Ultraviolet Spectroscopic Study of Interaction of Aromatic Molecules with Cationized and Decationized Zeolites

A. V. Kees'yel'yov, L. A. Koopcha, and V. I. Ligeen

Chemistry Department of M. V. Lomonosov State University of the City of Moscow

The spectra of aromatic hydrocarbons adsorbed on cationized NaX- and decationized Y-zeolites were studied by the ultraviolet spectroscopy. The spectra of the following aromatics were investigated: benzene, toluene, phenol, aniline, pyridene, and nitrobenzene. The directional consistency of the spectral shifts and the relatively small differences in the shift magnitudes, which are observed with the aromatics adsorbed on the hydroxylated aerosils and the cationized zeolites, point to similarity of the nature of interaction of the aromatics with the hydroxyl groups of the aerosils and with the exchangeable cations of the zeolites. The changes in the spectra of the molecules containing the oxygen and nitrogen atoms with free electron pairs indicate weakening of the bond between the π-electrons of the aromatic ring and the free electron pairs. The adsorption on decationized Y-zeolites results in the formation of coordination-bonded molecules and ions on the surface. Irradiation by ultraviolet light accelerates this process.

Optical and EPR Spectral Studies of Structure of the Adsorption Centers of Chromia-Alumina Catalysts

V. A. Shv'yetz and V. B. Kazansky

Institute of Chemical Physics of the Academy of Sciences of USSR

The surface structures of supported chromia-alumina catalysts were determined by means of EPR and reflected optical spectroscopy techniques. The results show that surface of the catalysts pretreated at high water-desorption temperatures contains coordination-unsaturated Cr^{+3} ions in the square-pyramidal coordination arrangement with Symmetry C_{4v}. These ions produce characteristic optical spectra and are the active sites for adsorption of water, methanol, and ammonia.

The Secondary Ion-Ion Emission Studies of Ammonia Decomposition Over an Iron Catalyst

V. I. Shvachko and Ya. M. Fog'yel'

A. M. Gor'ky State University of the City Khar'kov

The results of secondary ion-ion emission studies of ammonia decomposition over a pure iron catalyst show that the decomposition occurs only when the catalyst surface is free from the iron oxide impurities. Based on the experimental data, a mechanism is proposed to describe the process of ammonia decomposition over the iron catalyst. The hypothesized reaction mechanism is completely identical with that of NH_3 decomposition over a platinum catalyst, which was described in an earlier paper.

Radiative Chemisorption of Oxygen on γ-Al_2O_3

Yu. A. Kolbanovsky and M. N. Mast'yerova

Institute for Petrochemical Synthesis of the Academy of Sciences of USSR

A study of kinetics of radiative chemisorption of oxygen on γ-Al_2O_3 was carried out at a temperature of 20°. The results show that the initial reaction rate is independent of the oxygen pressure. A simple scheme is proposed to describe the chemisorption process. The irradiation-chemical yield of the adsorption centers was determined to be 4 per 100 ev and the ratio of the chemisorption rate constant to that of the rate of extinction of the active centers was found to be $(3.66 \pm 0.26)(10^{-16})$ cm^3.

BRIEF COMMUNICATIONS

Reactions of Atomic Hydrogen in an $H_2O + H_2SO_4 + FeSO_4$ System: The Reactions with Saturated Organic Compounds

N. M. Bajeen, E. V. Koozn'yetzov, N. N. Boobnov, and V. V. Voyevodsky

Institute of Chemical Kinetics and Combustion of the Siberian Division of the Academy of Sciences of USSR

The EPR studies of reaction of atomic hydrogen with molecules of alcohols and organic acids were made at temperatures near 90°K. The results show that atoms of the atomic hydrogen can abstract hydrogen atoms from the alcohol and organic acid molecules, with resulting formation of the corresponding radicals.

Behavior of Metal Oxide Additives in Thermal Decomposition of Ammonia Perchlorate

A. V. Boldir'yeva and V. N. Mozjova

Institute of Chemical Kinetics and Combustion of the Siberian Division of the Academy of Sciences of USSR

The micro-thermoreactor studies of ammonia perchlorate decomposition in the presence of admixtures of CdO, ZnO, and PbO (1–5% by wt) were carried out at a temperature of 300°, with concurrent recording of the infrared spectra. The results disclose the presence of chemical interaction of the components of the mixtures studied.

