ISSN 0023-1584, Kinetics and Catalysis, 2011, Vol. 52, No. 3, pp. 467–469. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © Editorial Board, 2011, published in Kinetika i Kataliz, 2011, Vol. 52, No. 3, pp. 478–480.

Vladimir Borisovich Kazanskii (On the Occasion of His 80th Birth Anniversary)

DOI: 10.1134/S0023158411030116

On June 28, 2011, Vladimir Borisovich Kazanskii, Academician of the Russian Academy of Sciences, Editor-in-Chief of *Kinetika i Kataliz*, and Head of the Laboratory of Radio-Frequency Spectroscopic and Optical Methods of Investigation of Heterogeneous Catalysis Mechanisms at the Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, celebrated his 80th birthday.

Academician Kazanskii is a prominent scientist in catalysis, spectroscopy, quantum chemistry, and surface chemistry and physics. Kazanskii's main interest is in investigation of homogeneous and heterogeneous catalysis mechanisms by advanced spectroscopic techniques and quantum chemical calculations. He began studies in these areas as early as the late 1950s, when he worked at the Institute of Chemical Physics, USSR Academy of Sciences. At that time, the arsenal of spectroscopic methods was very poor and, as applied to catalysis, was practically limited to IR spectroscopy. The development of electron paramagnetic resonance (EPR) spectroscopy inspired Kazanskii and his colleagues to devote their first works to introduction of this method into catalysis science.

After Kazanskii moved to the Zelinsky Institute of Organic Chemistry in 1967, he got an opportunity to employ a much wider variety of spectroscopic methods, including EPR spectroscopy, luminescence, UV–vis diffuse reflectance spectroscopy, and NMR spectroscopy. Diffuse reflectance spectroscopy in a wide spectral range has proved to be most fruitful. In collaboration with Prof. G.M. Zhidomirov, Kazanskii launched quantum chemical calculations on the mechanisms of various catalytic reactions. These calculations were also used in in-depth interpretation of spectroscopic data and in the detailed investigation of the nature of Brønsted and Lewis acid sites in zeolites

and of the mechanism of hydrocarbon conversion over heterogeneous and homogeneous acid catalysts. These studies have given impetus to wide use of spectroscopic methods and quantum chemical calculations in catalysis science and have provided a much deeper insight into the structure of the surface of oxide catalysts, into the nature of active sites, and into the mechanism of acid and acid–base catalyses.

The works carried out by Kazanskii in the 1980s contributed greatly to the understanding of the nature of surface acidic hydroxyl groups. Based on spectroscopic data and quantum chemical calculations, he suggested a rational systematization of acidic hydroxyl groups, which provided explanation for the dependence of their strength on the aluminum content of the zeolite crystal lattice. Using zeolites as an example, he put forward the radically new idea that, in many Brønsted acid–catalyzed reactions important in practice, there is no complete charge separation with the formation of separate carbenium ions and their role in acid catalysis is played by strongly polarized transition states of complicated concerted transformations. This idea accounts for the fact that, in spite of the acid character of the catalytic reactions, the attempts to detect carbenium ions by spectroscopic methods have failed. The conception suggested by Kazanskii aroused a keen discussion in the scientific literature and initiated extensive quantum chemical calculations on the mechanisms of Brønsted acid–catalyzed reactions. These calculations have proved that, on the whole, Kazanskii's ideas are quite correct.

Another area of Kazanskii's interest is the locus of divalent cations in high-silica zeolites. These ions impart the zeolites uncommon catalytic properties in paraffin dehydrogenation, selective nitrogen oxide reduction with hydrocarbons, and selective hydrocarbon oxidation. These studies demonstrated the formation of spatially separated acid–base pairs in which the positive charge of the divalent cations is only partly counterbalanced; as a consequence, these cations acquire the properties of a Lewis superacid.

Kazanskii's studies of the nature of liquid superacids and the mechanisms of superacid-catalyzed reactions have gained general recognition. In these works, Kazanskii explained the paradox that anhydrous superacids are dissociated only to a very low extent and, dissociating to a higher extent in water, they become weaker. This paradox was explained by the fact that the energy of solvation of protons by superacid molecules is lower than the energy of their hydration and, accordingly, the dissociation of anhydrous superacids is less favorable than the dissociation of the same acids in water. At the same time, the lower energy of solvation makes the protons of anhydrous superacids more reactive, thus outbalancing their lower concentration. Application of these ideas to isoparaffin alkylation with olefins in anhydrous sulfuric acid suggested a new mechanism for this reaction.

