2O_5-TiO_2 CATALYSTS DOPED WITH WO_3 AND Nb_2O_5

N.N. Sazonova, L.T. Tsykoza, A.V. Simakov, G.B. Barannik, Z.R. Ismagilov

React.Kinet.Catal.Lett.,
52 (1994) 101-106.

The performance of V_2O_5-TiO_2 catalysts doped by WO_3 and Nb_2O_5 in sulphur dioxide oxidation and in NO selective catalytic reduction (SCR) by ammonia has been studied.

At the tungsten addition to the catalyst the SCR activity rises and sulphur dioxide oxidation is suppressed in the presence of SO_2.

Niobidium doped catalysts loose their catalytic activity during the sulphur dioxide oxidation as well. For the catalysts doped with niobidium, the sulphur dioxide conversion is 10%, while for niobidium-free catalysts it is 12%.

Thus, tungsten and niobidium added to V-Ti catalysts significantly suppress sulphur dioxide oxidation and increase catalysts activity in NO selective catalytic reduction by ammonia.

EFFECT OF RAW MATERIAL NATURE ON THE PROPERTIES OF V-W-Ti-O CATALYSTS FOR EXHAUST GASES PURIFICATION FROM NITROGEN OXIDES

I.T. Tsykoza, V.F. Lyakhova, G.B. Barannik

1st Int. Conf. on Process in Inorganic&Organometallic
Chem., Polanica Zdroj, Poland. Abstracts, (1994) 98.

We have studied the physico-chemical properties and activity of mixed V-W-Ti-O catalysts at NO selective reduction with ammonia with regard to the chemical nature of initial V and W compounds and TiO_2 admixtures.

The data on NO conversion (a flow installation, T = 225°C, gas mixture content: 0.005 vol.% NO, 0.5 vol.% O_2, 0.005 vol.% NH_3; 3 mL/s mixture feed rate, 0.4 g sample; 0.5-1.0 mm particle size) for

V-Ti-O and W-Ti-O binary model systems and for V-W-Ti-O samples of various composition prepared from different TiO_2 (anatase) indicate that NH_4VO_3, $VOSO_4$ and WO_3 are better than V_2O_5 and K_2WO_4, respectively.

The activity of V-W-Ti-O catalysts appears to be markedly dependent of admixtures (SO_4^{2-} and Cl^--ions, etc.) formed at TiO_2 production. So, as Cl^--ions content increases, NO conversion linearly decreases. The samples containing SO_4 ions are usually more active than those with Cl^--ions. The NMR data permit to attribute this fact to the different nature and correlation of OH-groups on the TiO_2 surface causing a different distribution of active V and its environment.

Note that the raw material composition affects the extrudability of the catalyst mass, mechanical strength and thermal resistance of obtained catalysts. TiO_2 dispersity is of considerable importance here.

MONOLITH HONEYCOMB CATALYSTS ON MODIFIED ALUMINOSILICATE SUPPORTS

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1st Intern. Conf. on Process in Inorg. and Organometal. Chem., Polanica Zdroj, Poland. Abstracts, (194) 68.

In the present paper we report our results on the preparation of honeycomb catalysts on various aluminosilicate supports modified by amorphous alumina powder, obtained via gibbsite thermal pulse decomposition at 670 K. Modification was carried out during the the initial extrusion mixture preparation. Catalysts were prepared via the support impregnation with a solution of salts or oxides of Co, Cu, Mg in chromic acid without preliminary washcoat deposition. Catalysts thus obtained were studied by various instrumental methods. The genesis of the phase composition of monolith honeycomb catalysts with respect to the treatment temperature has been elucidated. The catalysts activity was determined in the model reactions of complete oxidation of butane and CO and of nitrogen oxide reduction with ammonia.

SOME ASPECTS OF EXTRUSION PROCEDURE FOR MONOLITH SCR CATALYST BASED ON TiO_2

V.F. Lyakhova, G.B. Barannik, Z.R. Ismagilov

6th Intern. Symp. on Scientific Bases for the Preparation of Hetergeneous Catalysts, Louvain-la-Neuve, Belgium. Proceed., 2 (1994) 371-378.

Honeycomb monilith catalysts attract intensive interest due to a high porosity of the contact layer forming (50-80%) and to a large diameter (2-30 mm) of hydraulic channels.

The qualitative and quantitative composition of these catalysts used for the SCR of NO_x with ammonia is often determined by the purified gas composition. Oxide V-Ti compositions doped with MoO_3 or WO_3 are widely used. Mixing oxides with proper inorganic and organic plasticisers, one can produce catalyst compositions suitable for the extrusive formation of honeycomb monoliths. Inorganic plasticizers give required mechanical strength to monoliths, organic plasticizers provide a necessary rheology to the catalyst mass, thus making its extrusion successful.

Here we report our study on the effect of organic plasticizers on the honeycomb catalyst extrusion formation and on the catalytic properties of oxide compositions.

Several types of honeycomb monoliths with a square side of 24.75-150 mm were prepared. After thermal treatment, catalysts with a 15-90 m^2/g specific surface area formed. The rheological properties of catalyst pastes were studied. In order to elucidate the effect of a plasticizer on the catalytic properties during the initail stage, the behaviour of catalyst pastes under heating has been studied. Organic additives appear to be susceptible to destruction under the thermal treatment of catalytic pastes.

The electron microscopy study has shown that the honeycomb catalysts prepared by different organic plasticizers have almost identical morphology peculiarities and remind the microstructure of TiO_2. Thus the catalyst morphology does not depend on the plasticizer nature and composition.

Our experimental data allow to choose a plasticizer for controlling the extrusion and catalytic properties of masses formed. Using the optimum combination we can produce highly active and rather strong SCR catalysts.

MODELING OF PERIODICALLY OPERATING PACKED-BED SO_2 OXIDATION REACTOR OF HIGH CONVERSION

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Chem.Eng.Sci.,
49 (3), 335-341 (1994).

Kinetic and mechanistic studies extending over a decade have led researchers at the Institute of Catalysis to a kinetic as well as a reactor model for SO_2 oxidation capable of describing the rate of SO_2 oxidation at a high SO_2 conversion and transient operating conditions.

Using kinetic parameters and transport properties obtained for a Russian commercial catalyst, this model was applied to simulate the experiments of Briggs et.al., when the feed to a packed bed of an industrial, potassium-promoted, vanadia/silica catalyst was periodically switched from an SO_3-SO_2-O_2-N_2 mixture to air. These experiments displayed rapid temperature excursions on the switching and SO_2 conversions that approached the equilibrium limit. A good agreement of the simulation with the measurements of Briggs et.al. was obtained.

This result demonstrates that the model developed at the Institute of Catalysis is robust and will be widely applicable.

MATHEMATICAL MODELING OF SO_2 OXIDATION REVERSE-PROCESS INCLUDING CRYSTALLIZATION OF ACTIVE COMPONENT OF LIQUID CATALYST

Yu.V. Malozyomov, G.A. Bunimovich, Yu.Sh. Matros, N.A. Chumakova and B.S. Bal'zhinimaev

Teor.Osn.Khim.Tekhnol.,
28 (1), 34-42 (1994).

The dynamics of crystallization process of vanadium catalyst active component has been studied with a reverse flow reactor model with high frequency reversals. The low values of input temperature and SO_2 concentration are considered.

The changes of the catalyst crystal phase fraction appear to be very slow. For instance, the process lasts for up to several days. Certainly, crystallization rate greatly depends on the temperature. The typical duration of the crystal phase changes under the temperature of 80-200 ^oC is approximately equal to months and even years. At a high temperature (in the central part of the catalyst bed) the primary crystallization is limited by the critical size of crystallite able to start crystallization, because this size is comparable with the pore diameter. The maximum crystallization rate occurs under 340-380 ^oC.

Provided for crystallization process for the reverse flow operation SO_2 conversion decreases within 1.5-2 % and the maximum bed temperature increases within 19-22 ^oC. The crystallization influence is especially pronounced, when the high temperature region reduces (at a lower height of catalyst bed and a smaller size of catalyst pellets).

COMPARATIVE ANALYSIS OF TWO TECHNOLOGICAL SCHEMES OF CATALYTIC PROCESS PERFORMANCE UNDER UNSTEADY-STATE REGIMES

Yu.Sh. Matros, A.S. Noskov, A.N. Zagoruiko and O.V. Goldman

Teor.Osn.Khim.Tekhnol.,
28 (2), 139-144 (1994).

We compare two different schemes for unsteady-state catalytic processes in a reactor with three packed beds including one catalyst fixed bed and two beds of an inert material. In the first scheme the periodical gas flow reversals have been done simultaneously in all the beds while in the other case the gas flow direction has been changed periodically in the inert beds only.

We consider a single exothermic first order reaction which is typical for many catalytic processes of waste gases purification. Mathematical modeling shows that for a wide range of technological parameters the first scheme provides significantly more efficient heat recover than the second scheme.

NITROGEN OXIDE (I): THE SOURCES

A.S. Noskov and I.R. Abdulin

Chemistry in sustainable development,
1 (1993) 403-405.

The paper presents the calculation and exploration of easy nitric acid production plants. Nitrous oxide concentration in exhaust gas is 0.5-0.15 % vol, as a rule 1 % vol. The global emission of nitrous oxide is about 1,000,000 ton provided for the world production of nitric acid (35 Mt of 100 % HNO_3 in 1985).

The paper includes chemical equations, diagram of sources correlation and table with the data of exhaust gas content analysis.

NITROUS OXIDE: SOURCES AND PURIFICATION METHOD

A.S. Noskov, I.R. Abdulin, Yu.Sh. Matros, G.V. Vanin

2nd Tokyo Conf. on Advanced Catalytic Science and Technology - "TOCAT-2", Tokyo, Japan. Abstracts, (1994) 329-330.

The correlations between the general industrial sources of nitrous oxide emission into the atmosphere base on earlier matter and authors analysis.

Here we report on the nitrous oxide impurities depletion from the initial gas in the REVERSE pilot tests. Initial N_2O concentration was 0.1-2.5 % vol. Despite that the inlet gas had the temperature of 20-25 °C it heated up to 600-610 °C in the catalyst bed and nitrous oxide conversion attained 99.5 %. As a catalyst synthetic zeolite Fe-HZSM-5 was used.

REVERSE FLOW CATALYTIC TECHNOLOGY FOR CONTROL OF NITROGEN OXIDES AND AMMONIA IN WASTE GASES

L.N. Bobrova, A.S. Noskov, Yu.Sh. Matros and E.S. Borisova

2nd Tokyo Conf. on Advanced Catalytic Science and Technology - "TOCAT-2", Tokyo, Japan. Abstracts, (1994) 311-312.

N-containing impurities like NO_x, NH_3, and so on, are involved in environment acidification.

The general-purpose control technology is a catalytic one. Additional heat-exchanger as well as energy consumption used for the treatment of low-temperature waste gases by the traditional technique can be excluded if unsteady - state method under REVERSE FLOW operation in the packed bed reactor is applied. Furthermore, the REVERSE technology for selective catalytic reduction of Nox by ammonia is more efficient than the common steady-state one, because both thermal and adsorptive properties of the catalyst bed are exploited.

The data of mathematical simulation, experimental tests and industrial operation experience of the process are presented.

MULTIPLICITY IN CATALYTIC REVERSE-PROCESS REACTORS

N.A. Chumakova and Yu.Sh. Matros

13th Intern. Symp. on Chemical Reaction Engineering, Baltimore, Maryland, USA. Abstracts. (1994) D3-3.

The recently developed theory of forced unsteady-state catalytic processes involves one of the most studied and widely applied REVERSE-PROCESS. The principal feature of the latter is a periodical change of gas flow direction through the catalyst fixed bed into the opposite one. The problem of solution multiplicity under such forced conditions was put forward. So, it was necessary to study conditions providing a stable high temperature regime preferable for practice.

We use the model of relaxed steady-state regimes to study the multiplicity regions for a single irreversible first order reaction.

We compare two different approaches: a) as usual the gas filtering velocity trough the catalyst layer is given, and b) the pressure drop on the bed is a priori fixed, the change of the physical and chemical gas properties inside the bed is taken into account, the linear gas filtering velocity is to be found. The second approach seems to be very important for practice, because it allows to deal with a new one-dimensional description to estimate the consequences of actual penetration inhomogeneity in the different regions of catalyst bed.

MATHEMATICAL MODELING OF SULPHUR CONDENSATION AND EVAPORATION INSIDE THE CLAUS CATALYST PELLET

A.N. Zagoruiko and Yu.Sh. Matros

Teor.Osn.Khim.Tekhnol., 28(1), 1-5 (1994).

A mathematical model of process inside a catalyst pellet in which the interaction between hydrogen sulphide and sulphur dioxide (the Claus reaction) occurs simultaneously with sulphur condensation/evaporation is proposed. The rate of phase transfer is assumed to be proportional to the difference between the current sulphur vapors and the equilibrium sulphur concentration in the saturated vapor.

Numerical estimations demonstrate that at high values of proportionality coefficient solution does not depend on this value itself. Mathematical simulation shows that under different conditions there may exist three quite different regimes of sulphur condensation inside the Claus catalyst pellet: condensation may take place over the whole pellet volume, in its central part only and in the pores mouth. The questions how the liquid sulphur distribution along the pellet radius and the observed rate of Claus reaction depend on type of the regime are discussed.

DEPARTMENT OF HYDROCARBON CONVERSION, OMSK

SORBENTS MOULDED FROM LIGNITES, THEIR PROPERTIES

O.N. Baklanova, V.Yu. Davydova, V.K. Duplyakin, V.V. Shim, M.L. Shchipko*, M.V. Trenikhin (Insitute of Chemistry and Chemical Engineering SB RAS, Krasnoyarsk, Russia)

2nd Symp. on Problems of Catalysis and Coal Chemistry, Krasnoyarsk, Russia. Abstracts. (1994) 88.

We have designed a new technology for moulding sorbents based on the lignites of Kansk-Achinsk basin. It allows to obtain the sorbents with a 290-380 m^2/g specific surface. Their total pore volume is 0.50-0.55 cm^3/g and resistance attains 25-30 kg/cm^2. These sorbents can be used as inexpensive capacious sorbents for diverse applications, including environmental protection.

THE ROLE OF A STOICHIOMETRIC COMPONENTS IN THE MEDIUM OF REFORMING PROCESS

Yu.N. Kolomytsev, E.M. Chalganov, D.M. Radko, O.N. Semenova, A.S. Belyi

1st Russia-Japan Symp. on Petroleum, Nature Gas and Petrochemistry, Yuzhno-Sakhalinsk, Russia. Proceed., (1993) 148-149.

