

than the energies of the same reactions in liquid phase. This difference is ascribed to specificity of the solid phase reactions, where mobility of the particles is greatly inhibited.

Radio-Chemical Decomposition of KClO_4

A. V. DOOSVEETZKY, G. B. MAN'YELEES

A Division of the Institute of Chemical Physics of the Academy of Sciences of USSR

EPR studies were made of the nature of the paramagnetic centers which are produced in potassium perchlorate by exposure to ionizing radiation at a temperature of 77–450°K. The kinetics of accumulation and recombination of the paramagnetic centers at these temperatures were also investigated. The results show that recombination of ClO_2 and O_3^- radicals is a reaction of second order.

Isotopic Oxygen Exchange Over Neodymium Oxide with Different Crystal Structures

L. A. SAZONOV, A. N. RATOV, T. G. RATOVA

Institute of Catalysis of Siberian Division of the Academy of Sciences of USSR

The study of isotopic oxygen exchange was made at temperatures of 300°–500° over neodymium oxides with cubic, hexagonal, and cubic-hexagonal crystal structures. The study also covered the exchange of isotopic oxygen with the oxygen of the hexagonal-form oxide.

Activity of the oxides in isotopic oxygen exchange was found to depend on the history of their pretreatment in vacuum and in oxygen atmosphere. The crystal structure of the oxides shows no effect on their activity.

Activation energy of the isotopic oxygen exchange reaction is 30 kcal/mol and that of the exchange of isotopic oxygen with the oxide oxygen is 20 kcal/mol.

Nature of Surface Defects of Irradiated Silica Gel: Catalytic Properties of Irradiated Silica Gel in Isotopic Hydrogen-Deuterium Exchange

YU. A. MEESHCHENKO, G. K. BOR'YESKOV

L. Ya. Karpov Physico-Chemical Institute

Catalytic activity of irradiated silica gel was evaluated in an isotopic hydrogen-deuterium exchange reaction. The apparent energy of activation and order of the reaction were determined on the mixture partition basis. The results show that activity of the samples studied is greatly affected by the admixed aluminum concentration and by

the activation and irradiation conditions. A faster method of activation was developed by tempering the samples in hydrogen atmosphere as compared to the activation by tempering in vacuum. A relationship exists between changes in the catalytic activity and the corresponding changes in the adsorption capacity for hydrogen; a relationship also exists between changes in the intensity of the sextet signals of the EPR spectra and the corresponding changes in (a) the aluminum content of the samples, (b) the conditions of activation and irradiation, and (c) the conditions of calcination in vacuum and in hydrogen media. It is concluded that in the irradiated silica gel, the "tinted" surface centers, due to the admixed aluminum, are the active centers catalyzing isotopic exchange of molecular hydrogen and adsorption of hydrogen.

Catalytic Properties of Chelated Polymers with bis-Thioamides of Quinaldine as the Carriers

N. P. KAYER, E. K. MAMAYEVA, G. M. ALEE-KEENA, L. I. T'YUL'YEN'YEVA, S. M. AFANAS'YEVA

Institute of Catalysis of Siberian Division of the Academy of Sciences of USSR

Catalytic properties of chelated polymers were investigated, using bis-thioamides of quinaldine and salts of the transition metals as the carriers. The effect of the metals and of the chain radicals on catalytic properties of the polymers was evaluated in oxidation of cumene. The results show that catalytic properties of the polymers and the reaction course are defined by the changes in electronic density on the sequestered metal and on the ligand.

Electronic Spacial and Surface Properties of Zinc Oxide

A. V. KRILOVA, L. YA. MARGOLEES, G. I. TCHEEJEEKOVA

Institute of Chemical Physics of the Academy of Sciences of USSR

The electronic work function, electroconductivity, and oxygen adsorption capacity of pure and modified zinc oxide were determined, using samples calcined at temperatures of 500°, 900°, and 1,300°. The results show that the electrophysical and adsorptive properties of the semiconductor are significantly affected by the preparation history. Depending on the pretreatment history, electroconductivity of the samples is either in direct or in inverse relationship with the electronic work function. A relationship was also established between the oxygen adsorption capac-

ity of the semiconductor and the intensity of its electrical surface charge.

Catalytic Properties of Metal Oxides of the IV-th Period of the Periodic Table in Oxidation Reactions: Oxidation of Methane

T. V. ANDROUSHK'YEVEETCH, V. V. POPOVSKY,
G. K. BOR'YESKOV

*Institute of Catalysis of Siberian Division
of the Academy of Sciences of USSR*

Catalytic activity of TiO_2 , V_2O_5 , Cr_2O_3 , MnO_2 , Fe_2O_3 , Co_3O_4 , NiO , CuO , and ZnO was determined in complete oxidation of methane in a recycle-continuous system. A temperature-reaction rate correlation and the order of the reaction with respect to methane were determined.

