

VI Russian Conference on the Scientific Foundations of Catalyst Preparation and Technology

V Russian Conference on Problems of Catalyst Deactivation

(With the Participation of CIS Countries)

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The VI Russian Conference on the Scientific Foundations of Catalyst Preparation and Technology and the V Russian Conference on Problems of Catalyst Deactivation were held on September 4–9, 2008, in one of the nicest places on the Black Sea coast near the town of Tuapse. The organizers of the conferences were the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences (Novosibirsk); the Institute of Hydrocarbon Processing, Siberian Branch, Russian Academy of Sciences (Omsk); the Scientific Council on Catalysis at the Division of Chemistry and Materials Science, Russian Academy of Sciences; and Novosibirsk State University. The forums were financially supported by the Russian Foundation for Basic Research and by Evrokhim Mineral and Chemical Company (Moscow).

The participants expressed deep interest in the subjects of the conferences: there were 169 specialists from Russia, Azerbaijan, Ukraine, Kazakhstan, Belarus, Uzbekistan, and Germany, including 115 representatives of academic research institutes and higher education institutions (20 post graduates and students) and 54 representatives from industrial enterprises, specialized research institutes, and companies.

The scientific program of the conferences-2008 included 5 plenary lectures by invited scientists, 8 key lectures, 64 oral reports (each 20- or 10-min-long), 12 oral reports by young scientists (each 10-min-long), and 41 poster reports.

The conferences took place on the 50th anniversary of the Institute of Catalysis and the 100th birth anniversary of Vera Aleksandrovna Dzis'ko, the founder of the Laboratory of the Scientific Foundations of Catalyst Preparation, one of the first laboratories of its kind in the Soviet Union. The achievements of the scientific schools of the Institute of Catalysis were adequately presented at the conferences: there were plenary, key, and oral reports by followers of V.A. Dzis'ko (A.S. Ivanova, E.V. Kul'ko, R.A. Buyanov (V.V. Molchanov, N.A. Pakhomov, B.P. Zolotovskii), G.K. Boreskov (A.A. Khassin, A.I. Boronin, Z.R. Ismagilov, M.S. Mel'gunov), V.A. Likholobov (A.S. Belyi, A.V. Lavrenov,

V.A. Drozdov), and Yu.I. Ermakov (B.N. Kuznetsov).

For the first time, the forum had young scientists' section, where expectant candidates of sciences and doctors made 10-min-long oral reports. The organizing committee of the conferences found it appropriate to institute awards from the scientific schools of the Institute of Catalysis for young participants who would carry out significant research in catalyst preparation.

The reports made at the conferences covered nearly all aspects of catalyst preparation and deactivation: physical chemistry and kinetics of the synthesis of heterogeneous catalysts and supports, including all preparation stages; targeted control of the formation of catalysts with preset properties; new methods of catalyst preparation; scientific principles of the design of integrated technologies, flexible production lines, and equipment for the main stages of catalyst and support preparation; scale-up problems; nature, regularities, and mechanisms of deactivation; and ways of extending the service life of catalysts. Notably, there have been an increasing number of studies dealing with the preparation of catalysts based on carbon nanomaterials, namely, nanotubes, Sibunit, and carbon xerogels.

The participants of the forum noted the disconnectedness between the catalyst developers and manufacturers. Nevertheless, they considered the conferences as the place to make joint decisions and found it necessary to hold the forum every three years. The forum accepted the application from Samara State Technical University for holding the next meeting (VII Russian Conference on the Scientific Foundations of Catalyst Preparation and Technology and VI Russian Conference on Problems of Catalyst Deactivation) in 2011 in Samara with organizational support from Novokuibyshevsk Catalyst Plant.

The scientific program of the conferences was opened by a plenary lecture by V.I. Pet'kov, M.V. Sukhanov (Nizhni Novgorod State University), M.M. Ermilova, N.V. Orekhova, and G.F. Tershchenko (Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow), entitled "Development and Production of Composite Membrane Catalysts Based on Framework Phos-

phates and Molybdates." This lecture demonstrated the possibility of obtaining framework phosphates of various compositions by sol–gel processing. It was also shown that, by varying the chemical composition of the framework compounds, it is possible to control the yield of the desired product in the production of environmentally friendly energy carriers (hydrogen, dimethyl ether).

