ISSN 0023-1584, Kinetics and Catalysis, 2010, Vol. 51, No. 6, pp. 783–787. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © E.P. Talsi, A.N. Startsev, L.Ya. Startseva, 2010, published in Kinetika i Kataliz, 2010, Vol. 51, No. 6, pp. 811–815.

VIII International Conference on Mechanisms of Catalytic Reactions,

Dedicated to the 70th Birth Anniversary of Academician K. I. Zamaraev

(June 29–July 2, 2010, Novosibirsk)

DOI: 10.1134/S0023158410060017

The VIII International Conference on Mechanisms of Catalytic Reactions, dedicated to the 70th birth anniversary of Academician K.I. Zamaraev, was held on June 29–July 2, 2009, in the House of Scientists, Akademgorodok, Novosibirsk.

Kirill Il'ich Zamaraev (1939–1996) was an outstanding scientist in the field of physical chemistry and catalysis. He was widely known both in Russia and abroad for his mechanistic studies of catalytic reactions at the molecular level. From 1984 till 1995, he headed the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences. He was President of the International Union of Pure and Applied Chemistry (IUPAC) and took an active part in the foundation of the European Federation of Catalysis Societies (EFCATS).

The conference was organized by the Boreskov Institute of Catalysis with the assistance of Moscow State University under the aegis of EFCATS. It was financially supported by the Russian Foundation for Basic Research and Russian Federal Agency for Science and Innovation. The VIII Conference was the first to be international. Owing to this new status, the organizers were able to draw in many great names in science from various countries. The conference welcomed about 250 scientists from 19 countries, including 180 participants from Russia.

The Conference on Mechanisms of Catalytic Reactions is unique in the world. Usually, only small sections of large chemical forums deal with this subject. The scientific program of the conference included 5 plenary lectures, 18 keynotes, 32 20-min-long oral reports, 39 10-min-long communications, 38 10-min-long oral reports by young scientists, and about 120 posters. There were three parallel sections: "Homogeneous and Heterogeneous Catalysis Mechanisms at the Molecular Level"; "Use of Physical Methods in Mechanistic Studies of Heterogeneous and Homogeneous Catalytic Reactions"; and "Theory and Quantum Mechanical Studies in Catalysis," including the subsection "Biomimetic Catalysis and Photocatalysis."

The conference was opened by Academician V.N. Parmon, who told the audience about the most important landmarks in Zamaraev's outstanding scientific and managerial activities.

The first item of the scientific program was the plenary lecture by M. Bochmann (University of East Anglia, Norwich, United Kingdom), which was devoted to the mechanism of the catalytic action of single-site olefin polymerization catalysts. Use of well-characterized activators and Croup IV metal complexes allowed the reporter to gain a detailed understanding of the structure of olefin polymerization intermediates, including complexes in which one of the ligands is a polymer chain, and to acquire information concerning the mechanism of the process and the main factors determining the polymerization activity of particular catalytic systems. These studies made it possible to obtain polymerization catalysts with hitherto unattainable catalytic activity and stereoselectivity.

The plenary lecture by A.G. Stepanov (Boreskov Institute of Catalysis, Novosibirsk, Russia) demonstrated the potential of solid-state NMR spectroscopy for elucidating the mechanisms of hydrocarbon conversion on solid acid catalysts and for investigating the complicated processes of hydrocarbon diffusion in catalyst pores and active site coking. These studies have recently elucidated the mechanism of coaromatization of methane with higher alkanes.

M. Sterrer (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany) reported the use of physicochemical methods in the study of model systems based on crystalline oxide films supporting metal nanoparticles. The structure, morphology, and adsorption properties of these systems were correlated with their reactivity in a number of catalytic reactions, such as alkene hydrogenation on palladium nanoparticles, methanol oxidation on supported vanadium, and hydrocarbon oxidation on gold nanoparticles.