Effect of chlorine concentration in a catalyst on coke deposition on platinum have been studied.

The data obtained indicate that chlorine acts as an inhibitor of coke deposition, and prevents coke deposition on the Pt atom, when its content approaches a certain level (0.7-0.8 mass.%). The results of catalyst investigations by several physico-chemical and absorption methods show that chlorine, hydrogen and sulphur can insert into the inner coordination sphere of ionic Pt forms, thus causing essential changes in the catalyst properties.

OXIDIZED PLATINUM SURFACE IN Pt/Al_2O_3 REFORMING CATALYSTS: IR STUDIES

M.D. Smolikov, A.V. Zaitsev*, N.M. Khabibislamova, A.S. Belyi, V.Yu. Borovkov*, V.K. Duplyakin, V.B. Kazanskii* (Zelinskii Inst. Org. Chem., Moscow, Russia)

React. Kinet. Catal. Lett., 53 (1994) 169-175.

The influence of haloid ions on the state of dispersed Pt in oxidized catalysts has been investigated, adsorbed CO being used as a probe. Charged Pt complexes form on catalyst oxidation, that exhibit CO bands at 2130, 2150, 2165, 2170 and 2180 cm^{-1}. The composition of the complexes depends on the oxidation temperature and the nature of halide ions.

PLATINUM STATE IN $Pt/\gamma\text{-}Al_2O_3$ (Cl) REFORMING CATALYSTS

M.D. Smolikov, A.S. Belyi, D.I. Kiryanov, V.Yu. Borovkov*, A.V. Zaitsev*, V.K. Duplyakin, V.B. Kazanskii* (Zelinskii Inst. Org. Chem., Moscow, Russia)

React. Kinet. Catal. Lett., 53 (1994) 161-167.

Particular properties of metal (Pt^o) and electron deficient (Pt^σ) platinum have been investigated by chemisorption and IR methods. The data on the catalyst resistance to sintering in hydrogen and to oxidizing media are reported.

MICRODISTRIBUTION OF IONIC AND METALLIC PLATINUM FORMS IN Pt/Al_2O_3 HYDROCARBON CONVERSION CATALYSTS

I.E. Udras, D.I. Kiryanov, M.D. Smolikov, A.S. Belyi

4th European East-West Conf.&Exhibition on Materials and Processes, St.Petersburg, Russia. Abstracts, (1993) 25.

The pioneer data showing the distribution of ionic platinum form (Pt^σ) over different size pores in the structure of reforming catalysts are presented.

Under particular conditions oxygen is found to adsorb selectively on both metallic and ionic Pt forms. The data on oxygen adsorption (regarding the P/P_s water curve) inform about the microdistribution of both platinum forms. As sulphur is selectively introduced into coordination sphere of ionic Pt^σ, the latter loses its ability to chemisorb oxygen. In this case microdistribution curve characterizes metallic platinum only. The difference between the first and the second curves shows microdistribution of the ionic platinum form.

PROPERTIES OF IONIC PLATINUM FORMS MODIFIED BY SULPHUR IN Pt/Al_2O_3 CATALYSTS

D.I. Kiryanov, Yu.N. Kolomytsev, E.M. Chalganov, D.M. Radko, A.S. Belyi, V.K. Duplyakin

4th European East-West Conf.&Exhibition on Materials and Processes, St.Petersburg, Russia. Abstracts, (1993) 25.

Adsorption measurements. Sulphur interacts with both ionic (Pt^{σ}) and metallic platinum (Pt^o), when the catalyst is exposed to a 1.0% H_2S mixture in H_2. A further treatment in hydrogen at 500°C provides sulphur deletion from the metallic platinum. Pt^{σ}-S binding is fast under these conditions, S/Pt^{σ} being 1. Such a selective sulphurization of Pt^{σ} changes a H/Pt^{σ} adsorption stoichiometry from 2 to 1, and decreases the rate of hydrogen binding.

Catalytic properties. Selective sulphurization of Pt^{σ} shows that the rate constant of cyclohexane dehydrogenation increases, and the activation energy grows by 5-7 kcal/mol. Aromatization selectivity in *n*-heptane reforming increases due to the decrease of hydrogenolysis rate constant. The better selectivity stabilizes the sulphur-containing catalyst operation. Basing on the "ligand effect" we have interpreted the obtained data.

ADSORPTION AND CATALYTIC PROPERTIES OF IONIC PLATINUM IN REFORMING CATALYSTS

A.S. Belyi, D.I. Kiryanov, N.M. Ostrovskii, L.A. Ishchenko, M.D. Smolikov, V.K. Duplyakin

4th European East-West Conf.&Exhibition on Materials and Processes, St.Petersburg, Russia. Abstracts, (1993) 26.

It has been found that the turnover number of the cyclohexane dehydrogenation increases linearly, while the activation energy increases by 2-5 kcal/mol. The turnover number calculated at 500°C equals 780 and 1255 mol/Pt atom/s, for Pt^o and Pt^{σ}, respectively. The data are confirmed by the presence of strongly bonded hydrogens on Pt^{σ} atoms. This leads to adsorption stoichiometry $H/Pt^{\sigma} = 2$ and low activity in the cyclohexane dehydrocyclization at 100-300°C. However, hydrogen mobility and ability of substitution sharply increase at $T > 320°C$ thus providing a high activity of Pt^{σ} atoms.

O_2 ADSORPTION AND (O_2-H_2) TITRATION ON ELECTRON DEFICIENT PLATINUM IN REFORMING CATALYSTS

A.S. Belyi, D.I. Kiryanov, M.D. Smolikov, E.V. Zatolokina, I.E. Udras, V.K. Duplyakin

React.Kinet.Catal.Lett., 53 (1993) 183-189.

Behavior of supported Pt in O_2 chemisorption and (O_2-H_2) titration has been studied. Pt/SiO_2, Pt/α-Al_2O_3 and Pt/γ-Al_2O_3 catalysts are characterized by the ratio between the stoichiometric coefficients of oxygen adsorption (X), hydrogen adsorption (Y) and oxygen-hydrogen titration (Z): X:Y:Z = 1:1:1.5. The coefficients differ for Pt-Cl/γ-Al_2O_3 reforming catalysts. This is explained by the presence of electron deficient platinum (Pt^o) with a coefficient ratio of X:Y:Z = 0.5:2:1.5.

DEVELOPMENT OF THERMOSTABLE CATALYSTS FOR TREATMENT OF EXHAUST GASES

P.G. Tsyrulnikov

4th European East-West Conf.&Exhib. on Materials and Processes, St.Petersburg, Russia. Abstracts, 3 (193) 18.

15th Mendeleev Meeting on General and Applied Chemistrtry, Chemical Problems of Environment, Minsk, Belorussia. Proceed., 3 (1993) 364.

D.I. Kochubey, T.G. Starostina, P.G. Tsyrulnikov, K.I. Zamaraev†

Kinet.Katal., 34 (1993) 716-720.

Catalysts based on MnO_x-Al_2O_3 (1) and Pt(Pd)-Ln-Al_2O_3 (2) conserve their activity after prolonged heating to 1000°C (1) and up to 750-850°C (2).

For (1) catalysts, the thermal stability is associated with the formation of a disperse phase of Mn(III) oxide on the corundum surface at 900-1000°C. The latter is formed via γ-oxide transformation, accelerated by the Mn oxide additives. Meanwhile, the activity of the system may increase by an order of magnitude as compared with the low-temperature samples (500°C), depending on the catalyzed reaction of deep oxidation.

For (2) system, the thermal stability is determined by the formation of highly disperse oxide complexes of the added lanthanide (lanthanum, cerium, etc.) platinum (palladium) in the ionic form, as well as by alumina support. According to the EXAFS data, palladium active formations on the lanthanated aluminium oxide are chain structures [Pd-O] with a changed Pd-Pd distance, compared to the phase palladium oxide. A rather low activity of Pt(Pd) in these complexes can be compensated by their high dispersity and thermal stability in a series of deep oxidation processes held at high temperatures.

Using an oxide Al-Mn system, we have developed a preparation procedure for the IC-12-40 catalyst, which was performed at AS "KATALIZATOR" (Novosibirsk).

The catalyst is produced on a large scale.

MODERN FCC CATALYSTS

V.P. Doronin, T.P. Sorokina, V.P. Konovalova, V.I. Gordenko

2nd Intern. Exhibition-Seminar "Catalysis-94", St.Petersburg, Russia. Proceed. of Seminar "Urgent Problems of Catalysts Manufacturing and Large-Scale Application of Catalysis", Novosibirsk, Russia. 2 (1994) 177-178.

In the present paper we discuss the main principles of the design of oil cracking catalysts, with regard to the size of zeolite particles, their morphology, matrix pore sizes and relations between the matrix pore size and the zeolite particle diameter.

Using the principles of design, we have compared the catalytic properties of a very promising catalyst for cracking with a widely-used one.

CARBON MONOLITHS FOR ENVIRONMENTALLY SAFE GALVANIC PROCESSES

V.K. Duplyakiin, O.N. Baklanova, V.V. Shim, V.K. Varentsov

4th European East-West Conf.&Exhibition on Materials&Processes, St.Petersburg, Russia, Abstracts, (1993) 20.

We have isolated electrochemically the ions of heavy metals from diluted aqueous solutions with a flow electrolyzer, containing a carbon monolith cathode, 13 mm in diameter with 0.35 mm cells. If the solution circulates at 1.0-1.8 mL/min through the electrode (cathode), the copper ion concentration decreases from 100 to 50 mg/L during one washing water exchange in the catholyte. Moreover, the content of organic admixtures drops to 0. The latter is associated with the porous structure of the material, whose specific adsorption surface is 200-300 m^2/g.

NEW CARBON AND CARBON CONTAINING MATERIALS FOR CATALYSIS, MEDICINE AND ENVIRONMENT PROTECTION

O.N. Baklanova, V.Yu. Davydova, V.K. Duplyakin, M.L. Shchipko* (Ins. of Chemystry and Chemical Technology SB RAS, Krasnoyarsk, Russia)

4th European East-West Conf.&Exhibition on Materials and Processes, St.Petersburg, Russia. Abstracts, (1993) 21.

We have designed technology producing honeycomb carbon materials. The channel diameter is 0.5 mm, wall width is 0.3 mm, outer diameter is 10-50 mm. These materials have a porous structure with the following parameters: total pore volume 0.6-0.8 cm^3/g, specific adsorption surface 200-400 m^2/g, efficient pore radius 300-500 Å, strength 30-50 kg/cm^2.

Honeycomb carbon materials were tested as hemosorbents for blood purification. They appeared to be very efficient for the isolation of various poisons. After one pass of blood through the hemosorbent, the content of blue pus decreases by 28-53%. Moreover, the formed elements (such as thrombocytes) are less deformed, as compared to the granulated hemosorbents, since there is no turbulence as blood runs through the monolith channels.

GAS-PHASE COMPOSITION INFLUENCE ON CATALYSTS DURING FUEL DEAROMATIZATION

K.S. Gulyaev, N.M. Ostrovskii, A.N. Startsev

1st Russia-Japan Joint Symp. on Petroleum, Natural Gas and Petrochemistry, Yuzhno-Sakhalinsk, Russia. Proceed., (1993) 130-131.

The activity of sulphided Ni-Mo(W) catalysts during fuels dearomatization (HDA) has been examined to elucidate the active sites poisoning by sulphur-organic compounds (RS). We suggest a mechanism of a mutual transformation of active sites for HDS and HDA. We have studied the effect of temperature and RS-, H_2 concentrations on the transition regimes.

LUMPING ANALYSIS OF COMPLEX REACTION MECHANISMS. I. EQUILIBRIUM SYSTEMS

S.L. Lebedeva, N.M. Ostrovskii, S.I. Spivak

Kinet.Katal.,
34 (1993) 171-175.

Here we consider the lumping analysis of complex reactions under equilibrium. For the first-order reactions, the expressions for the equilibrium constants of the lumping system were directly derived through the equilibrium constants of original system. We propose the lumping analysis procedure for the higher order reactions. Some examples are presented.

CATALYTIC REACTIONS ACCOMPANIED BY CAPILLARY CONDENSATION.
I. FORMULATION OF THE PROBLEM

N.M. Ostrovskii, N.M. Bukhavtsova, V.K. Duplyakin

React.Kinet.Catal.Lett.,
53 (1994) 253-259.

Capillary condensation was found to accompany gas-phase catalytic reactions, in particular motor fuel hydrotreatment. Reaction conditions appear to differ significantly in large pores (filled with gas) and in small ones (filled with liquid). Regarding capillary condensation we explain the "strange" dependences observed in this study or described in the literature. We have simulated jet fuel dearomatization taking into account capillary condensation.

THE ROLE OF ELECTRON-DEFFICIENT PLATINUM IN THE MECHANISM OF PARAFFIN DEHYDROCYCLIZATION

N.M. Ostrovskii, Yu.K. Demanov, V.K. Duplyakin

1st Russia-Japan Joint Symp. on Petroleum, Natural Gas
and Petrochemistry, Yuzhno-Sakhalinsk, Russia.
Proceed., (1993) 175-176.

Pt^o/SiO_2, Pt^o/Al_2O_3 and $(Pt^o+Pt^{2+})/Al_2O_3$ catalysts were tested. Hexane and heptane reactions as well as selective poisoning of active sites were examined by the pulse technique. The experimental data and calculation results allowedus to propose a reforming reaction network illustrating the role of Pt^o, Pt^{2+} and acid active sites. We have established that Pt^{2+} is responsible for $N_5 \rightarrow N_6$ isomerization thus increasing the aromatization activity

KINETIC MODEL FOR COKE DEACTIVATION OF SUPPORTED PLATINUM-ALUMINA CATALYSTS

O.A. Reutova, N.M. Ostrovskii

Izv. Vuzov, ser. Khim.Tekhnol.,
7 (1993) 64-71.

Kinetic model of deactivation by coking for polyfunctional platinum-containing reforming catalysts was proposed. It is based on a poisoning mechanism for each type of active sites: the active sites of Al_2O_3 support are coked according to the polylayer consecutive scheme; the active sites of electron deficient Pt^{2+} are coked according to the monolayer deposit with self-regeneration by H_2; the "metallic active sites (Pt^o) are deactivated according to "compensated break-up" mechanism.