The plenary lecture by K.D. Dosumov (Sokolsky Institute of Organic Catalysis and Electrochemistry, Almaty, Kazakhstan), entitled "Deactivation and Regeneration of Oxidation Catalysts," dealt with the role of sulfur dioxide in the deactivation of supported Pt and Pd catalysts, which are widely used in petroleum refining, neutralization of automotive and industrial toxic exhaust gases, etc. Use of a complex of physicochemical methods enabled the researchers to identify the sulfur dioxide adsorption species responsible for catalyst poisoning.

In their plenary lecture "Carbon Xerogels: Preparation, Properties, and Catalytic Applications," V.V. Molchanov, M.N. Shchuchkin, and N.A. Zaitseva (Boreskov Institute of Catalysis, Novosibirsk; All-Russia Research Institute of Experimental Physics, Russian Federal Nuclear Center, Sarov) suggested obtaining xerogels by carbonization of phenol formaldehyde resins prepared in a special way. The resulting xerogels possess unique properties and can be employed as catalysts for selective hydrogenation of acetylene and diene hydrocarbons into olefins and for selective methane chlorination and as adsorbents.

The plenary lecture by A.S. Ivanova (Boreskov Institute of Catalysis), "Physicochemical and Catalytic Properties of CeO₂-Based Systems," was devoted to the effect of synthetic conditions and the component nature and ratio on the phase composition, texture, and the redox and catalytic properties of complex cerium-containing systems. Promotion of cerium dioxide with zirconium, transition-metal, or rare-earth cations yields a cubic solid solution with a fluorite structure, whose stability depends on the synthetic procedure and treatment conditions. The introduction of these cations into cerium dioxide favors the formation of defects both on the surface and in the bulk. These defects enhance the mobility of oxygen and facilitate its diffusion in the fluorite lattice. The catalytic properties of the cerium-containing systems are due to the presence of anionic vacancies and the Ce⁴⁺ \rightleftharpoons Ce³⁺, M²ⁿ⁺ \rightleftharpoons Mⁿ⁺, and PM^{δ+} \longrightarrow PM⁰ conversions (M = transition metal; PM = Rh, Pd, Pt) occurring readily.

The plenary lecture by B.N. Kuznetsov (Institute of Chemistry and Chemical Technology, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk), entitled "Scientific Principles of Catalyst Selection for Deep Processing of Solid Fossil and Renewable Organic Raw Materials," demonstrated the possibility of employing catalysts in coal processing. The cata-

lysts in this application can be natural minerals, ores, and slags, which need not be recovered and regenerated because of their cheapness. The lecturer provided examples of successfully selecting catalysts for production of cellulose, monosaccharides, and levulinic acid and its derivatives.

A.A. Khassin (Boreskov Institute of Catalysis) delivered a key lecture entitled "New Approaches to the Preparation of High-Performance Oxide Catalysts from Metals: The Chemistry of the Processes." The lecturer summarized the latest advances in the preparation of some oxide catalysts having the desired cationic and phase compositions and meeting the environmental regulations. He suggested a new approach to obtaining iron and chromium precursors. This approach is based on the preparation of solutions of chromium(III) and nickel(II) or iron(III) and/or copper(II) nitrates using chromic anhydride, nickel metal (copper, cast iron), and nitric acid. The redox reaction occurring between, e.g., nickel metal and chromium(VI) in the presence of nitric acid yields a mixed solution of nickel and chromium nitrates. This provides a comparatively cheap, environmentally clean, and technologically convenient means of catalyst preparation.