V.I. Bukhtiyarov (Boreskov Institute of Catalysis, Novosibirsk, Russia) discussed problems of applying X-ray photoelectron spectroscopy (XPS) to the investigation of heterogeneous catalytic reactions. Main attention was focused on experiments at compara-

tively high reactant pressures close to those used in real processes. The reporter described experimental designs ensuring the most correct correlation between XPS data on the properties of surface species and the behavior of these species in ethylene epoxidation on silver catalysts and selective methanol oxidation on copper and vanadium catalysts. Both the structure of surface species and the chemical composition of the surface were probed, and the variation of the surface composition during the reaction was monitored. The mechanisms of the above reactions were derived from these data.

N. Rösch (Technical University of Munich, Germany) devoted his plenary lecture to DFT calculations for clusters and small metal particles modeling hydrocarbon hydrogenation and dehydrogenation catalysts. The lecturer discussed the structural and energetic properties of metal clusters varying in nuclearity, such as Rh_6 and Ir_4. It has recently been discovered that silver catalysts accelerate the regioselective hydrogenation of unsaturated aldehydes into unsaturated alcohols. For this reason, Rösch considered the activation of hydrogen molecules in this system.

Along with the plenary lectures, there were a number of keynote lectures delivered by invited scientists.

I.I. Ivanova (Moscow State University, Moscow, Russia) reported a mechanistic study of the aromatization of light alkanes by IR and NMR spectroscopy, gas chromatography, mass spectrometry, and thermogravimetry. Zn–methyl, Zn–ethyl, and Zn–propyl fragments resulting from alkane–catalyst interaction were detected by ^{13}C NMR spectroscopy on the surface of zinc-containing heterogeneous catalysts. ^{1}H NMR spectroscopy made it possible to observe the conversion of ZnO into ZnOH. Based on these data, it was hypothesized that alkane activation on the surface of the zinc-containing catalysts is due to dissociative adsorption. Methane adsorption yields species that are very strongly bound to the surface and thus deactivate the catalyst. The role of carbanions as possible coke precursor was discussed.

K.P. Brylyakov (Boreskov Institute of Catalysis, Novosibirsk, Russia) reported the structure of ion pairs appearing in three types of catalytic systems based on titanium and zirconium bis(phenoxyimine) complexes, iron bis(imino)pyridine complexes, and hafnium complexes with indenyl and fluorenyl ligands, respectively. In some cases, it was possible to correlate between the structure and conversion of the ion pairs, their catalytic activity, and the properties of the resulting polymers.

L. Palmisano (University of Palermo, Italy) discussed some aspects of use of heterogeneous photocatalysis in the selective oxidation of organic compounds in water. The lecturer considered the oxidation of hydrocarbons, the hydroxylation of aromatic compounds, the cyclization of amino acids, and the functionalization of heterocyclic compounds.

A. Knop-Gericke (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany) demonstrated in his lecture that the higher selectivity of Pd–Ga intermetallides as compared to palladium is due to the serious changes in the electronic state of the latter under the action of gallium. Furthermore, in the case of Pd–Ga intermetallides, segregation and near-surface interactions of C and H atoms typical of pure palladium are hampered. Owing to this fact, the Pd–Ga intermetallides are highly stable and selective in acetylene hydrogenation.

The lecture by F. Besenbacher (University of Aarhus, Denmark) dealt with investigation of a variety of catalytic objects by scanning tunneling microscopy. This method was shown to have a great potential for the study of diffusion, nanocluster agglomeration on oxide surfaces, and identification of new nanostructures possessing special catalytic properties. The lecturer demonstrated by a number of examples that studies at the atomic level can contribute to the synthesis of improved catalysts.

Ph. Sautet (Institute of Chemistry, Lyon, France) considered use of DFT calculations and XPS in the study of the nature of active sites in catalytic hydrogenation processes in the presence of transition metal complexes. Special attention was given to the effect of surface modification on hydrogenation selectivity, including the role of the thin carbide-like layer forming on the palladium surface during alkyne hydrogenation. This palladium–carbon phase was demonstrated to exert a strong effect on the selectivity of the process.