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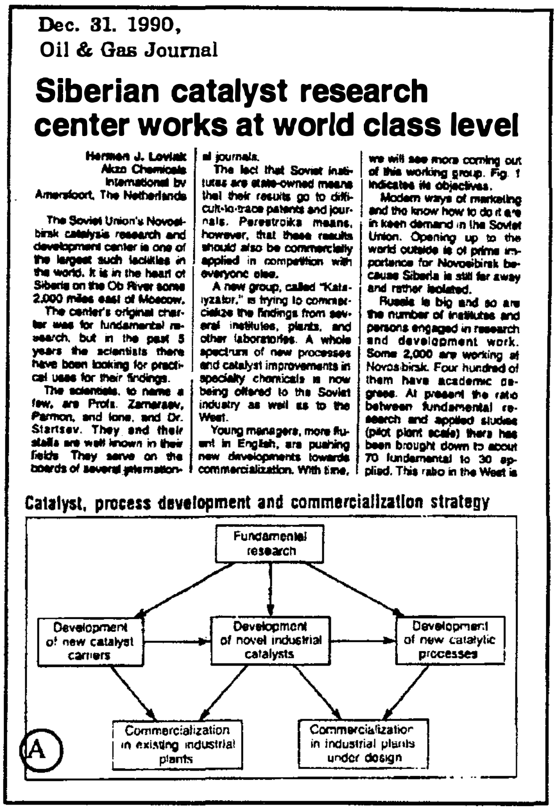
† J.H.Block deceased July 23, 1995
V.M.Mastikhin deceased February 8, 1995
V.Yu.Mashkin deceased October 21, 1994
A.L. Vishnevskii deceased March 3, 1995
K.I.Zamaraev deceased June 26, 1996

ADVERTISEMENT PAGES

INTERNATIONAL CENTER FOR CATALYST'S CHARACTERIZATION AND TESTING

INTRODUCTION

The International Center for Catalyst's Characterization and Testing was founded in 1992. In its work the Center uses the powerful potential of the Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences, which is the biggest in the world specialized institute working in the 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 catalysis, mathematical modeling and engineering of catalytic reactors and processes, development and commercialization of new industrial catalysts and processes. Sophisticated instruments for the *in situ* analytical control of catalyst state and reaction mixture composition, including the instruments for adsorption, kinetic, structural and spectral studies is available at the Institute. All this allows to obtain within a short time a unique combination of data about the structure of active centers, detailed reaction kinetics and mechanism, and to use these data for a purposeful design of new catalysts and catalytic technologies.



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

Fig. 1. This is a vivid illustration of the worldwide recognition of the Institute activity.

INTERNATIONAL ADVISORY BOARD

The International Advisory Board of the Center consists of the following specialists of the world renown:

1. Zamaraev K.I.†	Boreskov Institute of Catalysis	Chairman, Russia
2. Bal'zhinimaev B.S.	Boreskov Institute of Catalysis	Russia
3. Bell A.T.	University of California	USA
4. Block J.H. †	Fritz-Haber Institute	Germany
5. Gryaznov V.M.	Peoples Friendship University	Russia
6. Lovink H.J.	Akzo Chemical International	the 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 Institute	UK
13. Van Santen R.A.	Eindhoven University	the 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 Center is Academician Kirill I. Zamaraev†.
Executive Director of the Center is Professor Bair S. Bal'zhinimaev.

ACTIVITY

These are the main directions of the Center's activity in 1994:

- Standardization and certification of the physico-chemical properties of catalysts and supports as well as of various measuring devices;
- Characterization of catalysts and supports by modern physical methods;
- Execution of particular bi- and multilateral projects with foreign partners in the field of catalysis.

RESULTS OF ACTIVITY

The developed standard techniques for measuring the porous structure, chemical and phase composition of disperse materials, as well as their strength properties were generalized and matched with the Russian State Standard demands and international standards. Thus, a new Testing Center appeared, which was successfully accredited by the Russian State Committee for Standardization, Metrology and Certification in the following domains:

1. *Measurement of grain composition and bulk density.*
2. *Measurement of density and porosity.*
3. *Determination of chemical composition (mass fractions of moisture, metals, metal oxides, salts, ions, acid-insoluble sediments as well as of nitric-, oxygen- and carbon complexes).*
4. *Measurement of ash content and pH of water extracts.*
5. *Estimation of adsorption and dynamic activity.*
6. *Determination of permeability.*
7. *Determination of texture characteristics (specific surface, active specific surface, pore volume).*
8. *Measuring of mechanical strength (crushing and attrition strength).*

Research-methodological works on the preparation of standard porous-structure samples used, in particular, for the pore size distribution measurings, are still in progress. Presently, the calibration technique of setups measuring the specific surface area with the corresponding standard samples is used by foreign companies (Sy-Lab, Micromeritics).

A new home device SORBTOMETR-3.1 intended for the measuring of total and partial surfaces of dispersed materials has been metrologically certified.

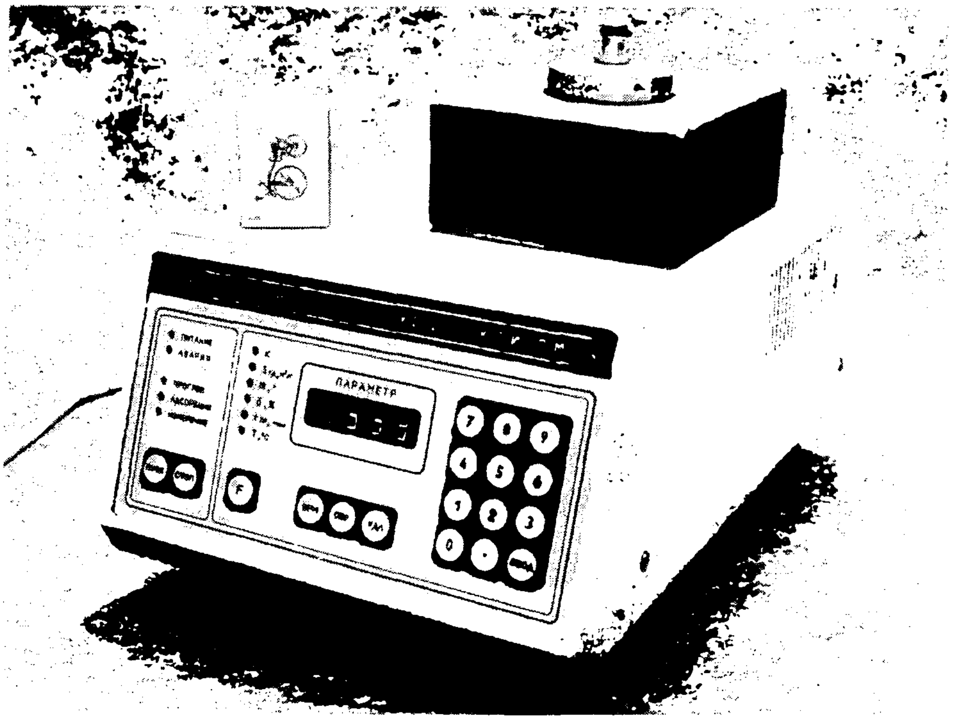


Fig. 2. The adsorber device of SORBTOMETR-3.1.

Particular scientific-research projects in the field of fundamental catalysis attract a lot of the Center's activity. Financial support of the International Association INTAS allowed to transform some traditional bilateral projects to multilateral one. Thus, the Leiden University (the Netherlands) and L'vov University (the Ukraine) has recently joined a conventional colloboration between the Institute of Catalysis and the Fritz - Haber Institute (Germany). In 1993 three projects were supported by INTAS:

Project 1. Heterogeneous Catalysis on the Atomic Scale: Oscillating Surface Reactions and Related Phenomena

Project coordinator:

Professor J.H. Block†	Fritz-Haber Institute	Germany

Participants:

Dr. V. Gorodetskii	Boreskov Institute of Catalysis	Novosibirsk, Russia
Dr. Yu. Sukorskii	L'vov University	the Ukraine
Professor V.K. Medvedev	Institute of Physics	the Ukraine
Dr. B. Nieuwenhuys	Leiden University	the Netherlands

Using the Field Ion Microscopy, the dynamic behaviour of hydrogen oxidation on a monocrystal Pt(100) and on a polycrystal platinum has been elucidated. On the latter, the reaction rate exhibits auto-oscillations as self-propagating autowaves, which are caused by dynamic interaction between various micro-faces. This fact is of prime importance for heterogeneous catalysis since it proves that the catalyst surface is not a superposition of catalytic properties of isolated faces. This experiment is nicely reproduced during numerical and simulation modeling of the system. Data are reported at the International conferences and published in some foreign journals.

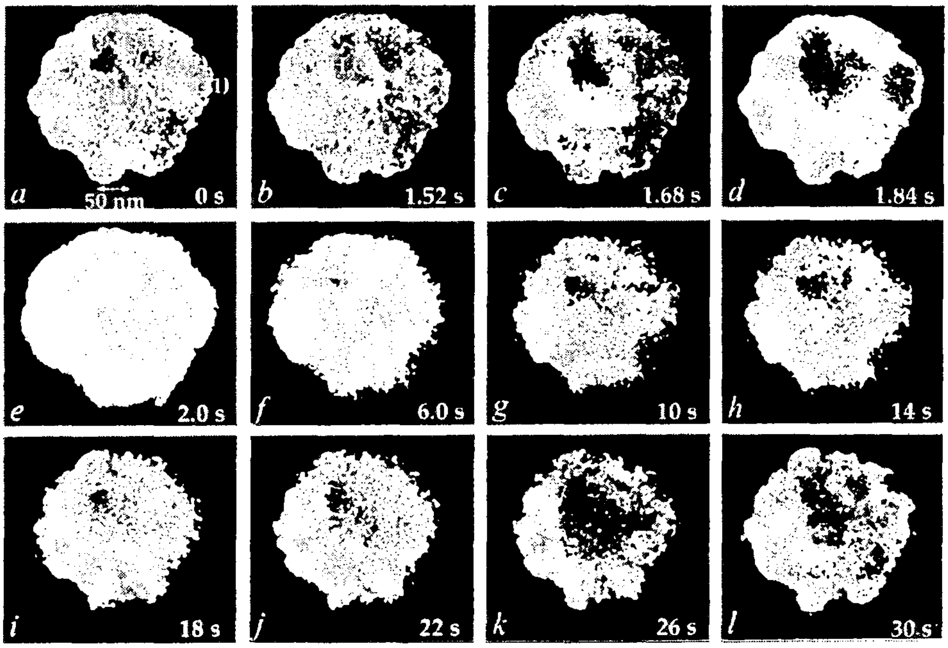


Fig. 3. Sequences of field ion microscopy (FIM) images from a Pt tip with 180 nm radius under constant conditions of catalytic oxidation of hydrogen.

Project 2. Pollution Control by Catalysis

Project coordinator:

Professor R. Fehrmann	Technical University of Denmark	Lyngby, Denmark

Participants:

Professor B.S. Bal'zhinimaev	Boreskov Institute of Catalysis	Novosibirsk, Russia
Dr. S. Boghosian	Institute of Chemical Engineering & High Temperature Chemical Processes	Patras, Greece
Dr. G. Hatem	Universite de Provence	Marceille, France

The goal of this project is to elucidate the molecular structure of vanadium catalysts, serving SO_2 and NO_x utilization from wet waste gases, in order to improve the latter. This year, new data on the alloy structure of vanadium catalysts, containing Cs additives, were obtained. A phase diagram of a system $KHSO_4$-$K_2S_2O_7$, simulating the alloy wetting, was built. Alloy phase conversions providing the catalyst deactivation were simulated with the Monte Carlo method.

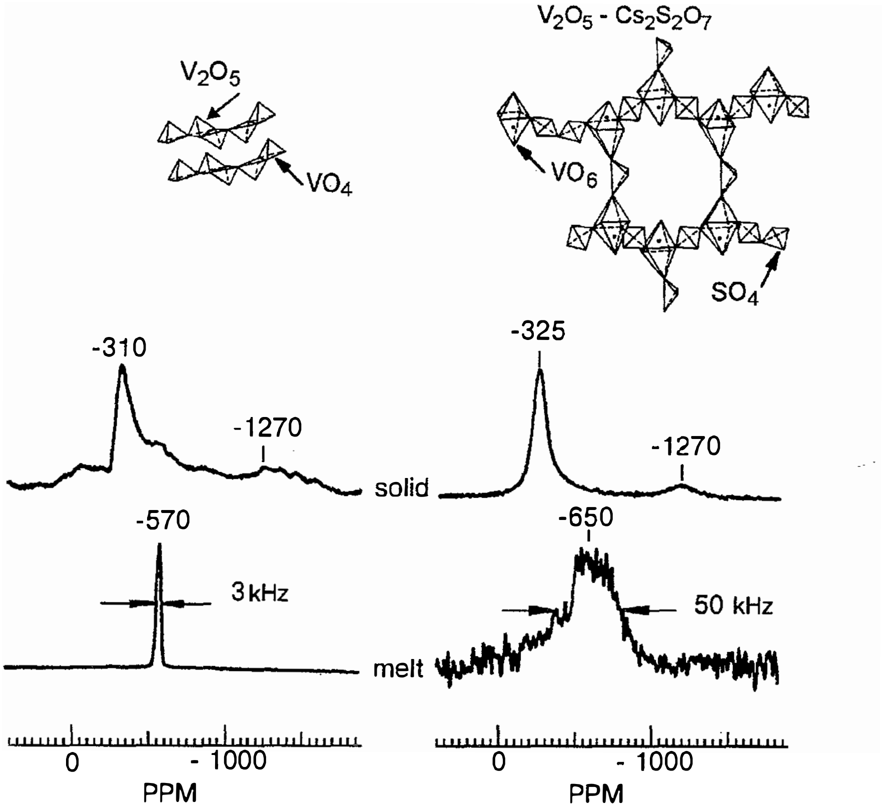


Fig. 4. Simulated structure of vanadium species present in V_2O_5-$Cs_2S_2O_7$ melts.

