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## Seventy-Five Years of the Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences

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The Institute of Petrochemical Synthesis was founded in 1934 as the Institute of Fossil Fuels (USSR Academy of Sciences) by merging the Institute of Sapropel (USSR Academy of Sciences) and the State Research Institute of Petroleum on the initiative and with active participation of the outstanding Russian scientists Academician Nikolai Dmitrievich Zelinskii and Academician Ivan Mikhailovich Gubkin. In 1948, the Institute of Fossil Fuels segregated the Institute of Petroleum (USSR Academy of Sciences). In 1958, the latter was reorganized into the Institute of Petrochemical Synthesis (IPS), USSR Academy of Sciences, under the guidance of Academician A.V. Topchiev.

The 75-year-long history of the IPS is inseparably associated with the names of many of the brilliant scientists that are the pride of Russian science. They include Academicians A.A. Balandin, S.S. Nametkin, A.V. Topchiev, V.A. Kargin, A.P. Krylov, S.I. Mironov, G.N. Flerov, and A.L. Chizhevskii and Corresponding Members M.I. Varentsov, M.A. Kapelyushnikov, M.F. Mirchink, S.F. Fedorov, and K.R. Chepikov. The following eminent scientists worked at the institute and created their scientific schools in later years: A.N. Bashkirov and K.P. Lavrovskii, corresponding members of the USSR Academy of Sciences and prominent petroleum chemists; the outstanding physical chemist A.V. Frost; Academician B.A. Dolgoplosk, the father of the Russian scientific school of metal complex catalysis and diene polymerization; Academician V.M. Gryaznov, the discoverer of membrane catalysis; and Academicians N.A. Plate and V.A. Kabanov, prominent macromolecular chemists.

As early as the 1930s, the institute, headed by Academician Zelinskii, the patriarch of Russian organic chemistry, carried out classical studies of the catalytic aromatization of paraffins. Professor Frost (1906–1952), who was head of the Laboratory of Kinetics and Catalysis, investigated both the formal kinetics of heterogeneous catalytic reactions (see the Frost equation) and a wide variety of catalytic reactions of hydrocarbons and alcohols, including gasoline synthesis from light hydrocarbons—a process that is still of commercial significance. The mechanisms and kinetics of catalytic reactions were of particular interest to Prof. Frost. Studies in this field at the institute were advanced by Corresponding Member A.N. Bashkirov and by Frost's followers Academician V.M. Gryaznov and Professor A.Ya. Rozovskii.

In 1946, Bashkirov founded the Laboratory of Synthetic Fuels (which was later renamed into the Laboratory of Catalytic Syntheses Based on Carbon Oxides). This laboratory carried out extensive studies of hydrocarbon oxidation, catalytic syntheses based on carbon oxides and hydrogen, the synthesis and conversion of nitrogen- and oxygen-containing organic compounds, and the metathesis of olefins and their functionalized derivatives. A specific feature of Bashkirov's school was that it combined in-depth fundamental studies with development of technologies for obtaining hydrocarbons and their functionalized derivatives.

Using a complex of chemical and physicochemical methods, Bashkirov's laboratory thoroughly studied the reactions taking place in the synthesis of organic compounds from carbon monoxide and hydrogen, the product formation sequence in this synthesis, the character and properties of the intermediates, the formation of an active surface, and the nature of catalysis on fused iron catalysts.

In Bashkirov's laboratory and, later, in the Laboratory of Kinetics of Catalytic Reactions, Prof. Rozovskii guided the investigation of the mechanisms, kinetics, and macrokinetics of catalytic reactions, primarily reactions of  $C_1$  compounds. The studies of the laboratory were focused on the development of the kinetic theory of catalytic reactions and construction of kinetic models for particular reactions (mechanism-based models). In some cases, this approach provided a reliable basis for process design.

Prof. Rozovskii and his colleagues suggested a new conception of the role of the medium in catalytic reactions and discovered the phenomenon of self-regulation in catalytic systems. Manifestations of this phenomenon were observed in a number of catalytic reactions, such as syntheses from CO and  $H_2$ , CO oxidation, alcohol sulfoesterification, and olefin hydroformylation. The theoretical advances and experimental data in this area provided a basis for the monograph *Katalizator i reaktsionnaya sreda* (Catalyst and Reaction Medium) by Rozovskii. The conception of self-regulation in catalysis was developed through studies in solid state chemistry and surface chemistry. These studies culminated in a theory of the kinetics and macrokinetics of reactions involving solids, which was presented in the monographs *Kinetika topokhimicheskikh reaktsii* (Kinetics of Topochemical Reactions) and *Geterogen-*

*nye khimicheskie reaktsii: Mekhanizm i makrokinetika* (Heterogeneous Chemical Reactions: Mechanism and Macrokinetics) by Rozovskii.