In recent years, Kazanskii and his colleagues have proposed a new spectroscopic criterion for estimating the degree of activation of adsorbed molecules as a result of their polarization by active sites of acid–base catalysts. It has been demonstrated that, along with the low-frequency shift of stretching IR bands, another possible index of reactivity is the intensity of absorption bands, which is directly correlated with the polarization of the corresponding chemical bonds. The fruitfulness of this approach was demonstrted by observing stronger absorption bands for more acidic hydroxyl groups and by recording uncommon IR spectra for adsorbed hydrocarbons. For the heterolytic dissipative adsorption of a number of light alkanes on Lewis acid sites of high-silica zeolites with divalent metal cations, a direct correlation was established between the reactivity of the adsorbed alkane and the intensity of the stretching band of the activated C–H bond. This approach proved very efficient in the systematic investigation of the mechanism of catalytic dehydrogenation of light alkanes over Zn- and Ga-substituted ZSM-5 zeolites. It was demonstrated that the intensity of the absorption bands of adsorbed reactants are usable as a reactivity index not only in Lewis acid catalysis, but also in some other catalytic reactions. Examples of such reactions are olefin oligomerization and cyclopropane destruction, in which extraordinarily strong absorption bands were observed for composite vibrations of reactant molecules. The latter observation opens up a qualitatively new, promising way of investigating molecular rearrangements in concerted reactions.

The laboratory headed by Kazanskii has developed a process for catalytic hydrocarbon conversion under supercritical conditions in the absence of a solvent. Comparative studies demonstrated the advantages of *n*-butane isomerization into isobutane, isobutane alkylation with butylene, and butylene oligomerization under supercritical conditions over the same reactions conventionally carried out in the gas or liquid phase. Conducting these reactions under supercritical conditions increases the productivity of the catalyst and makes the active sites more resistant to poisoning by by-products.

Responding to the current challenge of introducing innovations into economy, Kazanskii has organized a photocatalysis group in his laboratory. The purpose of this group is to design and implement integrated photocatalytic systems for air cleaning in dwellings. The new group is guided by the fundamental ideas developed in the laboratory as to the mechanisms of acid–base, redox, and light-initiated catalytic reactions in oxide systems. The project aimed at expanding the production of these systems and at carrying out further studies in photocatalysis has been financially supported by RUSNANO Corp. since 2010.

Kazanskii is the author of over 800 scientific articles, reviews, and patents. Many of them were published in prestigious international journals. The results

obtained by Kazanskii and his colleagues have been reported at nearly all important international and national conferences on catalysis. At many of these forums, Kazanskii delivered a plenary lecture. His works are renowned throughout the world, as is clear from the fact that, for a number of years, he has been a member of the editorial boards of various international journals, including *Journal of Catalysis, Applied Catalysis, Microporous and Mesoporous Materials, Advances in Catalysis*, and *Catalysis Letters*. A great authority in science, Kazanskii has been given grants from the Soros Foundation, NWO (Netherlands), and CRDF (United States). Studies by Kazanskii have been supported by many grants from the Russian Foundation for Basic Research, Presidium of the Russian Academy of Sciences, and Council of the President of the Russian Federation for Leading Scientific Schools.

Over many years, Kazanskii has been successfully combining his research and educational activities. Over several years, he delivered lectures on physical chemistry at the Moscow Institute of Physics and Technology and at the Higher Chemical College of the Russian Academy of Sciences. He has been the supervisor of more than 30 candidate of sciences dissertations. Ten of his pupils have received a doctoral degree and are now successfully working in Russia or abroad.

Academician Kazanskii is still taking an active part in the scientific life of the Institute of Organic Chemistry and his laboratory.

Dear Vladimir Borisovich, the editorial board of *Kinetika i Kataliz* sincerely congratulate you on the occasion of your jubilee and wish you good health and further success in all of your activities.