P.E. Strizhak (Pisarzhevskii Institute of Physical Chemistry, Kiev, Ukraine) considered the interrelation between the rate of a catalytic reaction and the fractal dimension of the catalyst surface, using some model reactions as examples. According to the lecturer, this approach can provide a more adequate description of size effects in heterogeneous catalysis. There is an alternative approach, based on the quantum chemical description of the electronic structure of the active site. Both approaches were used in the investigation of CO oxidation and the hydrogenation of CO, CO_2, ketones, and nitriles.

J.-M. Herrmann (Institute of Researches on Catalysis and Environment, Lyon, France) discussed the prospects of use of photocatalysis in the removal of organics (pesticides, herbicides, and dyes) from air and in air deodorization and disinfection.

A.V. Vorontsov Boreskov Institute of Catalysis, Novosibirsk, Russia) presented a systematic study of the products and kinetics of photooxidation of comparatively simple organic molecules and complex sulfur- and phosphorus-containing organic compounds. Titanium dioxide, both pure and platinum-modified, was used as the photocatalyst. Correlations were established between the diffuse reflectance spectrum of the

catalyst, the specific surface area of the catalyst, the charge state of the modifier, and catalytic activity. The effect of adding H_2O_2 to the gas phase on photooxidation was considered.

The lecture by C.L. Hill (Emory University, Druid Hills, Ga., United States) consisted of two parts. In the first, the lecturer presented a study of the first homogeneous water oxidation catalyst, $Rb_8K_2[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]$. The second part dealt with the reactivity of oxo complexes of noble metals (Pt, Pd, Au, and Ir). It has long been believed that these complexes are intermediate in catalytic processes occurring in the cathodes of fuel cells and on the surface of a n umber of supported automotive catalysts. Now these complexes have been synthesized and reliably characterized by various physical methods.

A.M. Khenkin (Weizmann Institute of Science, Rehovot, Israel) considered two classes of catalytic reactions, namely, the oxidation of alkyalaromatic compounds, primary alcohols, and diols with dioxygen under the action of polyoxometalates and the oxidation of alkenes in the presence of the $P_2W_{17}Mn(III)/F_5PhI(TFAc)_2$ system. Manganese(V) oxo complexes responsible for selective epoxidation were identified in the latter catalytic system.

A.T. Bell (University of California, Berkeley, United States) demonstrated how theoretical and experimental data can complement each other in mechanistic studies of important catalytic reactions, such as alkane cracking and dimethoxymethane carbonylation into monoethylene glycol catalyzed by zeolites.

H. Jobic (Institut de Recherches sur la Catalyse et l'Environnement, Lyon, France) reported use of neutron scattering in the study of the diffusion of organic molecules in porous systems. The discrepancy between the diffusion coefficients determined by NMR and neutron scattering arises from the fact that NMR spectroscopy gives an average value pertaining both to zeolite microcrystals and to the space between them, while neutron scattering characterizes only diffusion inside a microcrystal. As a consequence, smaller diffusion coefficient values are obtained by NMR.

A. Macchioni (University of Perugia, Italy) presented a number of interesting examples of use of the intermolecular nuclear Overhauser effect in the determination of the mutual orientation of fragments of complicated catalytic systems. The objects of this study were post-metallocene polymerization catalysts and cationic gold(I) complexes.

E. Roduner (University of Stuttgart, Germany) presented a study of benzene conversion to phenol on copper-containing zeolites. Use of FTIR, EPR, and EXAFS spectroscopy enabled him to suggest a well-substantiated mechanism for this reaction. Based on the data obtained in this study, the author outlined possible ways of modifying the catalyst in order to enhance its efficiency.

E. Lokteva (Moscow State University, Moscow, Russia) considered catalytic hydrodechlorination as a means to utilize various chlorine-containing substances. Main attention was focused on Co-, Fe-, Ni-, and Pd-based bimetallic systems supported on ultrafine diamonds; Ni and Pd systems supported on double oxides; and carbon- and oxide-0supported Ni and Pd systems prepared by laser electrodispersion and levitation melting of the metal.

