Oxidation of Naphthalene Over Vanadium Catalysts

V. Ya. Vol'fson and L. N. Gan'yuk

L. V. Peesarjevsky Institute of Physical Chemistry of the Academy of Sciences of Ukrainian SSR

A comparison of catalytic activities, chemical compositions, and EPR spectra of different vanadium catalysts shows that selectivity of the so-called complex Vd—K—SO_4-silica gel catalyst for oxidation of naphthalene to phthalic anhydride is improved when in addition to the lower oxides of vanadium it also contains vanadyl sulfate. The latter may be present in the catalyst either as a solid dilute solution or as a distinct solid phase. The effect of either form on catalytic activity is practically the same. The roles of potassium sulfate and of different carriers were determined to optimize activity and selectivity of the catalysts.

Activity Change of an Aluminum-Chromium Catalyst in Dehydrogenation of Butane

M. N. Shendreek, G. K. Bor'yeskov, and L. V. Keereel'yuk

State Institute for Synthetic Rubber Industry.
Institute of Catalysis of Siberian Division of the Academy of Sciences of USSR

A study of activity of an aluminum-chromium catalyst to dehydrogenate butane was made in a recycle-continuous unit, using a moving pseudo-fluidized catalyst bed. Initially, activity of the catalyst increases, reaching the maximum after 3–12 minutes; thereafter, the activity decreases, the rate of decrease being proportional to the space velocity. The low activity during the initial few minutes of operation is due to the presence in the catalyst of CrO_3 and of oxygen-containing compounds, which are formed in the course of its reduction. The decrease in activity following the point of peak activity is due to accumulation of carbonaceous deposits. The rate of carbon laydown decreases with increasing rate of butane conversion.

A Combined Radio-Chromatographic Method to Investigate Mechanism of Heterogeneous Catalytic Reactions

E. I. S'yem'yen'yenko, S. Z. Rog'eensky, and M. I. Yanovsky

Institute of Chemical Physics of the Academy of Sciences of USSR

A combined radio-chromatographic analytical method is described to study the mechanism of heterogeneous catalytic reactions. The method includes the use of a microcatalytic synthesis of tagged and non-tagged compounds (in mg amounts) and of a pulsed method to inject them into the catalytic reactor.

The outstanding features of the method are its rapidity, requirement of relatively small amounts of catalysts and charge stocks, and convenience to obtain a large number of compounds. As is well known, synthesis of these compounds by usual techniques presents appreciable difficulties.

Usefulness of this novel method to determine reaction mechanisms is illustrated by the case of dehydrogenation and isomerization of butylenes to divinyl.

Brief Communications

Kinetics of Destruction of Free Radicals by Ionizing Radiation

L. A. Teekhomeerov and N. Ya. Booben

Institute of Chemical Physics of the Academy of Sciences of USSR

EPR studies were made of the kinetics of decrease of paramagnetic particles in irradiation with fast electrons of stable radicals, such as 2,2,6,6-tetramethylpiperidine of nitric oxide. The results show that the destruction of the radicals is a first order reaction, with the reaction rate proportional to the dosage. At temperatures of 100°–300°K, the values of k increase with increase in the activation energy of 0.4 kcal/mol.

Multi-Step Super-Fast Reactions of Amines with Chloroanhydrides

S. G. Ent'yelees, E. Yu. B'yekhly, and O. V. N'yest'yerov

Institute of Chemical Physics of the Academy of Sciences of USSR

Thermometric measurements in continuous flow systems were employed to study the kinetics of interaction of different mono- and bifunctional amines with chloroanhydrides. These studies covered reactions at a temperature of 20° in homogeneous (heptane) and in near-heterogeneous (heptane-water) phases. The results show that the reactions studied occur in several steps. The rate constant values of the final, the slowest, reaction steps are 10^4–10^5 l/mol × sec.