It was an interesting and unexpected fact that the studies of surface reactions changed the researchers' view of the possible routes of heterogeneous catalytic reactions. It turned out that strong chemisorption is not a "dead end" of catalysis, contrary to classical theory. Conversely, the formation and reactions of stable surface compounds and strongly chemisorbed reaction products take place within the main route of many catalytic reactions. The mechanism of these reactions was studied in greatest detail for methanol synthesis.

In recent years, the Laboratory of Kinetics of Catalytic Reactions has investigated the kinetics and mechanism of methanol dehydrogenation into methyl formate, steam methanol reforming, methanol decomposition into a  $\text{CO} + \text{H}_2$  mixture, dimethyl ether synthesis, selective CO oxidation in the presence of hydrogen and water, and other reactions. Based on these studies, the researchers developed a highly efficient single-step technology for dimethyl ether synthesis from synthesis gas and a process for methyl formate synthesis from methanol. Both processes are superior to the hitherto suggested analogues.

Prof. Rozovskii's laboratory in collaboration with the laboratories headed by Prof. E.V. Slivinskii and Academician S.N. Khadzhiev has developed an original technology for obtaining antiknock gasoline from synthesis gas via dimethyl ether. The researchers created a catalyst allowing ultimate gasoline to be obtained from dimethyl ether and/or methanol in 60–75% yield at  $T = 340^\circ\text{C}$ ,  $P = 10 \text{ MPa}$ , and  $\text{GHSV} = 2000 \text{ h}^{-1}$ . A dimethyl ether conversion of 98–99% was attained. The resulting gasoline has the following average composition (wt %): isoparaffins, 60–70; *n*-paraffins, 3–6; cyclic hydrocarbons, 5–10; aromatic hydrocarbons, 22–30. This gasoline has an octane rating (RON) of 90 or above. The catalyst was subjected to long-term testing in a dimethyl ether conversion pilot plant and showed high stability over a long time of at least 700 h.

The organization of the Laboratory of Petrochemical Processes in 1997 opened up a new research area in heterogeneous catalysis. Headed by Academician Khadzhiev, this laboratory performs active studies in the refining of heavy oil residuals on molybdenum catalysts, the synthesis of motor fuel components by isobutane alkylation with olefins on zeolites, and the catalytic conversion of heavy oil residuals and rubber industry waste into light hydrocarbon fractions for fuel applications. At present, this laboratory is merged with the Laboratory of Catalytic Syntheses Based on Carbon Oxides and Hydrocarbons.

Academician Khadzhiev's laboratory has designed a radically new process for deep petroleum refining, namely, the hydrotreating of black oil (atmospheric-pressure petroleum distillation residual) on nanosized

catalysts. The degree of desulfurization of the hydrogenation product in this process is above 50%. Research, process design, and engineering calculations have been carried out for the cracking of vacuum gas oil to maximize the yield of the diesel fraction. Base data have been obtained for design of diesel fraction catalytic cracking and hydrodeparaffinization units.

Systematic studies have been carried out in the thermochemical conversion of black oil into ethylene, and performance specifications for a pilot plant have been developed. This technology is based on the thermochemical initiation principle. A heat transfer medium in which combustion reactions are incomplete is obtained, and black oil is introduced into a stream of this medium, which has a high temperature and a large quantity of highly active ions, electrons, and radicals. As compared to the conventional processes, this process allows the methane and hydrogen yields to be reduced and affords the highest ethylene yield. The synthesis of metal silicate heterogeneous catalysts with a nanosized porous structure, including modified ZSM-5 zeolites, was investigated in order to carry out basic petrochemical reactions, such as ethylbenzene disproportionation. Petrochemical synthesis reactions are studied in three-phase systems in which one of the phases is nanosized. In particular, the laboratory addresses isobutane alkylation with olefins on heterogeneous catalysts in a three-phase system in a film reactor. Another concern of the laboratory is fast technologies for motor fuel production from basic petrochemical products and petroleum.

