

Academician Kazansky Is 75

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On June 28, 2006, Vladimir Borisovich Kazansky, a full member of the Russian Academy of Sciences, Editor-in-Chief of *Kinetika i Kataliz*, Head of the Laboratory of Microwave Spectroscopy and Optical Methods for Mechanistic Studies in Heterogeneous Catalysis at the Zelinskii Institute of Organic Chemistry, celebrated his 75th birthday.

Kazansky is an eminent researcher in the fields of catalysis, spectroscopy, quantum chemistry, and surface chemistry and physics. Kazansky's main interest is the investigation of homogeneous and heterogeneous catalysis mechanisms using modern spectroscopic methods and quantum chemical calculations. Studies in this area were begun at the Institute of Chemical Physics (USSR Academy of Sciences) as early as the late 1950s. At that time, the choice of spectroscopic methods was very poor and, as regards catalysis, was virtually limited to IR spectroscopy. However, EPR spectroscopy was making progress, and the first studies by Kazansky and his colleagues were aimed at introducing this method into catalytic research. Those studies were unique in the Soviet Union and were far ahead of related studies carried out abroad. They demonstrated the great potential of EPR spectroscopy in the characterization of bulk and supported oxide catalysts and in the study of the properties of adsorbed free radicals. For example, EPR spectroscopy enabled the researchers to detect, on an oxide surface, coordinatively unsaturated transition-metal ions, whose spectral parameters appeared to be sensitive to the adsorption of molecules. Adsorbed O_2^- and O^- radicals were detected on oxide surfaces and in supported systems.

After Kazansky's laboratory was moved to the Zelinskii Institute of Organic Chemistry in 1967, the scientist gained access to a much wider variety of spectroscopic methods, including luminescence, UV–vis diffuse-reflectance spectroscopy, and NMR along with EPR. Diffuse-reflectance IR spectroscopy in a wide spectral range appeared to be the most fruitful. In collaboration with Prof. G.M. Zhidomirov, Kazansky took up quantum chemical calculations for the mechanism of various catalytic reactions. These calculations were also used to get a more profound interpretation of spectroscopic data. Thorough investigation was given to the nature of Brønsted and Lewis acid sites in zeolites and to the mechanisms of the catalytic conversion of hydrocarbons on heterogeneous and homogeneous acid catalysts. This investigation stimulated the wide use of spectroscopic techniques and quantum chemical



calculations in catalytic research. Furthermore, it provided a much deeper insight in the surface structure of oxide catalysts, in the nature of active sites, and in the mechanism of the acid and acid–base homogeneous catalysis.

In the 1980s, Kazansky contributed greatly to the understanding of the nature of surface acid hydroxyl groups. His inference that these groups are covalently bonded has gained universal acceptance. Based on spectroscopic data and quantum chemical calculations, he suggested a rational systematization of acid hydroxyl groups that explained the dependence of the strength of these groups on the aluminum content of the zeolite lattice. A spectroscopic study of proton transfer from a Brønsted acid site to an adsorbed olefin molecule has demonstrated that, contrary to earlier assumptions, the coordinate of this elementary step is not simply the elongation of one O–H bond. Rather, it is related to a concerted reorganization of many chemical bonds, including changes in the geometry of adsorbed olefin molecules. This deduction has been confirmed by quantum chemical calculations, which have provided a new

understanding of the nature of adsorbed alkylcarbenium ions.

One of Kazansky's current concerns is the location of divalent cations in high-silica zeolites. It is these cations that are responsible for the specific catalytic properties of the zeolites in paraffin dehydrogenation, in the selective reduction of nitrogen oxides with hydrogen, and in the selective oxidation of hydrocarbons. Kazansky's studies have proved the formation of spatially separated acid-base pairs in which the positive charge of the divalent cation is compensated only in part. As a consequence, these cations acquire the properties of Lewis superacids.

Kazansky's studies on the nature of liquid superacids and on the mechanism of acid catalysis involving these superacids have won universal recognition. These studies were first to explain the paradox that anhydrous superacids are dissociated only to a very small extent, while their aqueous counterparts are dissociated to a larger extent and are weaker at the same time. This paradox is explained by the fact that the proton solvation energy is lower for the superacids than for water and, therefore, superacid dissociation is more favorable in an aqueous solution. On the other hand, due to a lower solvation energy, the protons of the anhydrous superacids are so reactive that their lower concentration is overcompensated. The development of these conceptions has suggested a new mechanism for the alkylation of isoparaffins with olefins in anhydrous sulfuric acid.

Kazansky has recently advanced a new spectroscopic criterion for evaluating the extent of activation of adsorbed molecules due to their polarization by active sites of acid-base catalysts. It is suggested to use, as a reactivity index, not only the bathochromic shift of stretching IR bands but also the intensities of these bands, which are directly related to the polarization of the corresponding chemical bonds. The efficiency of this approach has been proved by the fact that the higher the acidity of the hydroxyl group, the stronger the corresponding absorption band, and that adsorbed olefin molecules give rise to unusual IR spectra.

Kazansky's team has developed a procedure for catalytic hydrocarbon conversion under supercritical conditions in the absence of a solvent. Comparative studies of *n*-butane isomerization into isobutane, isobutane alkylation with butene, and butene oligomerization have highlighted the advantages of supercritical reactions over ordinary gas- and liquid-phase reactions. Under supercritical conditions, catalysts are more productive and function longer than they do in the same reactions in the gas phase.

Kazansky is the author of more than 650 scientific articles, reviews, and patents. About 200 of these have been published in international journals. He has made reports at all of the most important international and national conferences on catalysis and has delivered plenary lectures at many of them. His works have received international recognition, as is evident from the fact that, for several years, he was on the editorial board of *Journal of Catalysis*, *Applied Catalysis*, *Microporous and Mesoporous Materials*, and *Advances in Catalysis*. Today, he sits on the editorial board of *Catalysis Letters*. Kazansky is a scientist of worldwide reputation: his studies have been supported by grants from various foundations, including ISF, NWO (the Netherlands), and CRDF (the United States), the Russian Foundation for Basic Research, and the RF President's Support to Leading Scientific Schools Program.

Kazansky successfully combines research and educational activities. For several years, he delivered lectures on physical chemistry and catalysis at the Moscow Institute of Physics and Technology. At present, he heads the Department of Physical Chemistry and lectures on catalysis at the Higher Chemical College, Russian Academy of Sciences. He has been the supervisor of more than 25 candidate of sciences dissertations, and eight of his followers has won a doctoral degree.

Kazansky is now at the peak of his powers and is energetically putting his ideas into effect. The editorial board of *Kinetika i Kataliz* (*Kinetics and Catalysis*) heartily congratulates V. Kazansky on his birthday and wishes him good health and every success in his activities.