Kinetics of Heterogeneous Catalytic Reactions Retarded by Side-Reaction Intermediates

J. J. Yoffé, L. S. Kamen'yeva, and V. A. Slaveenskaya

Scientific Research Institute of Organic Intermediates and Dyes.
Institute of Organic Synthesis of the Academy of Sciences of Latvian SSR

This paper describes a study of kinetics of heterogeneous catalytic reactions which are being retarded by intermediate products of the side-reactions. A differential kinetic equation is presented; it was developed for the reactions of this type by assuming steady-state conditions. Usefulness of electronic computers to solve this equation is illustrated for the case of oxidation of furfural to maleic anhydride.

Regenerability of Palladium-Polyvinyl Alcohol Catalyst

O. A. T'YUR'YENKOVA AND V. V. BONDAR'YUK
Farm Institute of the City of Koorgansk

The studies of regenerability and activation of a colloidal palladium-polyvinyl alcohol catalyst involved its precipitation with ethyl alcohol and dissolution of the precipitate in water.

The rate of allyl alcohol hydration over the regenerated catalyst is doubled compared to the fresh catalyst. Each fresh catalyst charge can be advantageously regenerated three times. However, beginning with the fourth regeneration the activity progressively decreases.

Chemisorption of Nitrogen and Hydrogen on Iron Catalysts Used in Ammonia Synthesis

R. B. CHESNOKOVA, A. I. GORBOONOVA, S. S. LACHEENOV, G. K. MOORAVSKAYA, AND G. A. ERDEDEE
Scientific Research Institute for Nitrogen Industry

Adsorption of nitrogen and hydrogen at respective temperatures of 475° and 200° was studied, using promoted and unpromoted iron catalysts. For systems in equilibrium at a wide range of pressures, the catalysts studied have similar specific chemisorptive capacity for nitrogen and hydrogen.

Catalytic Properties of Germanium Metal Films Formed by Pyrolysis of GeH_4

V. M. FROLOV
Institute of Chemical Physics of the Academy of Sciences of USSR

A study of dehydrogenation kinetics of ethanol was carried out over germanium metal films produced by thermal decomposition of GeH_4 on powdered quartz. The activation energy of dehydrogenation of about 10 kcal/mol exceeds that for powdered germanium metal, which has its own inherent conductivity. At a temperature of 235°, specific catalytic activity of the film is about one fourth that of the powdered metal. Variation of electrical resistance of the film with temperature was also established. At temperatures of 150°–250°, the electroconductance activation energy is 0.30–0.38 ev.

Chemistry of Conversion of Alkylphenyl Esters at High Temperatures and Pressures

B. V. TRDJETZKAYA AND J. V. KAL'YECHEETZ
Institute for Coal- and Petrochemical Synthesis of the City of Angarsk

The compositions of typical products were determined in high temperature and pressure liquid phase hydrogenation of alkyl-phenyl esters over an iron catalyst. The schemes to interpret the reactions assume a radical interaction mechanism.

Kinetics of Ammonia Synthesis Over a Steam-Poisoned Iron Catalyst Promoted with Al_2O_3

I. A. SMEERNOV, N. M. MOROZOV, AND M. I. T'YOMKEEN
L. Ya. Karpov Physico-Chemical Institute

Applicability of the kinetic equation describing ammonia synthesis over a reversibly steam-poisoned iron catalyst was determined when the catalyst used in the synthesis is promoted by Al_2O_3.

Effect of Thermal Pretreatment on Porosity of a Vanadium Catalyst

E. I. DOBKEENA, V. I. D'YER'YUJKEENA, AND I. P. MOOKHL'YENOV
Lensoviet Technological Institute of the City of Leningrad

The pore radii of a physically-rugged vanadium catalyst for use in oxidation of sulfur dioxide are a function of thermal pretreatment temperatures, the pore-size increasing with the temperature. The catalyst with the optimum pore radius of 1,000 A is produced at the pretreatment temperatures of 500°–600°.

A Nickel-Titanium Hydrogenation Catalyst

N. K. NADEEROV
Pedagogical Institute of the City of Khabarovsk

Experimental results demonstrate that titanium dioxide to support nickel formate catalyst is not an inert base but is an active catalytic component. Activity of the titanium dioxide-based catalyst is superior to the nickel formate catalyst now in industrial use.