V. Ostrovskii (Karpov Institute of Physical Chemistry, Moscow, Russia) reported the catalytic activity of Cr_2O_3 in C_3H_8 dehydrogenation and correlated it with the heats of adsorption of H_2, O_2, and CO_2. This correlation proved Boreskov's rule concerning the effect of the reaction medium on catalytic activity.

The lecture by J. Fraissard (University of P. and M. Curie, Paris, France) was devoted to the application of NMR spectroscopy with an ultrathin detection coil to the investigation of gas diffusion into a zeolite.

Since we cannot overview all sectional reports here, we will dwell on the most interesting of them.

At the meeting of the section "Homogeneous and Heterogeneous Catalysis Mechanisms at the Molecular Level," A.Yu. Kostrova (St. Petersburg Department of the Boreskov Institute of Catalysis, St. Petersburg, Russia) made a 20-min-long report on olefin polymerization mechanisms in the presence of various post-metallocene catalysts and on the synthesis of novel dinuclear bis(phenoxyimine) complexes showing high thermal stability and activity.

O.A. Kholdeeva (Boreskov Institute of Catalysis, Novosibirsk, Russia) reported the catalytic properties of the polyoxometalate $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O]_8$, which had recently been synthesized by her German colleagues, and demonstrated that this compound possesses unique catalytic activity. Under optimum conditions, the selectivity of alkene epoxidation and sulfide oxidation with hydrogen peroxide was close to 100%. H. Schulz (University of Karlsruhe, Germany) systematized information about the complicated processes taking place in Fischer–Tropsch synthesis. Global interest in these reactions has risen considerably in recent years because of the drastic fluctuations in energy carrier prices. A.N. Startsev (Boreskov Institute of Catalysis, Novosibirsk, Russia) discussed the concept of acid–base catalysis, within which he considered the mechanism of action of sulfide catalysts for petroleum hydrodesulfurization and described, in detail, the structure of their active component, which includes occluded hydrogen. The oxidative addition of hydrogen to an active metal atom brings the latter to an

extraordinarily high oxidation state (Ni(IV), Co(III)) with the electronic configuration d^6. It is the resulting metal ions that serve as the Lewis acid sites activating the S-containing molecules.

At the meeting of the section "Use of Physical Methods in Mechanistic Studies of Heterogeneous and Homogeneous Catalytic Reactions," M.V. Tsodikov (Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia) reported the reductive dehydration of alcohols on nanostructured polymetallic catalysts. I.R. Subbotina (Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia) presented a new approach to the study of the activation of chemical bonds in adsorbed hydrocarbons. This approach is based on the changes in band intensities in the IR spectrum due to the polarization of the hydrocarbon molecules. S.A. Yashnik (Boreskov Institute of Catalysis, Novosibirsk, Russia) reported the electronic state of Cu ions in zeolites studied by diffuse reflectance UV spectroscopy under NO adsorption conditions. This study revealed the formation of the N_2O_4 dimer with a short N–N bond. E. Stavitski (Utrecht University, the Netherlands) reported a study of thiophene conversion on acidic zeolites by multifunctional microspectroscopy. V.V. Kaichev (Boreskov Institute of Catalysis, Novosibirsk, Russia) reported use of a combination of complementary methods, such as XPS combined with mass spectrometry and gas chromatographic analysis of reaction products, in the investigation of the oscillations of the rate of propane oxidation on nickel. H. Idriss (University of Aberdeen, United Kingdom) reported obtaining hydrogen by ethanol reforming on Rh–Pd/CeO_2 clusters. T. Maniecki (Technical University of Lodz, Poland) made a 20-min-long report on the thermal stability of aluminum–chromium oxide systems.