Project 3. The Partial Oxidation of Light Hydrocarbons in Electrochemical Devices under Mild Conditions

Project coordinator:

Professor N. Giordano	Institute of Energy Transformation&Accumulation	Messina, Italy

Participants:

Professor V.N.Parmon	Boreskov Institute of Catalysis	Novosibirsk, Russia
Professor S. Coluccia	University of Turin	Italy
Dr. K. Vakulov	Institute of Organic Chemistry	Moscow, Russia
Professor G. Fierro	Institute of Catalysis&Petrochemistry	Spain

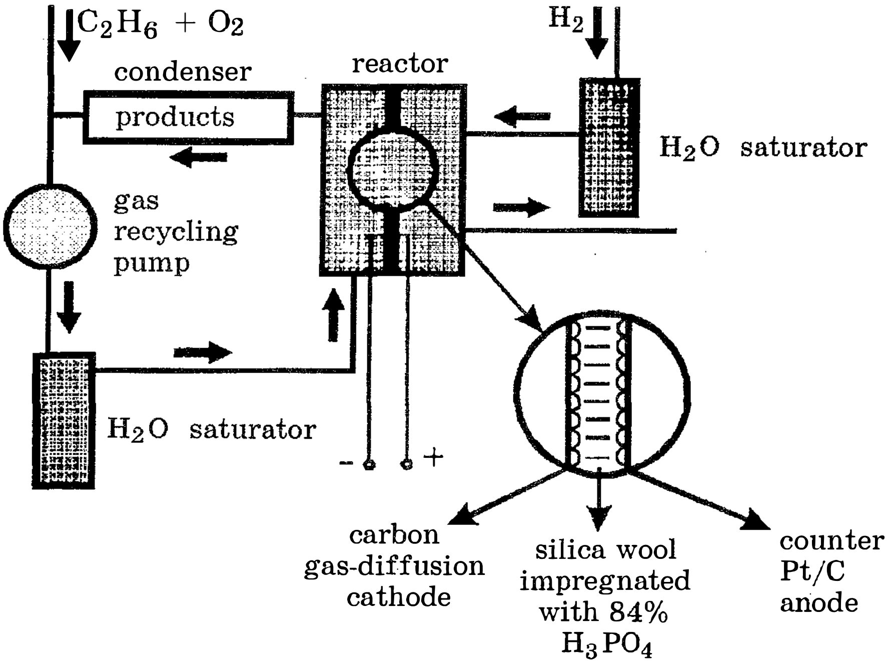


Fig. 5. Schematic diagram of the experimental set-up with gas electrochemical cell.

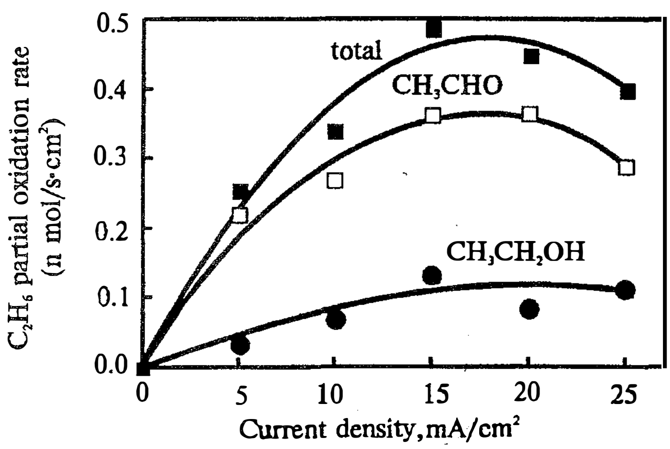


Fig.6. Effect of current density on C_2H_6 partial oxidation rate in gas electrochemical cell over carbon membrane (Teflon content 30 wt %. Nafion loading 20 wt %) at 343 K.

This project is focussed on the development of new technologies of lower paraffins selective oxidation in electrochemical devices of a fuel-cell type.

A 95% selectivity towards useful products (acetaldehyde, 65%; ethanol, 35%) can be obtained, when ethane is oxidized by molecular oxygen, previously activated via the cathode current flow through a carbon gas-diffusion electrode. The molecular oxygen activation appears to proceed through the hydrogen peroxide formation on the carbon cathode. Reaction is assumed to proceed via the radical chain mechanism.

Additional financial supply of these projects by INTAS has enabled to intensify the scientific exchange, both short- and long term, thus to accelerate research studies. In the framework of this multilateral collaboration 7 visits have been done, 15 works with joint results were accepted for publication.

In 1994 five more projects were supported by INTAS:

1. Fundamental Studies of Electrochemical Promotion in Heterogeneous Catalysts

Project coordinator:		
Dr. S. Bebelis	University of Patras	Greece
Participants:		
Prof. V.A. Sobyanin	Boreskov Institute of Catalysis	Novosibirsk, Russia
Prof. W. Gopel	Universitat Tubingen	Tubingen, Germany
Prof. R.M. Lambert	University of Cambridge	UK

2. The Role of Peroxometal Complexes in Oxidations Related to Synthetically, Environmentally and Biologically Relevant Processes

Project coordinator:		
Prof. G. Modena	Universita'di Padova	Padova, Italy
Participants:		
Prof. K.I. Zamaraev†	Boreskov Institute of Catalysis	Novosibirsk, Russia
Prof. I.L. Moiseev	Kurnakov Institute of Inorganic&General Chemistry	Moscow, Russia
Prof. J. Muzart	Universite de Reims Champahne	Ardenne, France

3. Novel Membrane Materials for Environmental Protection Control

Project coordinator:		
Prof. F. Drioli	University of Calabria	Italy
Participants:		
Dr. O.M. Ilinitch	Boreskov Institute of Catalysis	Novosibirsk, Russia
Prof. N. Plate	Topchiev Institute of Petrochemical Synthesis	Moscow, Russia
Prof. V. Soldatov	Institute of Physical Organic Chemistry	Minsk, Belarus
Prof. H. Strathmann	University of Twente	the Netherlands

4. Polysiloxanes: Promising Materials for the Preparation of new Absorbents, Catalysts and Metal-Extractants

Project coordinator:		
Dr. V. Parish	University of Manchester Institute of Science&Technology	Machester, UK
Participants:		
Prof. N.N. Kundo	Boreskov Institute of Catalysis	Novosibirsk, Russia
Prof. Yu.L. Zub	Institute of Surface Chemistry	Kiev, the Ukraine
Prof. V.A. Kogan	Rostov State University	Rostov, Russia
Prof. U. Schubert	Technische Universitat	Wien, Austria

5. Optimization of Parameters Intervening under Construction of Ergonomic Reactor Efficient in the Degradation of Industrial Pollutants

Project coordinator:

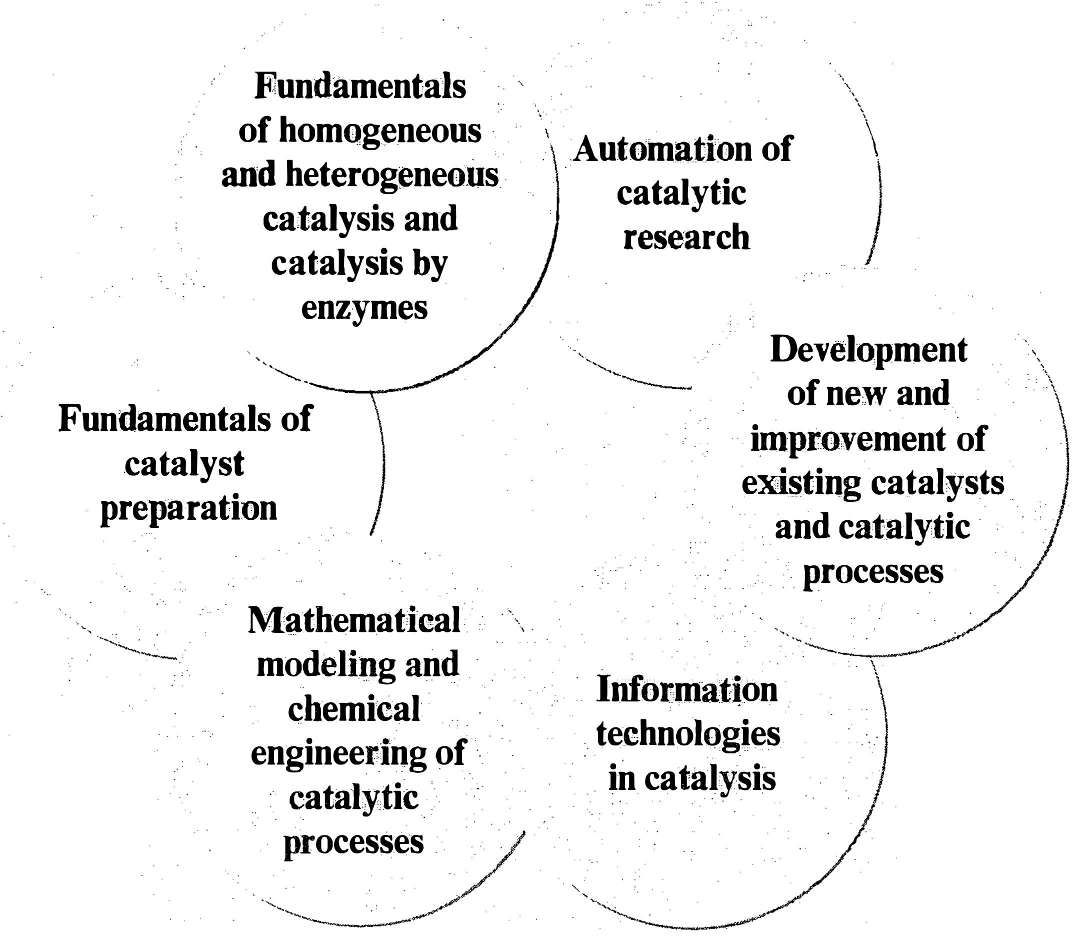
Dr. J. Kiwi	Institute of Chemical Physics	Losanna, Switzerland

Participants:

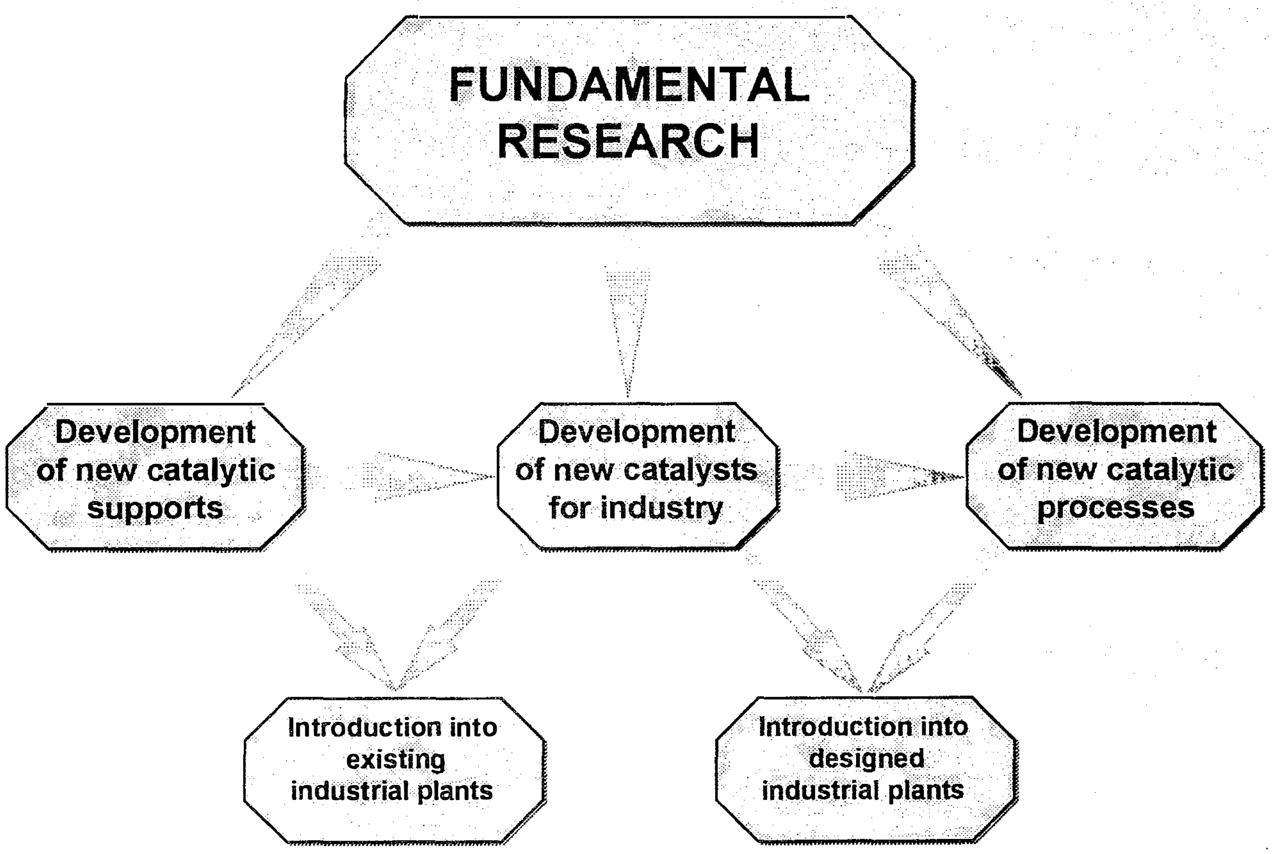
Prof. E.N. Savinov	Boreskov Institute of Catalysis	Novosibirsk, Russia
Prof. D. Bonemann	Institute of Transformation of Solar Energy	Gannover, Germany
Dr. S. Pulgarin	Institute of Bioengineering	Losanna, Switzerland
Dr. V.V. Nikandrov	Institute of Biochemistry	Moscow, Russia
Prof. V.N. Troitskii	Institute of New Chemical Problems	Chernogolovka, Russia

In 1994, traditional bilateral collaboration with several European institutions persisted. The most promising connections are with the Munich University (Germany), Royal Institution (UK), Institute of Transformation of Solar Energy (Italy), Universities of Bologna and Turin (Italy) and University of Zhirone (Spain). More than 30 publications are published and accepted for publication in home and foreign magazines. Commercial agreements for searching research works are concluded with companies of USA, Europe and South Korea.