Kinetics of Disproportionation of Dimethyl Dioxymethyleneglycol Ether

V. V. Eevanov, V. P. Volkov,
V. N. Eevanov, and N. S. Yeneekolop'yan
Institute of Chemical Physics of the Academy of Sciences of USSR

A study of the disproportionation kinetics of dimethyl dioxymethyleneglycol ether was made, using etherate of boron trifluoride as the catalyst. Calculations of the reaction kinetics were based on the scheme analogous to that used in determination of the kinetics of chain continuation-chain interruption processes.

Effect of Fluorination on Acidity of Aluminum Oxide

V. A. Tchernov and T. V. Anteepeena
Chemistry Department of M. V. Lomonosov State University of the City of Moscow

Acidity of "pure" and fluorided aluminum oxide was determined by: titration with n-butylamine in the presence of Hammett indicators; thermometric titration with ethylacetate; high-temperature adsorption of vaporized organic bases. The results show that the samples of unpromoted and promoted aluminum oxide have closely similar properties.

Pretreatment of Al_2O_3 with boron fluoride and with hydrogen fluoride produces no noticeable increase in the acid strength of the surface sites, but it is accompanied by the formation of new relatively weak centers. These centers, apparently of a different chemical nature, catalyze cracking and isomerization reactions.

Oxygen-Initiated Heterogeneous Catalytic Condensation of Olefins in the Presence of Hydrogen: Conversion of Pentene-2

Ya. T. Eidoos, N. I. Yershov,
and V. R. Yerokheena
N. D. Z'yeleensky Institute of Organic Chemistry of the Academy of Sciences of USSR

The results of hydrogenation of pentene-2 over a precipitated Co/clay catalyst at a temperature of 100° show that the reactant hydropolymerizes to the hydrocarbons of C_8, C_9, and higher carbon number. In the absence of oxygen, the polymer yields of up to 24% are realized, based on the olefin charge; in the presence of 1.3% of added oxygen the yields of up to 30% are obtained, on the same basis. Increasing the operating temperature to 190°, decreases the product yields to as low as 5%. In the absence of hydrogen, polymerization of pentene-2 at a temperature of 100° does not occur.

Influence of the Conditions of Cooling of a Nickel-Alumina Alloy on Activity of the Skeletal Nickel Catalyst Produced

A. B. Fasman, T. Kabyeeyev,
D. V. Sokol'sky, and G. A. Pooshkar'yova
S. M. Keerov State University of the Kazakh SSR

Activity of skeletal nickel catalysts is dependent in a complex way upon the pretreatment temperature, duration of the pretreatment, and the rate of cooling of the Ni-Al alloy, the starting material. The catalyst with the greatest activity for the hydrogenation-in-solvents reactions is produced by crystallization of the alloy at nonequilibrium conditions. The nature of the active centers of the catalyst is not altered by changes in the crystallization conditions.

Effect of High Frequency Currents on Kinetics of Catalyzed Synthesis of Ammonia

M. V. Tovbeen and T. P. Kozlova
T. G. Shevchenko State University of the City of Keeyev

The experimental data of the effect of high frequency currents on catalytic synthesis of ammonia show that (a) High frequency currents do not alter performance of the iron catalyst used; and (b) Activity of the catalyst is significantly increased at temperatures of 300°–350°, the effect increasing with increasing frequency of the current.

Catalytic Activity of Aluminum Oxide and Acidic Properties of Its Surface

E. N. Rosolovskaya, O. L. Shakhnovskaya,
and K. V. Topcheeyeva
Chemistry Department of M. V. Lomonosov State University of the City of Moscow

The effect of the degree of dehydration of aluminum oxide on its activity was determined in isomerization of allylbenzene to propenylbenzene at a temperature of 300°. Acidic properties of the catalyst surface were determined concurrently by titration with butylamine containing different Hammett indicators and by adsorption of butylamine at high temperatures. In the double-bond shift reactions, properties of the acidic and catalytic centers are identical. A comparison of properties of the acidic and catalytic centers indicates