Among the reports presented to the section "Theory and Quantum Mechanical Studies in Catalysis," of particular interest was the communication by V.I. Elokhin (Boreskov Institute of Catalysis, Novosibirsk, Russia), who presented a stochastic model of CO oxidation on palladium nanoparticles. C.H. Christensen (Haldor Topsøe A/S, Denmark) demonstrated the potential of the DFT method for surface reactin calculations in the design of industrial reactors. The report by V. Bykov (University of Karlsruhe, Germany) dealt with mathematical modeling of complicated catalytic systems. D. Murzin (Abo Akademi University, Turku, Finland) presented a thermodynamic analysis of the nanoparticle size effect on the kinetics of catalytic processes. I.V. Yudanov (Boreskov Institute of Catalysis, Novosibirsk, Russia) reported a DFT study of the mechanism of acrolein hydrogenation on silver. V.S. Muzykantov (Boreskov Institute of Catalysis, Novosibirsk, Russia) made use of the kinetic isotope effect in his study of the mechanism of isotope exchange in multiatomic molecules.

In the subsection "Biomimetic Catalysis and Photocatalysis," considerable interest was attracted by the oral report by A.I. Kokorin (Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia), who carried out an EPR study of Fe–TiO_2 catalysts. B.N. Kuznetsov (Institute of Chemistry and Chemical Technology, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, Russia) reported the oxidative delignification of wood on a TiO_2 catalyst under the action of UV light. T.S. Dzhabiev (Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Russia) reported the multielectron water oxidation reaction in photosynthesis. E.G. Chepaikin (Institute of Structural Macrokinetics and Materials Science Problems, Russian Academy of Sciences, Chernogolovka, Russia) presented a study of the biomimetic oxidation of alkanes on metal catalysts in a homogeneous medium. M.P. Fedotova (Tomsk State University, Tomsk, Russia) reported the photocatalytic purification of water on Au/TiO_2–SiO_2 catalysts. The report by M. Hussain (Politecnico di Torino, Italy) was devoted to the photocatalytic decomposition of ethylene on TiO_2 nanoparticles.

The young scientists' session, which included 38 10-min-long reports made by researchers from Russia, Poland, Germany, France, Switzerland, Bulgaria, Ukraine, and Azerbaijan, was very informative. Many of the reports dealt with the mechanisms of CO, methanol, and hydrocarbon oxidation on various catalysts.

The following five reports made by young participants were warded diplomas from the International Organizing Committee:

(1) D. Ivanov (Boreskov Institute of Catalysis, Novosibirsk, Russia), "The Effect of Oxygen Mobility in La–Sr–Mn–O Oxides on Their Activity in Methane Burning and High-Temperature N_2O Decomposition";

(2) A. Michalak (Institute of General and Ecological Chemistry, Lodz, Poland), "Low-Temperature CO Oxidation on Cobalt Catalysts";

(3) A. Aloui (Chemical Process Engineering Laboratory, Lyon, France), "Kinetic and Theoretical Study of the Asymmetric Methacrylate Hydrogenation Using Rh(I)/(R, R)-Me-BPE";

(4) I. Grishin (Lobachevsky State University of Nizhni Novgorod, Nizhni Novgorod, Russia), "Catalysis of Free-Radical Polymerization by Ruthenium Carborane Complexes: Mechanism and Specific Features";

(5) K. Bawolak (Technical University of Lodz, Poland), "Au–Cu/Al_3CrO_6 Catalyst for Methanol Synthesis."

A big audience was attracted by poster reports, which gave rise to active discussions.

An analysis of the totality of reports presented at the conference demonstrated that fundamental research in mechanisms of catalytic reactions is becoming innovative, addressing challenging problems. Increasingly more attention is being given to nanostructured catalysts and to establishing structure–catalytic activity and structure–selectivity correlations. Researchers are seeking not only to gain the deepest possible insight into the mechanisms of catalytic processes, but also to use their knowledge in the design of improved catalysts.

The International Program Committee decided to hold the next, IX International Conference on Mechanisms of Catalytic Reactions in 2012 in a Western Europe country.

E.P. Talsi, A.N. Startsev, and L.Ya. Startseva