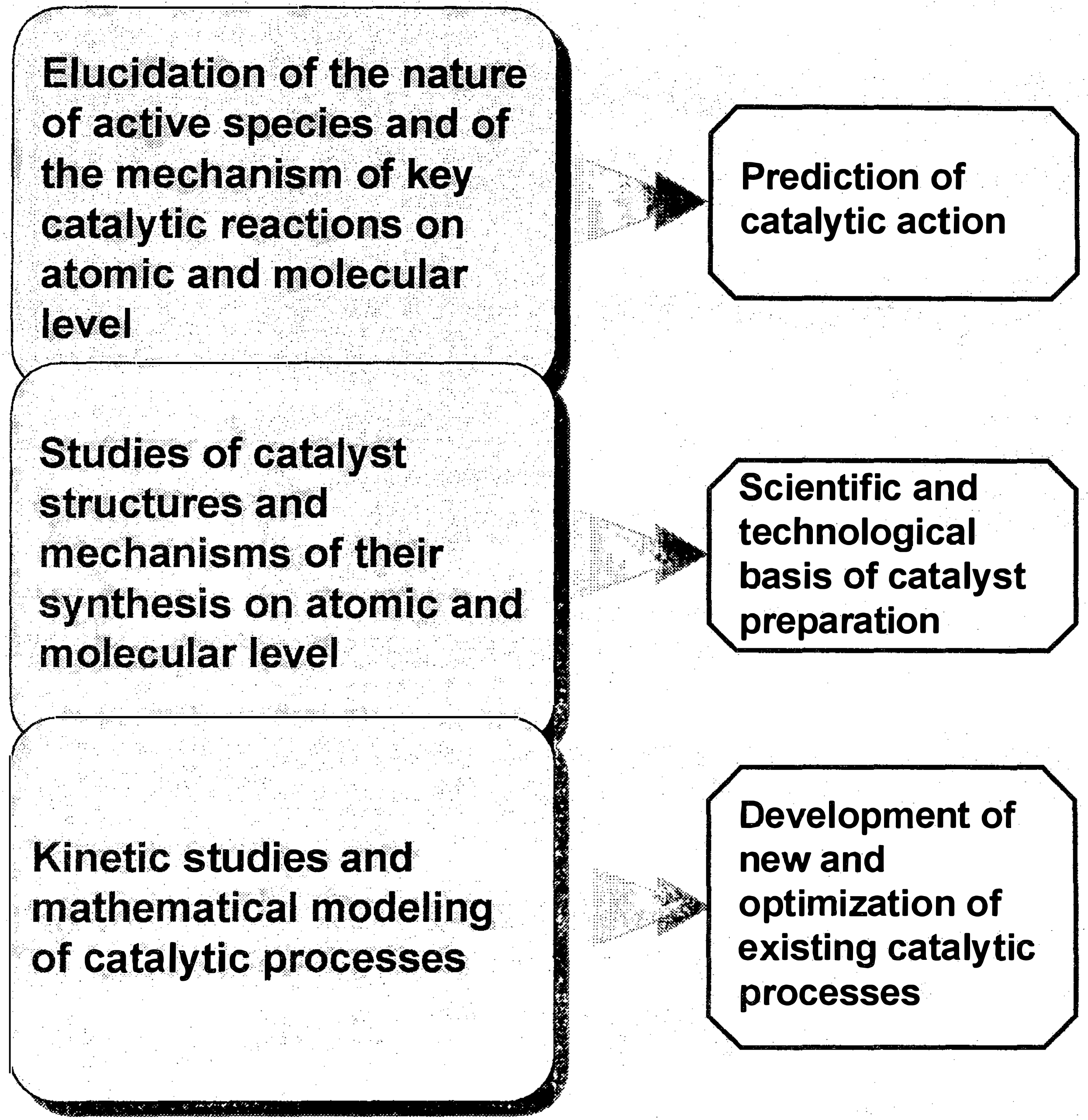
R&D activity areas



Strategy for new generation catalysts and catalytic processes



Strategy for fundamental research



Elucidation of the nature of active species and of the mechanism of key catalytic reactions on atomic and molecular level

Prediction of catalytic action

Studies of catalyst structures and mechanisms of their synthesis on atomic and molecular level

Scientific and technological basis of catalyst preparation

Kinetic studies and mathematical modeling of catalytic processes

Development of new and optimization of existing catalytic processes

R&D capabilities

Analytical *(composition of catalysts and catalytic reaction products)*

- Differential dissolution
- Chromatography
- Superrapid chromatography
- Mass spectrometry

Adsorptive *(specific surface area, pore structure, adsorption heat)*

- Porosimetry
- Calorimetry

Kinetic

- Gradientless and integral differential reactors
- Fast relaxation technique
- Stop flow technique

Physical

- X-Ray diffraction
- Electron microscopies
- EXAFS
- X-Ray spectroscopy
- VUV electron spectroscopy
- UV-VIS electron spectroscopy
- Vibrational spectroscopies (IR and Raman)
- ESP
- NMR
- ESCA (XPS and UPS), Auger spectroscopy
- LEED
- HREELS
- Ionic Cyclotron Resonance
- Radiochemical methods
- Flash photolysis and radiolysis
- X-Ray tomography

New catalyst supports

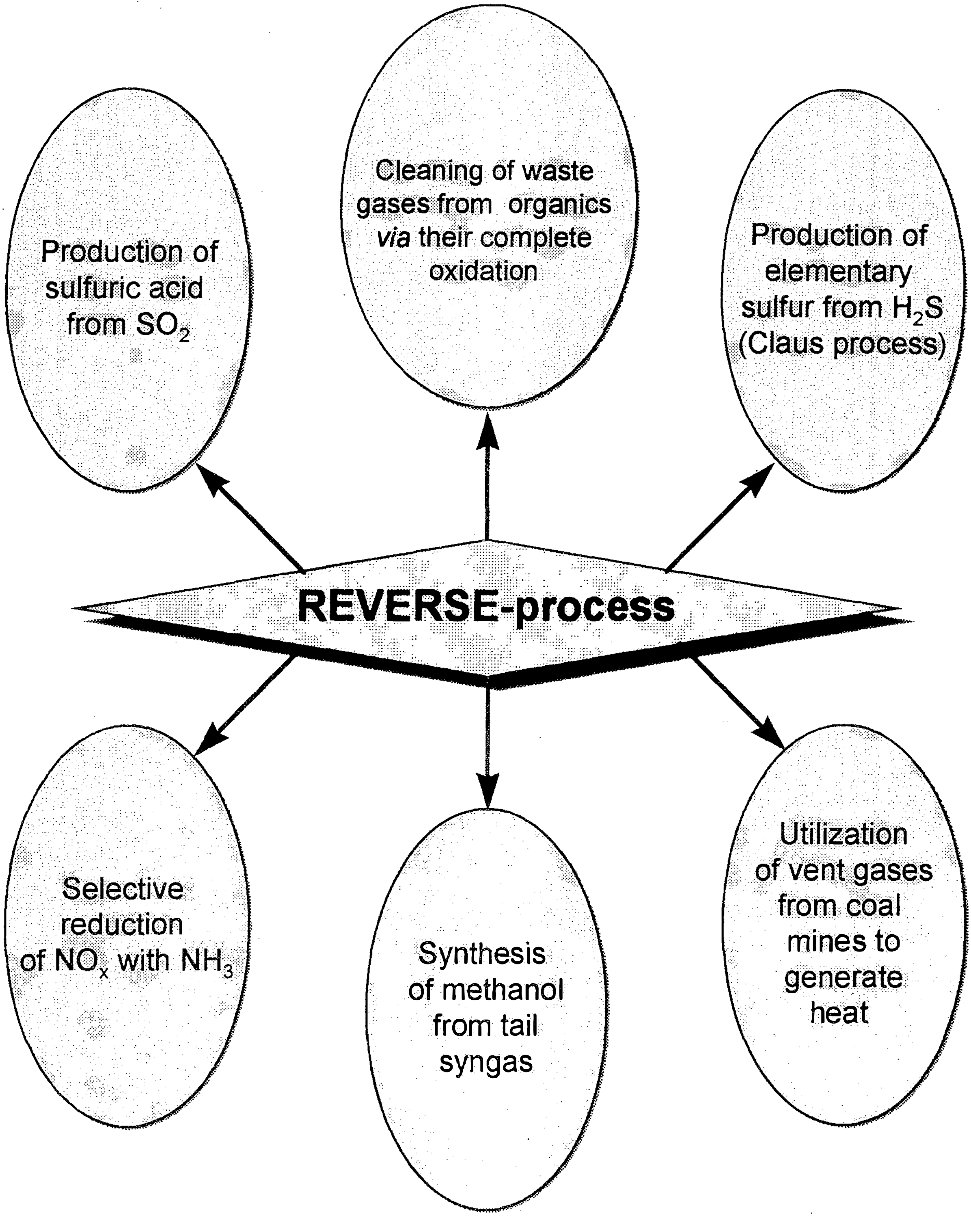
- A systematic set of alumina supports prepared through the same technology
- Catalyst supports of very high mechanical strength for fluidized and moving catalyst beds
- Ceramic and carbon monoliths
- Mechanically strong carbon supports with adjustable porous structure
- Mechanically strong supports for immobilization of enzymes
- Aerogels

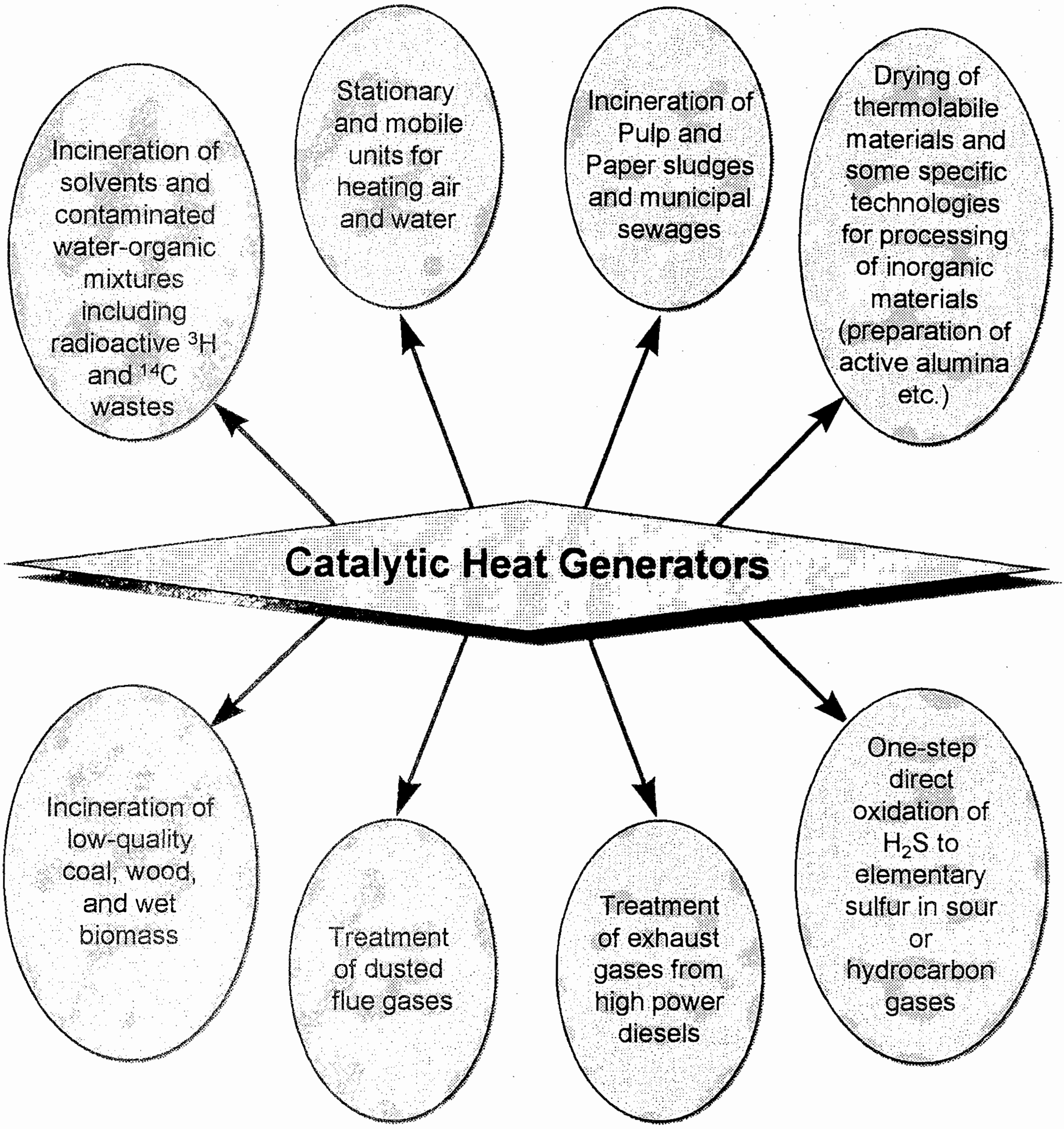
New industrial catalysts

- Catalysts for inorganic synthesis
- Catalysts for organic and fine synthesis
- Catalysts for olefin polymerization
- Catalysts for oil processing
- Catalysts for treatment of gaseous and liquid wastes of industries, energetics, transport, etc.
- Catalysts for treatment of technological gases
- High silica zeolites

New catalytic technologies owned by BIC

- ➢ A family of new unsteady-state technologies in catalysis - "Reverse- process"
- ➢ A family of technologies based on combustion in a fluidized catalyst bed ("Catalytic Heat Generators")
- ➢ Catalytic combustion using honeycomb and mat catalysts
- ➢ "Chemical Heat Accumulators"
- ➢ Processing of oil, natural gas and coal
- ➢ Large-scale inorganic synthesis
- ➢ Catalytic technologies for environmental protection
- ➢ Production of food, medicines and biopreparations:
  - ✓ Direct gas-phase oxidation of β-picoline to nicotinic acid
  - ✓ Synthesis of vitamins K and E
  - ✓ Synthesis of xylidine and other fine organics
- ➢ Catalytic partial oxidation:
  - ✓ Oxidation of methanol in an adiabatic catalyst bed to produce formaldehyde
  - ✓ Direct oxidation of methanol to formic acid
  - ✓ Partial oxidation of aromatics with N_2O
- ➢ Purrification of hydrocarbon-containing gases from H_2S via its partial oxidation to sulphur


REVERSE-process
Production of sulfuric acid from SO_2
Cleaning of waste gases from organics *via* their complete oxidation
Production of elementary sulfur from H_2S (Claus process)
Selective reduction of NO_x with NH_3
Synthesis of methanol from tail syngas
Utilization of vent gases from coal mines to generate heat


Catalytic Heat Generators
Incineration of solvents and contaminated water-organic mixtures including radioactive ^{3}H and ^{14}C wastes
Stationary and mobile units for heating air and water
Incineration of Pulp and Paper sludges and municipal sewages
Drying of thermolabile materials and some specific technologies for processing of inorganic materials (preparation of active alumina etc.)
Incineration of low-quality coal, wood, and wet biomass
Treatment of dusted flue gases
Treatment of exhaust gases from high power diesels
One-step direct oxidation of H_2S to elementary sulfur in sour or hydrocarbon gases

R&D activities for ecology

Impurity	Contributor	BIC's technology
SO_2	• Waste gases from metallurgy and chemical industry • Natural gases • Oil-refinery flue gases • Effluents of power plants	• REVERSE unsteady-state processing of sour gases to produce sulfuric acid**** • Liquid-phase purification to produce sulfur commercially*** • New catalysts for Claus process**** • REVERSE-Claus process** • Catalytic treatment of waste gases of Claus processes***
H_2S	• Flue gases of metallurgy and chemical industry • Natural gases • Oil-refinery flue gases • Geothermal gases • Offgases from wells	• Liquid-phase purification to produce sulfur commercially*** • New catalysts for Claus process**** • Catalytic treatment of waste gases of Claus processes*** • One-step cleaning of H_2S-containing gases in a fluidized catalyst bed
NO_x	• Technological and industrial flue gases • Exhausts from internal combustion engines • Flue gases of power plants	• REVERSE unsteady-state cleaning**** • Honeycomb and granular DeNOx catalysts*** • Selective catalytic reduction with ammonia** • Liquid-phase catalytic reduction**
As_2O_3	• Waste gases of sealteries	• Liquid-phase treatment to produce arsenicum sulfide***
CO	• Technological and industrial flue gases • Exhausts from internal combustion engines	• REVERSE unsteady-state cleaning**** • Cleaning in a fluidized catalyst bed*** • Adsorptive and catalytic treatment*** • Honeycomb and granular catalysts for converters***
organics	• Technological and industrial flue gases • Products of incomplete combustion of organic fuels • Wastewater (including municipal sewages) • Sludges of water cleaning units	• REVERSE unsteady-state cleaning**** • Cleaning in a fixed catalyst bed**** • Cleaning in a fluidized catalyst bed*** • Catalytic gas heaters*** • Mixing gaseous air heaters****

**** commercial scale;
*** semi-works scale;
** pilot installation;
* R&D

LEADING SCIENTISTS
OF THE BORESKOV INSTITUTE OF CATALYSIS

ANDRUSHKEVICH Tamara Vitalievna, doctor of chemical sciences (1994)[1], Head of the Laboratory.