In their key lecture entitled "Heteronuclear and Homonuclear Nanosized Clusters and Alloys from Molecular Complexes: A new Approach to the Synthesis of Catalytic Materials," I.I. Moiseev, M.N. Vargaftik, N.Yu. Kozitsyna, and S.E. Nefedov (Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow) suggested a new approach to the synthesis of bimetallic heterogeneous catalysts. This approach employs heteronuclear complexes in which one palladium atom and an "extra" metal are bonded by carboxylate bridges. Investigation of the thermolysis of supported and free complexes in a controlled atmosphere demonstrated that they are readily reducible between 150 and 250°C, yielding nanosized intermetallides, such as Pd–Zn and Pd–Co, or nanocomposites based on palladium and CeO₂. The possibility of obtaining a catalyst for acetylene hydrogenation into ethylene was also reported.

In his key lecture "State of the Art in the Manufacture of Petroleum Refining Catalysts in Russia," V.M. Kapustin (OAO VNIPIneft, Moscow) presented an in-depth analysis of the Russian market of petroleum refining catalysts. The lecturer noted that this market is dominated by foreign companies (for some processes, they supply 100% of the catalysts) and proposed creating a catalyst manufacturers association. He considered the ways of ousting foreign catalysts from the market and replacing them with domestic analogues. He noted also that petroleum refining catalysts are in very high demand in Russia. In addition, there is a shortage of cracking and hydrodesulfurization catalysts and interest in membrane and metal complex catalysts is shown.

The key lecture by A.V. Lavrenov and V.K. Duplyakin (Institute of Hydrocarbon Processing, Siberian Branch, Russian Academy of Sciences, Omsk), entitled “Solid Acid–Catalyzed Alkylation of Isobutane with Butenes: The Way from Understanding the Cause of the Rapid Deactivation of the Catalysts to Process Design,” was devoted to the deactivation processes occurring in isobutane alkylation with butenes. Sulfated zirconia was considered as the solid acid catalyst. It was found that various solid acid catalysts are deactivated in similar ways. Although researchers put great effort into optimization of the acidic and structural properties of catalysts, the problem of ensuring their stable performance remains unsolved.

The key lecture by N.A. Pakhomov (Boreskov Institute of Catalysis), “Fundamental and Applied Problem of Preparation and Use of Aluminum–Chromium Catalysts for the Dehydrogenation of Lower Paraffins,” dealt with the synthesis of chromium oxide catalysts for the dehydrogenation of lower paraffins. Although these catalysts have been extensively studied and used in industry for more than 70 years, the nature of the active component and active sites has not been elucidated. The lecturer presented a critical analysis of the studies of various states of supported chromium oxide and their role in the dehydrogenation reaction, and their changes during operation. He reported the main factors and parameters allowing the states of supported chromium oxide to be controlled and noted that the most significant role is played by the interaction between chromium oxide and the support.

In his plenary lecture “Scientific Foundations of the Preparation and Production of Reforming Catalysts: Development of Technology,” A.S. Belyi (Institute of Hydrocarbon Processing, Omsk) presented a systemic approach to the preparation of reforming catalysts, to the study of the structure of their active sites, and to catalyst design. Designing these catalysts includes synthesis of surface platinum compounds based on knowledge of the active site structure; optimization of the active component topography; optimization of the pore structure; optimization of the pellet shape, size, and mechanical strength; and development of a catalyst production technology. This approach enabled the researchers to design the PR catalyst series and to start the production of these catalysts at two catalyst plants in Angarsk and Ryazan.

In his key lecture “Deactivation of Catalysts in Heterogeneous Reactions under Supercritical Conditions,” V.I. Bogdan (Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow) reviewed the existing catalyst regeneration methods, which are mainly based on burning out the condensation products with atmospheric air at 500–700°C, and noted the drawbacks of these methods. In the reporter’s opinion, carrying out the heterogeneous reaction under supercritical conditions will ensure the regeneration of the catalyst *in situ* and, accordingly, its high activity and stability.

A.I. Boronin (Boreskov Institute of Catalysis) delivered a key lecture entitled “Mechanisms of Carbon Formation on the Surface of Platinum Interacting with Hydrocarbons,” in which he considered investigation of the nature of carbon deposits on the surface of platinum-containing catalysts and elucidation of the coking mechanism by advanced physical methods. A significant stage of coking is the condensation of an elementary carbon layer yielding various aggregated layers with a diamond-, graphite-, or fullerene-like structure. The formation of these structures is governed by a variety of factors, such as the orientation of the platinum surface, the nature of the hydrocarbon, temperature, and carbon segregation and diffusion in platinum.

