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FTIR spectroscopy for the studies of catalysts and catalytic reaction mechanisms

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IR spectroscopy became a classical method of solid catalysts characterization. The paper deals with the advances in the studies of mechanisms, establishing the structure of intermediates and the nature of active sites of the reactions catalyzed by oxides and zeolites using FTIR spectroscopy at variable temperatures. Variable temperature spectroscopy broadens the number of test molecules for acid sites. At low temperatures, besides ammonia, pyridine and nitriles, we can use CO, NO, H₂ or other molecules that do not adsorb at 300 K. Low-temperature adsorption of weak CH proton-donating molecules such as CHF₃, enables one to characterize the basicity of surface electron-donating sites. Carrying out simultaneous measurements of spectra, pressure and temperatures one can obtain thermodynamic characteristics of surface species, while spectrokinetic data provide information about the height of activation barriers. To trap the unstable intermediates of catalytic reaction, we can follow spectra evolution with temperature and observe the chain of reactant transformations. In particular, the method can be applied to the studies of photocatalytic reactions, modeling the processes at the surface of atmospheric aerosol particles. The structure of intermediates can be clarified using isotopic substitution and finally the detailed mechanism of catalytic processes could be established. Some adsorption products, however, cannot be stabilized at low temperatures, but arise at the surface as a result of thermal excitation. So, CO forms, with the cations in zeolites, two kinds of complexes. Besides the usual C-bonded structure the energetically less favorable O-bonded species arise and exist in thermodynamic equilibrium with usual form. These species have the excess of energy and can be considered as an activated state, which can play a role of intermediate in catalytic reactions. Surface isomeric states were established for some other adsorbed species, such as cyanide ion CN⁻ produced by HCN dissociation. The linkage isomerism can be explained by an electrostatic model, or quantum mechanical calculations. The strength of surface sites can be affected by lateral interactions between the adsorbed species, which modifies the catalytic properties of solids and shift the bands of test molecules, distorting the data on surface acidity. Co-adsorption of acidic and basic molecules leads to mutual enhancement of adsorption. This can be evidenced by protonation of bases, such as NH₃ or 2, 5-dimethylpyridine (DMP) on silanol groups in the presence of SO₂ or NO₂. This effect suggests an explanation of the promoting action of these gases in the reactions catalyzed by Brønsted sites. Besides the above effect of induced Brønsted acidity, induced basicity in the presence of adsorbed bases has also been detected spectroscopically. Lewis acidity can also be influenced by adsorbed acidic molecules. This effect was illustrated by CO adsorption on CaO pre-exposed to CO₂, SO₂, SO₃, showing higher electron accepting ability of salts as compared with oxides. It is consistent with superacidity of oxides doped with (SO₄)²⁻ and explains much higher Lewis acidity of cationic sites in zeolites than that of oxides of the same elements. Quantitative spectral analysis of surface sites is not possible without the knowledge of absorption coefficients of test molecules. Quantum chemical calculations and electrostatic approach predict the correlation between the frequency shifts on adsorption and the absorption coefficients, in a fair agreement with the published data on CO adsorption on ionic surfaces.

Biography

Alexey Tsyganenko is currently working as Full Professor of Physical Faculty of St. Petersburg State University and graduated from the same university in 1971. Since then, he worked at the same faculty, got his PhD in Molecular Physics in 1975 and gave lectures on molecular spectroscopy, adsorption and catalysis. From 1983, he is the Head of the research group of Infrared Spectroscopy in the Department of Photonics of V.A. Fock Research Institute of Physics. He supervised 7 PhD works defended in Russia and two more in France. He participated at many international conferences in a dozen of countries and plenty in the former USSR. He gave lectures at the universities and scientific centers in the native country and abroad. In 1987, and later, he worked in the University of Caen, France as an Investigator or as Invited Professor. He participated in scientific researches in the Universities of Hamburg, Germany, Delft, Netherlands, the Balear Islands, Palma, Spain and Helsinki, Finland. In 2006, he served as Chairman of the Organizing Committee of International Symposium of Molecular Photonics, St. Petersburg from June 28th to July 2nd. His whole list of publications include more than 110 scientific papers in scientific journals. His main field of scientific activity is spectroscopy of surface species, adsorbed molecules and mechanism of surface reactions. He contributed to the spectral studies of hydroxyl cover of oxides, acidic and basic sites of catalysts, lateral interaction between the adsorbed molecules and linkage isomerism of adsorbed species. He developed the methods of low temperature spectroscopy of dispersed ice or ozone adsorbed on solid surfaces, photocatalytic processes and technique of quantitative surface site characterization by the spectra of test molecules.

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