Tamara 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, N-containing heterocycles belong to the sphere of her activities. She has established the redox mechanism for selective reactions. The principles of catalyst selection to oxidize 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.

Tamara V. Andrushkevich contributes considerably to the design of commercial catalysts for the two-stage propylene oxidation to acrylic acid and for propylene ammoxidation.

At present, she designs the processes of the heterogeneous-catalytic gas-phase oxidation of formaldehyde to formic acid and of β-picoline to nicotinic acid.

ANIKEEV Vladimir Il'ich, doctor of technical sciences (1992), senior researcher.

The research interests of Vladimir I. Anikeev include the mathematical simulation of multiphase processes, catalytic reactors and chemical-technological schemes, experimental kinetic studies of catalytic processes and catalyst activity; characterization of heat- and mass transfer, studies in the fields of nontraditional power engineering, as well as development of new energy resources and energy saving plants and technologies on the basis of thermochemical catalytic reactions, coal and biomass thermochemical conversion.

Vladimir I. Anikeev has initiated and developed a new scientific direction - an application of thermochemical catalytic processes in power engineering. He developed novel catalytic reactors/receivers of the concentrated solar flux and proposed new experimental and theoretical methods to analyze the efficiency of these reactors; guided the construction of pilot plants for energy conversion and transfer of energy based on the closed thermochemical cycles proposed new schemes of heat-recovery installations; designed soft ware to calculate and analyze exergy efficiency and to optimize numerous chemical catalytic processes and schemes.

ANUFRIENKO Vladimir Feodosievich, doctor of chemical sciences (1993), Head of the Research Group.

Vladimir F. Anufrienko is an expert in the 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 unpaired electron in the chelate complexes. Vladimir F. Anufrienko has registered the effect of ligand exchange on the ESR spectra of copper(II) complexes in solutions. He was the first to prove the equatorial forms of copper(II) complexes to form.

Vladimir F. Anufrienko revealed the effect of a concerted arrangement of copper ions and other paramagnetic ions caused by the Jahn-Teller cooperative effect in various oxide systems and oxide catalysts.

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[1] 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

During 20 years of his research activity he described some important peculiarities of the ESR spectra of titanium catalysts for polymerization.

He is also known for his fundamental results concerning the ESR of carbons, cokes and carbon mesophase structures. These results were used to understand deactivation in methanol conversion over zeolite catalysts.

AVDEEVA Lyudmila Borisovna, candidate of chemical sciences (1977), Head of the Research Group.

Lyudmila B. Avdeeva has developed the technique for a nonoxidative catalytic conversion of methane (natural gas) to carbon and hydrogen.

She has developed the principles for obtaining coke-resistant metal catalysts and for producing a novel graphite-like carbon material - catalytic filamentous carbon (CFC).

BAL'ZHINIMAEV Bair Sadypovich, doctor of chemical sciences (1991), Executive Director of the International Centre for Catalyst Characterization and Testing.

Kinetics of heterogeneous catalytic reactions, reaction and chemical engineering belong to the sphere of his activities. His knowledge of kinetics and catalytic reaction mechanisms allows him to design and improve catalysts, catalytic processes and techniques of catalyst testing.

Bair S. Bal'zhinimaev has developed experimental procedures to characterize the kinetics of fast processes on heterogeneous catalysts. He studied the recently developed unsteady state kinetics of ethylene epoxidation, SCR of NO_x and SO_2 oxidation, as well as the oxidation of o-xylene to phthalic anhydride based on the detailed knowledge of active sites structure, and reaction mechanism.

BARANNIK Georgii Borisovich, candidate of chemical sciences (1977), Head of the Laboratory.

The domain of his research acitivity includes the effect of reaction medium on the heterogeneous-catalytic reaction mechanism, synthesis and study of oxide catalyst active component, processes and catalysts for environmental control.

Recently he became deeply involved in a new trend - chemical design and formation of structured heterogeneous catalysts - ceramic and composite monoliths.

Original monolith catalysts for DENOX process and complex purification of industrial waste gases have been developed on the basis of domestic raw materials. Studies of several new monolith supports and catalysts for some novel catalytic processes are in progress.

BOBROV Nikolai Nikolayevich, candidate of chemistry (1974), Head of the Laboratory.

Nikolai N. Bobrov is the expert in experimental kinetic methods applied for catalysis. His nowadays activity concerns the standardization of control over catalysts and supports; equipment for testing catalysts activity, overall and active surface of catalysts and supports. Nikolai N. Bobrov is also occupied by designing the express analyzers of gas and gas/vapor compositions, devices for reference gas mixtures preparation. His scientific activity concerns kinetics of oxidative conversion of methane and other hydrocarbons. He designs the education accessory software to investigate the formal kinetics of steady-state heterogeneous processes.

BUYANOV Roman Alekseevich, doctor of chemical sciences (1972), Professor (1976), Honoured Scientist of Russia, the Associate Member of the Russian Academy of Sciences, Lenin Prize Winner, Head of the Laboratory.

Professor Roman A. Buyanov developed a basis for building the theory of low-soluble hydroxides crystallization via the 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 ortho-para hydrogen conversion. He studied also the radical chain mechanism of catalytic pyrolysis. Thus, the role of the heterogeneous initiation, chains break and propagation over the catalyst surface has been elucidated.

Prof. Buyanov also investigated the mechanism of the carbide cycle in coke deposition and the stage mechanism of carbon oxidation in catalyst regeneration. He developed the scientific principles for the synthesis of carbon-mineral supports, adsorbents, catalysts and composites. Prof. Buyanov studied the reasons of catalyst deactivation and destruction and accomplished their first scientific classification. New mechanisms of activation were applied to prepare and process the catalysts. He made a significant contribution to the development of the general theory of catalysts preparation. He supervises various all-Russian conferences concerning the scientific principles of preparation and technologies of catalyst, and the problems of catalysts deactivation also. Many commercial catalysts have been obtained in his laboratory, among them are the catalysts for dehydrogenation and sulphur removal via the Claus method etc.

DAVYDOV Anatolii Aleksandrovich, doctor of chemical sciences (1990), Professor (1990), Head of Laboratory.

Using the IR spectroscopy, Prof. Anatolii A. Davydov studies the structure and properties of surface and surface complexes forming as simple and complex molecules adsorb on the oxide catalysts, and as reactions proceed on the surface of solids. He studies the mechanism of heterogeneous catalytic reactions by the IR spectroscopy analysis of surface intermediates.

DUPLYAKIN Valerii Kuzmich, doctor of chemical sciences (1990), Director of Omsk Department of the Boreskov Institute of Catalysis.

Valerii K. Duplyakin is an expert in the field of hydrocarbons catalytic conversion.

His research activities concern the design of oil-refining and petrochemical catalysts. He contributed magnificently to the chemistry and technology of the main stages of supported catalysts preparation; to molecular design of the catalyst active component for reforming and isomerization. He commercialized a series of reforming catalysts and new technologies for supported catalysts production.

He initiates the design of new materials based on carbon and complex oxides, which have unique properties. He suggested a new method of hydroxides production allowing to design complex oxides and catalysts at the atomic level.

FEDOTOV Martin Aleksandrovich, doctor of chemical sciences (1991), senior researcher.

Martin A. Fedotov is a top specialist in NMR application to studying the structural and catalytic properties of coordinated compounds of molybdenum, tungsten and metals of Pt group in solutions. He has studied a generation of hydroxides obtained from pure and mixed solutions of salts of aluminium and transition elements of the 1st row. He also investigated the structure and catalytic properties of heteropoly molybdates in solutions and tungstates of various composition possessing transition metal ions, as well as the structure and catalytic properties of platinum metal complexes in solutions.

FENELONOV Vladimir Borisovich, doctor of chemical sciences (1986), Head of Laboratory.

In his research activities he studies and simulates the porous structure (texture) and adsorption properties of catalysts and adsorbents, mechanism of their structure formation at different synthesis stages, develops the methods of adsorption and mercury porosimetry to study the structure of porous solids.

Vladimir B. Fenelonov has developed the physico-chemical principles of texture generation for a set of standard catalysts and supports via successive technological stages of their synthesis; elucidated the surface-capillary and colloidal mechanisms of texture formation taking into account various geometry in the dispersed system. He also developed methods for interpreting the data of adsorption and mercury porosimetry.

At present he studies how the texture of porous carbon materials forms. His monograph "Porous Carbon" dedicated to this subject will be published in 1996.

GORODETSKII Vladimir Vladimirovich, candidate of chemical sciences (1974), senior researcher, Head of the Research Group.

The main object of his scientific interest is to understand fundamentally the mechanism of low temperature surface processes related to catalysis by platinum metals. Rate oscillations and related concentration wave propagation, the activity of different adsorption states of reactants (molecular or atomic) and induced-surface structural changes in the course of reactions are now the hot topics in model reaction studies (H_2+O_2, $CO+O_2$, $NO+H_2$, NH_3+O_2). The primary emphasis is to attack deeper the insights of catalytic processes at the atomic and molecular levels.

IONE Kazimira Gavrilovna, doctor of chemical sciences (1981), Professor (1988), Head of Laboratory, Director of Scientific Engineering Center "ZEOSIT".

Prof. Kazimira G. Ione focusses on developing scientific approaches to the synthesis and characterization of acid-base zeolite catalysts. She has magnificantly contributed to the creation of scientific basis of zeolite synthesis, design of zeolite catalysts and zeolite-based catalysis in the basic and fine organic syntheses.

Under her supervision her team has developed catalytic systems and process principles to produce unleaded high-octane-number gasolines from different hydrocarbon raw materials. Many reactions of basic and fine organic syntheses to produce alkyl aromatics, nitrogen containing compounds using environmentally friendly technologies were designed.

The industrial production of zeolite catalysts and commercial installations catalytically synthesizing motor fuels, designed and patented by Prof. Ione and co-workers, successufully operate now.

ISMAGILOV Zinfer Rishatovich, doctor of chemical sciences (1988), Professor (1990), Head of the Department of Environmental Catalysis.

Prof. Zinfer R. Ismagilov is a well-known specialist in the field of environmental catalysis. His scientific interests are focussed on the development of environmentally friendly technologies, catalytic methods of wastes utilization and environmental control. He has elucidated the mechanism of hydrogen oxidation on oxides; the kinetics and mechanism of oxidation of organic substances and the mechanism of heterogeneous-homogeneous free radical reactions; designed new technologies to purify waste gases, utilize and recycle liquid and solid residues; developed new spherical alumina supports and catalysts for gas processing and petrochemistry.

Prof. Zinfer R. Ismagilov initiated the development of honeycomb monolith supports and catalysts, used for VOC control, purification of automotive exhausts, DENOX of tail gases from power plants. He supervized the organization of the first line producing monoliths in Russia.

He has invented and patented a new process of the direct catalytic oxidation of hydrogen sulphide to elementary sulphur both in fluidized bed and on a monolith catalyst.

Commercial production of a series of catalytic heaters and appliances was organized using the results of his persistant R&D activities in the field of catalytic combustion.

IVANOV Aleksei Alekseevich, candidate of chemical sciences (1964), Head of Laboratory.

Aleksei A. Ivanov contributed significantly to the studies of catalysts and processes to oxidize sulphur dioxide and aromatic compounds. He investigates the mechanism of catalyst action and catalysis under unsteady-state conditions.

Aleksei A. Ivanov has developed a physico-chemical and mathematical concept to control the effective nonstationary state of catalysts in catalytic oxidation.

He has developed the transition response techniques to study reactions and detailed mechanisms of a series of industrial catalytic processes such as sulphur dioxide oxidation, o-xylene oxidation to phthalic anhydride.

KERZHENTSEV Mikhail Anatolyevich, candidate of chemical sciences (1979), Head of the Research Group.

Mikhail A. Kerzhentsev is an expert in the catalytic combustion, oxidative heterogeneous catalysis using catalysis for environmental protection. His research activities include the study of kinetics of complete oxidation of various organic compounds over solid catalysts, fluidized bed catalytic combustion of organic compounds and wastes, development of catalysts and processes for the direct oxidation of hydrogen sulphide to elemental sulphur.

KHASIN Aleksandr Viktorovich, doctor of chemical sciences (1989), Head of the Research Group.

Aleksandr V. Khasin investigates the isotope exchange of oxygen and nitrogen, ammonia synthesis, reaction of nitric oxide with carbon monoxide, 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 using 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.

Valerii A. Kirillov is engaged in the mathematical simulations of chemical reactors; studies on hydrodynamics of multiphase fluids, phenomena of heat and mass transfer upon chemical and phase conversions and application of catalysis to ecology and power engineering.

Prof. Kirillov has developed the theory of simultaneous processes of chemical and phase conversion on a porous grain and in the catalyst layer; suggested a set of technologies for the 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 catalysis..

KOCHUBEY Dmitrii Ivanovich, doctor of physico-mathematical sciences (1994), Head of Laboratory.