The key lecture “Deactivation of Automotive Catalysts” by N.M. Danchenko and A.V. Porsin (Ural Electrochemical Integrated Plant) drew the attention of the audience to the fact that automotive catalysts typically operate between –30 and 1100°C and are exposed to catalyst poisons in the gas stream. These circumstances impose stringent requirements on the heat resistance and durability of the catalysts in addition to the toxic emission limits. Basic catalyst deactivation processes (sintering, poisoning, active site blocking) and the ways of solving the deactivation problem were considered.

The key lecture “Problems of Catalyst Deactivation in Aryl Halide Coupling Reactions” by A.F. Schmidt, A.A. Kurokhtina, A.N. Svechkarev, V.V. Smirnov, and A. Al-Halaiqa (Irkutsk State University and Irkutsk State Technical University) pointed out that the main obstacle to wide industrial use of aryl halide coupling reactions is the insufficient reactivity of the readily available aryl bromides and chlorides. This is commonly believed to be due to the agglomeration of the unstable complexes of zero-valence palladium. Another cause of catalyst deactivation is the formation of palladium halide complexes accompanied by palladium oxidation. Ways of improving the performance of homogeneous and heterogeneous catalytic systems were suggested for Heck and Suzuki reactions involving aryl chlorides and bromides.

There were two “round tables” in the framework of the conferences. The round-table meeting on the Results and Prospects of the Innovation-Oriented Competitions of the Russian Foundation for Basic Research was guided by Academician I.I. Moiseev (Kurnakov Institute of General and Inorganic Chemistry) and I.P. Tikhonov (Russian Foundation for Basic Research, RFBR). Participants could gain valuable information concerning project examination and financing. The chairmen of the round table drew the participants’ attention to typical drawbacks and mistakes that should be avoided when applying for a grant. It was noted that the RFBR competitions and RFBR purpose-oriented fundamental research projects had been of great importance for supporting of fundamental studies and promising R & D works. A suggestion

was made that the project financing in the framework of the RFBR competitions should be increased.

The round-table meetings on the Current State and Prospects of Russia's Catalyst Industry were guided by Doctor of Engineering, Professor A.S. Noskov (Boreskov Institute of Catalysis) and Doctor of Chemistry V.M. Kapustin (OAO VNIPINeft', Moscow). Brief reports were made by representatives of Russian enterprises and organizations manufacturing or consuming catalysts and by leading researchers whose R & D works are almost ready for commercialization. The following representatives of industrial enterprises and companies took an active part in the discussions: I.D. Reznichenko (Angarsk Catalyst and Organic Synthesis Plant), G.R. Kotel'nikov (Yarsintez Research Institute), O.V. Levin (Novokuibyshevsk Catalyst Plant), V.A. Tyshchenko (Srednevolzhskii Research Institute of Petroleum Refining), E.Z. Golosman (Novomoskovsk Institute of Nitrogen Industry), O.A. Parakhin (Altai Krai Clearing Agency), and A. Malyshev (Sasol Germany GmbH). N. Tolkachev (Russian Nanotechnology Corporation, Moscow) reported the outlooks for, and the requirements imposed on, the projects submitted for exami-

nation by the Corporation. He informed the audience of the science-and-technology and investment examination of projects. A number of possible joint projects involving catalyst developers and manufacturers were discussed at the around-table meetings and behind the scenes. The participant came to the agreement that it is necessary to hold regular consultations on the commercial products of the most important domestic catalysts.

Despite the heavy schedule of the forum, the participants had time for rest. The "velvet" season did not upset them by frequent rainfalls. They enjoyed a golden sandy beach, pure mountain air, and warm sea water, in which one could watch the fascinating swimming of a dolphin family early in the morning. There were interesting excursions to the dolphinarium and aqua park. After the conferences were closed, everyone was invited to make an interesting mini tour of the Black Sea Coast and Caucasus mountain masses.

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