Study of Chromium Oxide—Oxygen System by Infrared Spectroscopy

D. M. SHOPOV, A. N. PALAZOV

*Institute of Organic Chemistry of Bulgarian
Academy of Sciences, Sophia, Bulgaria*

A study of the infrared spectra of a chromium oxide-oxygen system at different temperatures shows that interaction of the oxide with oxygen leads to formation of individual compounds on the surface and in the adjacent underlying layers. Chromic anhydride and a product of its thermal decomposition were identified. Based on the spectral analyses, thermal preactivation with hydrogen does not result in formation of a new solid phase on the chromium oxide surface.

Kinetics of Dehydrogenation of Cyclohexane in a Non-Gradient System

A. A. ANDREI'YEV, S. L. KEEPERMAN

*N. D. Z'yeleensky Institute of Organic Chemistry
of the Academy of Sciences of USSR*

Using a recycle-continuous unit, kinetic data were obtained in dehydrogenation of cyclohexane over a nickel catalyst on zinc oxide carrier at the far-from-equilibrium conditions. At partial pressures of cyclohexane of over 100 mm Hg, the reaction rates conform to the equation of the zero order reactions; at partial pressures below 100 mm Hg, the rates are described by the equation, $\omega = kP_{\text{C}_6\text{H}_{12}}^{0.5}$. Activation energy of the reaction is 14.2 kcal/mol. The results obtained are interpreted by assuming that the reaction has no limiting stage at high and moderate surface coverages and the far-from-equilibrium conditions. Transition from a high to a moderate surface coverage changes the (observed) order of the reaction.

Bismuth-Molybdenum-Phosphorus Catalysts for Oxidation and Oxidative Ammonolysis of Propylene

I. K. KOLCHEEN, E. L. GALT'YEREN,
S. S. BOBKOV, L. YA. MARGOLEES

Institution—Not given

A study was made of the effect of phosphorus addition on the structure and catalytic properties of bismuth molybdates differing in structure and having the following compositions: $\text{Bi}_2\text{O}_3 \cdot 3\text{MoO}_3$ (α); $\text{Bi}_2\text{O}_3 \cdot 2\text{MoO}_3$ (β); $\text{Bi}_2\text{O}_3 \cdot \text{MoO}_3$ (γ). The results show that introduction of 0.2–0.8% of phosphorus at the conditions to form the α -phase, produces structural and phase changes in the $\text{Bi}_2\text{O}_3 \cdot 3\text{MoO}_3$. Here, the α -phase is partially transformed into the β -phase, which is characterized by the greatest catalytic activity. Addition of phosphorus in amounts greater than 4% (wt), leads to formation of the compound, $2\text{Bi}_2\text{O}_3 \cdot 3\text{MoO}_3 \cdot \text{P}_2\text{O}_5$. This substance has lower catalytic activity than either the $\text{Bi}_2\text{O}_3 \cdot 3\text{MoO}_3$ or the $\text{Bi}_2\text{O}_3 \cdot 2\text{MoO}_3$ forms.

Oxidation of Methanol to Formaldehyde Over a Silver Catalyst: Properties of the Process

V. N. GAVREELEN, B. I. POPOV

*Institute of Catalysis of Siberian Division
of the Academy of Sciences of USSR*

Air-oxidation of methanol was studied over a silver-on corundum catalyst at temperatures of 510°–920°K. At temperatures of 510°–570°K and 750°–850°K, the respective activation energies are 21–22 and 2–3 kcal/mol. At temperatures of 570°–650°K, the process is unstable and the reaction temperature spontaneously increases or decreases, reaching the temperature values outside the interval of unstable conditions. Qualitatively, the kinetic correlations for the process in the high temperature range differ from those in the low range. It is concluded that at temperatures above 650°K, the reaction is not diffusion-limited. Calculation of surface temperature of the catalyst qualitatively supports this conclusion.

Kinetics of Ethylene Polymerization to a Crystalline Polymer Over a Chromium Oxide Catalyst

YU. I. YERMAKOV, L. P. IVANOV

*L. Ya. Karpov
Physico-Chemical Institute
Institute of Catalysis of Siberian Division of
the Academy of Sciences of USSR*

A study of ethylene polymerization kinetics was carried out at temperatures below 90°, using suspensions of a chromium oxide in cyclohexane as the catalyst. The reaction rate-on-stream time