Dmitrii I. Kochubey contributed a lot to the EXAFS studies of ultradispersed metal clusters, oxides and sulphide materials, and to scanning tunnel microscopy on surfaces.

Dmitriy I. Kochubey has developed the following EXAFS techniques: fluorescence, transmission, overall photocurrent, XEOL (in the International Siberian Centre of Synchrotron Radiation). He also directs the EXAFS studies at this Centre.

He has developed a technique for characterizing 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 Research Group.

Prof. Ivan V. Kozhevnikov is a distinguished scientist known for his expertise in catalysis for organic synthesis. His research interests lie in the area of metal complex and acid catalysis in homogeneous and heterogeneous liquid-phase reactions. He contributed to the mechanistic studies of homogeneous catalysis by the Lewis acids. He also performed an extensive research on palladium catalyzed oxidation of organic compounds (olefins, alcohols, arenes, carbohydrates, etc.).

Prof. Ivan V. Kozhevnikov has made a significant contribution to the acid and oxidation catalysis by heteropolyacids; preparation and characterization of HPA catalysts. He studied the mechanisms of HPA catalytic performance, development novel catalytic methods for the synthesis of fine chemicals (stabilizers, medicines, vitamins (E, K, C, etc.). Some of his innovations were commercialized. In his recent studies he aimed at designing advanced solid acid catalysts based on HPA and related compounds incorporated in novel mesoporous M41S zeolites.

He is the author of more than 150 works, including 32 Russian Patents, 9 reviews and monograph "Catalysis by Acid and Bases".

Since 1993, he works as a visiting professor (joint program on catalysis by HPA and related systems) at the Delft University of Technnology, the Netherlands.

KRIVORUCHKO Oleg Petrovich, doctor of chemical sciences (1990), Head of Laboratory.

Oleg P. Krivoruchko develops theoretical principles of heterogeneous oxide catalysts preparation and related technologies.

He has also developed nontraditional methods for preparing supports and catalysts via thermochemical, mechanochemical and electron-beam activation of solids under coniditions far from equilibrium.

He has discovered and studied experimentally the phenomenon of unusual liquid metal-carbon particles formation during the solid-phase interaction between Fe, Co, Ni and amorphous carbon at the temperatures by 500-900°C lower than the melting point of metals and their carbon eutectics. These particles constitute solutions that exhibit abnormally high saturation by carbon (to 50 at.%) and extremely high flowing into the carbon support. When moving, these metal-carbon particles catalyze the transformation of amorphous carbon to graphite.

KUNDO Nikolai Nikolaevich, doctor of chemical sciences (1991), Head of Laboratory.

Nikolai N. Kundo successfully develops catalytic processes in the gas phase and solutions for detoxicating wastes containing sulphur compounds, searches for catalysts resistant to sulphur compounds, and studies catalytic reaction mechanisms.

He has developed the processes for the liquid phase catalytic purification of gases from hydrogen sulphide, yielding elementary sulphur. He pioneered the use of catalysts based on cobalt phthalocyanines for this purpose. Test experiments provided a 95% yield of sulphur and practically complete gas purification from hydrogen sulphide. Heterogeneous catalysts on the basis of cobalt phthalocyanine allow to detoxicate wastes from hydrogen sulphide and mercaptanes.

Studies of H_2S+SO_2 reaction in aqueous solutions produced efficient catalysts for sulphur generation. The process of sulphur removal from the effluent gases containing sulphur dioxide was designed using the data obtained.

KUVSHINOV Gennadii Georgievich, doctor of technical sciences (1992), Head of the Research Group.

The field of his research activities unites the engineering of chemical, mechanical and thermal processes.

Gennadii G. Kuvshinov results come from the mathematical simulation and design of chemical reactors, hydrodynamics and heat- and mass transfer in dynamic dispersed systems (fluidized-, circulating-, moving, vibrant beds), as well as from catalysis application to ecology, power engineering and processing of new carbon materials.

KUZIN Nikolai Alekseevich, candidate of chemical sciences (1982), Head of the Research Group.

Nikolai A. Kuzin designs metal based catalysts, studies microkinetics of chemical reactions with phase transformations and develops chemical technologies related.

He is an expert in catalysis, especially in the design of catalysts for highly exothermal processes, and in macrokinetics theory and chemical technology.

He obtained key results when designing metal based catalysts for the liquid-phase decomposition of hydrogen peroxide and hydrazine. These catalysts are mechanically stable in the gasogeneration. Dr. Kuzin also studies macrokinetic regulations of such processes on the catalyst grain. His studies allowed him to elucidate the essence of physical chemical phenomena proceeding in the gas-phase catalytic decomposition of hydrogen peroxide and hydrazine and to give a mathematical description of these processes in a reactor.

Nikolai A. Kuzin has designed the methods to obtain catalytically active armoured metal membrane materials. These methods in turn allowed him to develop three ways of catalytic gas fuel combustion to produce heat. Such materials are used in catalytic devices (or heaters) allowing to burn the stoichiometric fuel-air mixtures at 800-850^{o}C producing no nitrogen oxides. Moreover, the heaters act as heat exchangers.

KUZNETSOV Vladimir L'vovich, candidate of chemical sciences (1978), Head of the Research Group. Director of Information Center of BIC SB RAS.

Vladimir L. Kuznetsov is the expert in synthesing and studying highly dispersed compounds. His scientific interests are focussed on the research and design of supported catalysts immobilizing metal complexes and clusters on the supports of different origin (oxides, carbon). He has also developed the method for transforming disperse diamond to curved graphitic structures (onion-like carbon, surface carbon nanotubes), methods for preparing ultra-disperse magnetic materials.

Vladimir L. Kuznetsov is the organizer and decision maker of the Information Center of BIC SB RAS, responsible for supporting of the databank on catalysis.

LIKHOLOBOV Vladimir Aleksandrovich, doctor of chemical sciences (1983), Professor (1985), Head of Laboratory, Head of the Chair "Catalysis and Adsorption" at the Novosibirsk State University.

Prof. Vladimir A. 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 magnificently to the research of processes for activating dihydrogen, carbon monoxide, dioxygen, olefin molecules by transition metal ions, as well as of ligand rearrangements yielding the products of hydrogenation, oxidation and carbonylation of various organics.

Now he is desgning methods for synthesing the surface-functionalized carbon materials which are catalysts and sorbents of a new generation (they serve as key materials to produce dyes, biologically active substrates, fine organics).

MALAKHOV Vladislav Veniaminovich, doctor of chemical sciences (1988), Head of Laboratory.

Vladislav V. Malakhov contributed significantly to the development of such methods as atomic-emission spectroscopy with inductively related plasma; X-ray fluorescence spectroscopy; atomic-absorption spectrophotometry; local X-ray microanalysis; chemical methods of elemental and phase analyis; 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. He 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 varius genesis and application.

He has designed a new chemical method for the phase analysis - stoichiographic method for differentiated dissolving allowing to analyze solids of unknown phase composition not using the reference samples of individual phases.

Vladislav V. Malakhov has designed a new type of polycapillar chromatography columns accelerating the chromatographic separation of materials by several orders as compared to the conventional ones.

MASHKINA Anna Vasilievna, doctor of chemical sciences (1973), Professor (1988), Head of Laboratory.

Taking into account the chemical nature of the heterogeneous catalysis, Prof. Mashkina has established a general approach to predicting the catalytic action of materials with respect to sulphur compounds interactions. Her studies of chemical interactions between the reagents and the surface allowed to perform thermodynamically possible but previously unknown reactions and to select efficient catalysts for some particular processes in the inert media involving hydrogen, oxygen and hydrogen sulphide. She supervised the design of efficient catalysts and processes for synthesing alkane thiols, aliphatic- and cyclic sulphides and sulfoxides, sulfolane, thiophenes, methylthiazole.

MASTIKHIN† Vyacheslav Matveevich, doctor of chemical sciences (1986), Professor (1994), senior researcher, Head of the Research Group.

Prof. Vyacheslav M. Mastikhin studied catalysts and catalytic reactions with radiospectroscopy methods, such as electron spin resonance (ESR) and nuclear magnetic resonance (NMR). At the initial stage of his work he studied with ESR the active component structure in almost all important catalysts. He was the first to investigate how vanadium catalysts for sulphur dioxide oxidation behaive *in situ* and obtained the data on the change of their phase composition as the gas mixture composition and temperature change. Then he turned his efforts towards the NMR spectroscopy. Using the high performance solid state NMR he has developed new approaches to study heterogeneous catalysts. In order to study the sites on heterogeneous catalysts surface, he has developed probes and rotors allowing NMR measurements in sealed tubes rotated at magic angle, and was the first in the field. His work initiated similar studies abroad and helped in their development. To study the catalyst performance *in situ*, he designed probes allowing to analyze at high temperatures (up to 650°C) in reacting gases media. Approaches designed by Prof. V.Mastikhin helped to obtain unique results important for catalysis fundamentals and application. These results help to create new efficient catalysts and to understand the mechanisms of catalytic reactions.

MATVEEV Klavdii Ivanovich, doctor of chemical sciences (1970), Professor (1982), Head of the Research Group.

Prof. Klavdii I. Matveev magnificently contributed to the design and studies of homogeneous catalysts for oxidation in the basic and fine organic syntheses. He pioneered in the homogeneous catalysis with heteropolyacids, which resulted in the production of more than 25 catalysts for various reactions of organic synthesis. He is the author of 48 patents in USSR and 2 patents in 6 European countries.

Nowadays he is predominantly engaged with catalytic synthesis of vitamins K and E.

MOROZ Ella Mikhailovna, doctor of chemical sciences (1989), senior researcher.

X-ray diffraction of highly-dispersed systems is the main field of her research work. Using this method Ella M. Moroz studies the structural and substructural properties of catalysts and supports.

With the up-to-date experimental and numerical methods she has developed X-ray methods to study the multicomponent highly-dispersed materials. The methods are based on the integral analysis of the X-ray intensity curves. Method of radial atomic distribution (RAD) was used to study the phase composition, structure and size of the crystallites of multicomponent catalysts. The criterion of RAD curves reliability was found. The harmonic analysis of diffraction peaks profile was used to identify the 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 importance for supported catalysts. Ella M. Moroz characterized the mechanism of interaction between these compounds and promoters.

Ella M. Moroz has studied the structural and substructural characteristics of a series of monometallic supported catalysts Me/(Al_2O_3, C, SiO_2, spinels). (Me = Pt, Ir, Pd, Re, Ni) and bimetallic catalysts of Pt-Me type (Me = Sn, Re, Ru, Ir, Ce, etc.) prepared via various procedures.

NOSKOV Aleksander Stepanovich, doctor of technical sciences (1993), Head of the Chemical Engineering Department.

The main fields of his scientific interests are the mathematical modeling of catalytic fixed bed reactors and forced unsteady-state catalytic processes, development and commercialization of catalytic processes used to protect the environment from wastes containing VOC, SO_2 and NO_x.

At present his interests are focussed on the use of the catalyst surface unsteady state in catalytic processes. He supervises the design and commercialization of new catalytic processes for gas purification under unsteady-state regimes.

PANOV Gennadii Ivanovich, doctor of chemical sciences (1985), Head of Laboratory.

Dr. Gennadii I. Panov studies the mechanism of molecules activation on solid surfaces and its manifestation in heterogeneous catalysis. Using the isotope techniques for the mechanistic studies, he has revealed some general regularities in the activation of diatomic molecules (N_2, O_2, H_2).

His recent activity relates to the oxidation catalysis over zeolites and searching for new routes in the oxidation organic synthesis.

He and his colleagues has discovered an efficient way for the direct hydroxylation of benzene and other aromatics with nitrous oxide N_2O. This way uses a biomimetic strategy using on a remarkable ability of Fe-complexes stabilized in the zeolite matrix to produce reactive oxygen species similar to the active oxygen in enzyme monooxygenases.

PARMON Valentin Nikolaevich, Corresponding Member of the Russian Academy of Sciences (1991), doctor of chemical sciences (1984), Professor (1991), Head of Laboratory.

Prof. Valentin N. Parmon has developed and studied a large amount of catalysts and photocatalysts for dihydrogen production from water, thermocatalytic systems and devices for the 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.

Prof. Parmon carried out the fundamental study on the design of catalysts for water conversion to dioxygen and elucidated the mechanism of this action, unusual adsorption and catalytic properties of high-temperature superconductors, gas phase electrocatalytic reactions of CO_2 reaction and oxidation of light hydrocarbons under mild conditions.

Among his recent works one should mention papers concerning a possible impact of photocatalysis over tropospheric aerosols on the global chemistry of the Earth atmosphere, conceptual basis of application of renewable and nontraditional energetics in Siberia, the role of chemistry and catalysis in the sustainable development of future energetics as well as design of new catalysts and catalytic technologies for the biomass conversion to valuable fuels.

PAUKSHTIS Eugenii Aleksandrovich, doctor of chemical sciences (1992), senior researcher.

Eugenii A. Paukshtis uses the quantitative IR spectroscopy to study the surface of catalysts. He has evaluated the methods for acidity measurements regarding thermodynamic scales. He suggested to use the proton affinity scale to measure the acid sites strength. Now he is working in the field of zeolite surface properties estimation.

He has studied the acidity of different types of zeolites including HY, H Mordenite, H-erionite, *beta*-zeolites, H-ZSM-5. Studying the catalytic reaction mechanisms, he and his co-workers suggested that carbenium ion in aliphatic compounds behaves as a "transition state". He has established a relationship between the catalytic activity and PA (proton affinity) of acid sites.

Now he also works in the field of fluorescence analysis of dispersed metal (Ag) on supports.

PLYASOVA Ludmila Mikhailovna, doctor of chemical sciences (1993), Head of Laboratory.

The domain of her scientific interests encompasses X-ray diffraction for studying polycrystal materials, their development with regard to catalyst peculiarities. Among these methods is the high-temperature X-ray diffraction analysis in controlled media (*in situ* X-ray diffraction analysis); methods studying how the complex oxide catalyst structure forms during all stages of catalyst preparation and operation; methods studying the crystal-chemical peculiarities of complex oxides exhibiting catalytic properties.

Ludmila M. Plyasova has studied how the phase composition and structure of a number of Mo-, Fe-, Cu-containing oxide systems form. Data on the phase transformation, crystal-chemical nature of phases, their thermal stability, reaction medium effect on the phase composition and structure of the phases forming help to understand the mechanism of the catalyst active state formation and to control the catalyst properties.

ROMANNIKOV Vyacheslav Nikolaevich, candidate of chemical sciences (1978), Head of the Research Group.