The 1960s were the years when membrane catalysis, a novel area of heterogeneous catalysis, was born in the IPS. Prof. V.M. Gryaznov, a pupil of Prof. A.V. Frost, unambiguously determined the mechanism of hydrogen redistribution in cycloolefins on metal catalysts. This mechanism has been the subject of debate for nearly half a century. In a later series of works, Gryaznov theoretically substantiated experimentally confirmed the thermodynamic, energetic, and kinetic advantages of combining catalytic reactions with selective introduction of withdrawal of one of the reactants through a membrane. Gryaznov and his colleagues discovered the phenomenon of reaction conjugation on membrane catalysts. The Laboratory of Membrane Catalysis comprehensively studied a wide variety of hydrogenation and dehydrogenation reactions on monolith and composite membrane catalysts based on palladium alloys, investigated the kinetics of these reactions, and designed unique catalytic membrane reactors.

Today, the studies in membrane catalysis and catalytic membrane reactors are guided by Academician G.F. Tereshchenko and include both search for new hydrogen-permeable alloys with a low palladium content and development of asymmetric composite membranes containing various nanostructures, including complex framework phosphates, low-dimensional

metal oxides introduced into pores of inert supports by molecular layering, and hydrophobic porous carbon films with immobilized nanosized particles of transition metals. The laboratory has designed a catalytic membrane module with palladized polypropylene hollow fibers for the reduction of oxygen dissolved in water with hydrogen. This economic efficiency of this technology is 40% higher than the efficiency of the other water degassing technologies.

The achievements of modern high technologies are also used in the Laboratory of Catalytic Nanotechnologies, headed by Prof. M.V. Tsodikov. This laboratory has laid the scientific foundations of the directed synthesis of ultrafine mixed-oxide materials from alkoxide, chelate, and other metal complex precursors. The structural sensitivity of these materials was studied in the liquid-phase oxidation of hydrocarbons, liquid-phase hydrogenation of the organic mass of brown coal into fuel components, and carbon dioxide and methane activation involving intermetallides. These studies revealed template coreactants capable of yielding structurally organized oxides under mild conditions ( $T = 350\text{--}400^\circ\text{C}$ ). Another basic research area of the laboratory is gas-phase catalytic reactions involving carbon dioxide in microchannels of porous ceramic membranes. Studies in this field demonstrated that, in the narrow pores of ceramic membranes, the direct oxidation and carbon dioxide reforming of methane proceed much more intensively. The same is true for the carbon dioxide reforming of the products of biomass conversion into hydrogen-containing gases.

The environmental works of the laboratory are aimed at obtaining highly active catalysts for the selective oxidation of hydrogen sulfide into sulfur, fast destruction of analogues of toxic pesticides and herbicides using hybrid technologies involving catalysis and microwave radiation.

In the late 1950s, the IPS successfully started research in metal complex catalysis. A large contribution to this research was made by studies of olefin, cycloolefin, and diene polymerization under the guidance of Academicians B.A. Dolgoplosk and V.A. Kabanov and Professors B.A. Krentsel' and V.V. Frolov.

Academician Dolgoplosk (1905–1994) and his colleagues suggested original stereospecific polymerization catalysts based on transition metal  $\pi$ -allyl complexes for. An analysis of extensive experimental

data concerning a multitude of homogeneous and heterogeneous catalytic reactions enabled Dolgoplosk to formulate a new conception of organometallic intermediates in heterogeneous catalysis. The essence of this conception is that the substrate is coordinated on the heterogeneous contact surface, which results in an organometallic compound, and this compound then decomposes into molecular products. This conception was corroborated by experimental data for deuterium exchange, self-hydrogenation, and other reactions.

In recent years, Prof. Frolov (1931–2006) and his colleagues have designed original binary catalysts for olefin and diene polymerization. These catalysts are titanium–magnesium or chromium-containing systems modified with nickel or zirconium oligodienyl complexes. The catalysts are extraordinarily active, thus providing way to significantly reduce the consumption of heavy metals and, accordingly, their discharge into the environment.

Academician Kabanov (1934–2006) and his colleagues studied gel-immobilized catalytic systems based on variable-valence metal complexes, a new class of metal complex catalysts, and suggested them for conversions of unsaturated hydrocarbons. These catalysts, which are very stable and can readily be separated from the reaction products, are of considerable interest to those concerned with the polymerization, oligomerization, and dimerization of lower olefins.

Thus, the IPS has carried out fruitful catalytic studies aimed at solving particular problems of petroleum chemistry and petroleum refining and has made a considerable contribution to the theory of catalysis. The results of these studies are widely known in Russia and abroad and have allowed the institute to rank high in the catalytic community. At present, the IPS, which belongs to the Division of Chemistry and Materials Science of the Russian Academy of Sciences, is a universally avowed scientific center in the fields of petroleum chemistry, petroleum refining, catalysis, polymer physics and chemistry, and membrane science and technology.

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