Vyacheslav N. Romannikov is occupied with zeolite synthesis, study of mechanisms of reactions catalyzed by zeolites and with the design of zeolite containing catalysts.

He has developed the principles of zeolite acidity regulation using chemical modification. The corresponding catalytic system has been elaborated for the highly-selective alkylation of aromatics.

RYNDIN Yurii Alekseevich, candidate of chemical sciences (1977), Head of Laboratory.

Yurii A. Ryndin is engaged in catalysis by the anchored metal complexes. He studies the nature of active sites of supported oxide and metal catalysts via a purposeful synthesis of molecular models of sites resulting from organometallic precursors.

SADYKOV Vladislav Aleksandrovich, candidate of chemical sciences (1978), Head of Laboratory.

Vladislav A. Sadykov studies environmental molecular catalysis, detailed mechanisms of heterogeneous catalytic oxidation and NO reduction, defects of oxide catalyst structures, new routes of catalyst preparation (plasmochemical, hydrothermal, mechanochemical treatments), supported noble metal catalysts promoted by oxides.

He studies the nature of bulk and surface defects of transition metal oxides and their role in the oxidation catalysis; elucidates the 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 using wastless technologies.

SAVCHENKO Valerii Ivanovich, doctor of chemical sciences (1985), Professor (1988), Head of Laboratory.

Using up-to-date physical methods for surface studies, i.e. LEED, Auger and photoelectron spectroscopy, mass-spectrometry and mathematical modeling of catalytic processes, Prof. Valerii I. Savchenko deals with the atomic structure and electronic properties of single crystal and powdered catalysts; studies the kinetics of adsorption and catalytic reactions, mechanisms of chemisorption and catalysis on metals.

He has 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 reconstruction under the influence of the reaction media.

Mathematical modeling methods (differential equations integration, homotopy and Monte Carlo) allowed him to show that during CO oxidation on heterophase systems there may appear super-additive activity at the kinetic conjugation of surface different patches, caused by the surface diffusion (spillover) of CO molecules adsorbed.

SAVINOV Evgenii Nikolaevich, doctor of chemical sciences (1994), Assistant Professor of Physical Chemistry at the Novosibirsk State University (1981).

His research activities concern particulate photoelectro-chemistry, photochemistry, photocatalytic transformations of organic compounds as well as the synthesis and characterization of ultrasmall semiconductor particles. He is also engaged in the heterogeneous photocatalysis, solar- and environmental chemistry. He is the author of more than 70 publications and 5 patents.

SEMIKOLENOV Vladimir Aleksandrovich, doctor of chemical sciences (1994), senior researcher, Head of the Research Group.

Valdimir A. Semikolenov focuses his research activities on the development of new porous carbon-graphite materials, design and study of metal complex and highly disperse metal catalysts of platinum group supported on carbon, and on the design of new catalytic processes for fine organic synthesis.

Here are the key results of his studies. (i) He has developed and obtained a new family of porous carbon materials, whose size and volume of pores, chemical composition and microcrystal surface structure can be varied within a wide range. (ii) He also developed new methods for preparing supported palladium particles of various geometry and size. He suggested the way, how to control the active metal distribution over the carbon support grain. The data obtained helped to create a series of commercial catalysts "palladium on carbon". (iii) A set of new processes to obtain valuable organic semiproducts, used to synthesize medicines, herbicides, food-stuffs, dyes, to separate isotopes and to produce thermally stable polymers, was designed.

SIMONOV Aleksandr Dmitrievich, candidate of chemical sciences (1979), Head of Laboratory.

Aleksandr D. Simonov studies the catalytic combustion and processing of solid fuels. At present he pays a particular attention to the processes of catalytic utilization of solid organic waste and vegetable feedstocks; design of technology and equipment for bringing these processes to practice and technology commercialization. He is the author and co-author of more than 70 scientific publications.

SOBYANIN Vladimir Aleksandrovich, doctor of chemical sciences (1991), Head of Laboratory, Dean of the Natural Sciences Department at the Novosibirsk State University.

Vladimir A. Sobyanin is active in the surface science, adsorption and catalysis by metals, solid state electrochemistry and electrocatalysis.

Using EELS, FEM, AES and TDS techniques, he has carried out the detailed study of the mechanisms of oxygen isotope exchange, hydrogen oxidation and ammonia decomposition on metals.

He is engaged in the development of fuel cell systems with solid H^+- and O^{2-}-conducting electrolytes to perform various catalytic reactions, methane conversion to valuable chemicals in particular.

SOLOVIEVA Lidiya Pavlovna, doctor of geology-minerological sciences (1991), senior researcher.

Lidiya P. Solovieva uses X-ray diffraction based on monocrystal data to study inorganic compounds, designs mathematical basis for X-ray diffraction calculations.

At present she studies polycrystal structures, develops precise investigation techniques using the synchrotron radiation. She has also established the program systems to solve structural problems using mono- and polycrystal diffraction data. For 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 as well.

STARTSEV Anatolii Nikolaevich, candidate of chemical sciences (1977), Head of the Research Group.

The field of his scientific interest includes the detailed mechanism and active component structure of sulphide HDS catalysts; anchored metal complexes; synthesis and characterization of metal complexes of Mo, W, Re, Ni and Co; design of supported catalysts; catalysts and unsteady-state process for dearomatization of oil fractions; carbon supported catalysts for hydrodemetallization of heavy crude oils; catalysts for bio-oils upgrading.

Anatolii N. Startsev has promoted the concerted mechanism of hydrodesulphurization catalysis, proposed the unsteady-state process of dearomatization, developed a new approach to synthesizing supported bimetallic catalysts via the "surface assembling" of direct precursor of the HDS catalyst active component.

STOYANOV Eugenii Stepanovich, doctor of chemical sciences (1991), senior researcher.

His research interests comprise studying the composition and structure of all-type complexes and associates formed in solutions, their solvation and hydration, intermolecular interactions, and the problems related to the very strong H-bonds formation.

Eugenii S. Stoyanov uses various spectroscopic techniques, namely IR, Raman and NMR, in his studies.

TALSI Eugenii Pavlovich, doctor of chemical sciences (1991), senior researcher.

Eugenii P. Talsi is occupied with the 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 $O_2^{\cdot-}$ coordination to palladium (σ or π) were found. Superoxide complexes (σ-mode) appear to oxidize quantitatively ethylene to ethylene oxide.

Using ^{95}Mo, ^{51}V, ^{59}Co, ^{17}O, ^{1}H NMR spectroscopy and EPR technique, metal complexes formed in catalytic oxidation of alkanes by organic hydroperoxides and hydrogen peroxide were characterized. Alylperoxo and peroxo complexes of Mo, V, Co and Ti were detected and studied *in situ.*

Peroxotitanium(IV) complex $Ti(O_2)(OEt)_2(EtOH)_2$ was characterized in the reaction of $Ti(OEt)_4$ with 95% HOOH. The complex can selectively epoxidize cyclohexene and hydroxylate phenol. New low-spin peroxoiron(III) complexes $Fe(bpy)_2(OOH)Py$, $Fe(phen)_2(OOH)Py$, active towards cyclohexane, were found in the Gif-type catalytic systems. Using ^{59}Co, ^{13}C and ^{1}H NMR it has been shown that the so-called cobalt(III) acetate is a mixture of two types of oxo-centered trinuclear cations $[Co_3O(OAc)_6(AcOH)_3]^+$ and $[Co_3O(OAc)_5(OH)(AcOH)_3]^+$.

TOLSTIKOV Aleksandr Genrikhovich, doctor of chemical sciences (1993), Winner of Leninskiy Komsomol Prize (1986), Winner of Russia State Prize (1993), expert in the fine organic synthesis.

His research interest is the enantiospecific synthesis of low-molecular bioregulators such as prostaglandins, leukotrienes, ferromones and allomones of insects, pyretroids, glycosphingolipides, alkaloids of urea type.

Recently he designed available methods to synthesize chirale biologically active complexes and their semiproducts using the principles of asymmetric homogeneous catalysis by metal complexes.

VENIAMINOV Sergei Alekseevich, candidate of chemical sciences (1963), Head of Research Group.

Sergei A. Veniaminov studies the mechanism of a set of model and industrially important catalytic reactions over oxide catalysts based on molybdenum and antimony. He uses a complex of kinetic methods including steady state kinetics, pulse microcatalytic method, temperature programmed surface reaction (TPSR), temperature programmed desorption (TPD), the method of gas-phase titration of oxygen and other surface complexes. To study the kinetics and mechanism of individual stages, he used the pulse microcatalytic method simultaneously measuring the surface oxygen binding energy with a calorimetric method *in situ* and ESR *in situ*.

This data on the kinetics of individual stages allowed to develop a technique to calculate steady-state and dynamic regimes for the oxidation reactions proceeding via the redox mechanism.

YERMAKOVA Anna, doctor of technical sciences (1986), leading researcher.

Anna 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), and to modeling macrokinetic complex chemical reactions. She has established a new set of numerical methods to identify and analyze the kinetic models adapted for IBM PC. She developed a mathematical model of a new complex liquid-phase catalytic purification of process gases from the admixtures of sulphur dioxide, nitrogen oxides, arsenic oxides. Now she is occupied designing new simulation computer models mimicing the engineering schemes of chemical processes, including the Fischer-Tropsch process performed in a slurry reactor.

YUDANOV Valerii Fedorovich, doctor of chemical sciences (1992), Head of Laboratory.

The main field of his scientific interest is the application of Electron Spin Resonance to chemical problems. He carried out thorough studies of the mechanism of modulation phenomena in Electron Spin Echo and investigated the structure of trapped electrons, H-atoms and other paramagnetic species in disordered vitrous systems.

At present he studies the mechanism of free radical processes in zeolites, rheology of dispersed systems, electrokinetics measurements and the theory of dissipative structures.

YURIEVA Tamara Mikhailovna, doctor of chemical sciences (1984), Professor (1990), Head of Laboratory.

Prof. Tamara M. Yurieva is an expert in heterogeneous catalysis with oxides, she studies the mechanism of the oxide catalytic action in redox reactions. Prof. T. Yurieva has studied the peculiarities of oxides genesis and dependence of their catalytic properties on the structure of environment of metal ions determined experimentally. In accordance with a developed low-temperature catalyst preparation method Prof. T. 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.

ZAGORUIKO Andrei Nikolaevich, candidate of technical sciences (1991), Head of Laboratory.

Andrei N. Zagoruiko is an expert in mathematical modeling and development of catalytic processes in a packed catalyst bed, performed under forced unsteady state conditions. The field of his research interest includes unsteady and steady-state kinetics of catalytic reactions, influence of the state of catalyst surface on the catalyst activity, mathematical modeling of unsteady state processes in the packed catalyst bed, software design to simulate the processes. His applied interests are elemental sulphur production from hydrogen sulphide, removal of volatile organic compounds (VOC) from waste gases by catalytic reverse-process and adsorption-catalytic methods, oxidation of sulphur dioxide, deep oxidation and partial oxidation of organic compounds.

ZAKHAROV Vladimir Aleksandrovich, doctor of chemical sciences (1982), Professor 1988), Head of Laboratory.

Prof. Vladimir A. Zakharov studies the catalytic polymeriztion of olefins, synthesizes and studies solid catalysts of various types (supported organometallic systems, Ziegler supported catalysts, supported metallocene catalysts), investigates the kinetics and mechanism of catalytic polymerization.

He has studied the composition, structure and reactivity of surface transition metal species in polymerization catalysts and developed a set of new highly active supported catalysts to produce polypropylene, polyethylene and copolymers of ethylene with a-olefins of controlled molecular structure and morphology.

ZAMARAEV Kirill Il'ich[†], Full Member of the Russian Academy of Sciences (1987), Member of the Academia European (1990), Foreign Fellow of the Indian National Science Academy (1990), doctor of chemical sciences (1972), Professor (1977), Director of the Boreskov Institute of Catalysis (1984), General Director of MNTK KATALIZATOR, Head of the Chair of Physical Chemistry at the Novosibirsk State University.

Prof. Kiril I. Zamaraev is a well-known specialist in the area of catalysis, kinetics of chemical reactions in condensed media, photochemistry and magnetic resonance spectroscopy.

He has carried out detailed studies on the mechanism 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. Kirill I. Zamaraev has characterized with various spectroscopic techniques, in particular with EPR, NMR and EXAFS, the structure of numerous homogeneous and heterogeneous catalysts and has elucidated the mechanism 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 physical and mathematical sciences (1988), Professor (1988), senior researcher.

The main field of his scientific interest is the theory of elementary rate processes on solid surface. Prof. Vladimir P. Zhdanov has studied in detail vibrational relaxation of adsorbed particles via the 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 and mathematical sciences (1975), Professor (1986), Full Member of the Russian Academy of Natural Sciences (1992), Member of the Board of Directors of the International Society for Theoretical Chemical Physics, Head of Laboratory.

Prof. Georgii M. Zhidomirov develops the theoretical basis of quantum chemistry, elaborates and modifies semiempirical quantum chemical methods of calculations, performs quantum chemical studies using spectroscopic parameters (NMR, ESR, IR, electron spectroscopy, XPS, UPS, XANES, EXAFS), theory of magnetic resonance (NMR, ESR) form lines, theory of electron spin echo phenomena, theoretical surface sciences and molecular theory of heterogeneous and metal complex catalysis.

He is systematically engaged in analyzing how magnetic resonance parameters (isotopic and anisotropic hyperfine coupling constants, g tensors and etc.) depend on the structure peculiarities of paramagnetic centers (free radicals, transition metal compounds), in elaborating semiempirical approaches to the quantum chemical studies of chemisorption and catalysis (MINDO/3-HB, CNDO-S2, NDDO/MC), and widely uses the cluster approximation to study the electronic structure and reactivity of active site on oxides (zeolites, Al_2O_3, SiO_2, MgO, ZnO and oxides modified by enclosed transition elements).

ZOLOTARSKII Il'ya Aleksandrovich, Head of Laboratory.

He deals with the mathematical modeling of catalytic processes, from the kinetic models simulation to flow-sheeting evaluation with an intent to design new catalytic processes and to improve the efficiency of the existing plants.

ZOLOTOVSKII Boris Petrovich, doctor of chemical sciences (1993), Head of Laboratory.

Boris P. Zolotovskii designs new alumina adsorbents and catalyst supports. In particular, he studies the catalysts for gaseous sulphur recover (the Claus processes). He supervised the design and commercialization of microspherical and spherical alumina supports and catalysts, including the catalysts for the Claus process; the design of a unique titanium oxide catalyst for the Claus process.

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