

relationship indicates that the degree of overlap of the s- and p-electron functions, which effect the bonding between a metal and an organic moiety, changes with the character of the radical in the moiety. Aliphatic and aromatic radicals have opposite effect on the spectral structure of copper in Cu-polychelates. The changes in catalytic activity of the polychelates studied, correlate well with the experimental X-ray spectral data on the effect of the radicals in these polymers.

Kinetics of Isotopic Oxygen Exchange in Molecular Oxygen—Solid Oxide Systems

V. S. MOOSIKANTOV, V. V. POPOVSKY,
AND G. K. BOR'YESKOV

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

A study was made of generalized kinetics of simultaneous isotopic and homomolecular exchange of molecular oxygen with the oxygen in the oxides. The differences in the kinetic correlations obtained lead to definite conclusions regarding the nature of exchange mechanism on each oxide.

Determination of Acidity of Some Silicate Catalysts by Use of Spectral Methods

L. G. KARAKCHEYEV, V. A. BARACHEVSKY,
AND V. E. Kholmogorov

*A. A. Jdanov Scientific Research Institute
for Physics in Leningrad.
Institute of Catalysis of Siberian Division
of the Academy of Sciences of USSR*

Acidity of catalytically-active double oxide systems of $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$; $\text{MgO} \cdot \text{SiO}_2$; $\text{ZrO}_2 \cdot \text{SiO}_2$; and $\text{TiO}_2 \cdot \text{SiO}_2$ was determined from the adsorption spectra and EPR analyses of molecular anthracene ions adsorbed on these oxide systems. Direct relationship exists between protonic and aprotic acidities and the composition of the double oxides studied. The maximum acidity of the $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ and $\text{MgO} \cdot \text{SiO}_2$ catalysts corresponds to the maximum concentrations of the four-coordinated Al^{+3} and Mg^{+2} ions in them. The peak acidity in $\text{ZrO}_2 \cdot \text{SiO}_2$ catalysts occurs at near equimolecular concentrations of the two oxide components.

Reaction of Formylglycine with n-Toluene Sulfonate Cyclohexyl β -[N-(N-Methyl Morpholinium)] Ethylcarbodiimide

D. G. K'NOPPE AND T. N. SHOUBEENA

*Institute of Organic Chemistry of Siberian
Division of the Academy of Sciences of
USSR in (the City of) Novosibirsk*

The kinetics of interaction of aqueous solutions of n-toluene-sulfonate cyclohexyl β -[N-(N-methyl

morpholinium)] ethylcarbodiimide with formylglycine was studied by determining the cumulative yields of products with positive hydroxamic reaction. The study shows that the formylglycine-carbodiimide interaction yields two products: one of them is stable in acid media and gives positive hydroxamic reaction with alkaline NH_2OH solutions; the second product, on the other hand, disintegrates in acidic media and gives positive hydroxamic reaction with neutral NH_2OH solutions only.

Kinetics of Ethyl Ester of Formylglycyl Glycine Synthesis in Aqueous Solutions Containing a Carbodiimide Promoter

D. G. K'NOPPE, O. A. MEERGORODSKAYA,
AND T. N. SHOUBEENA

*Institute of Organic Chemistry of Siberian
Division of the Academy of Sciences of
USSR in (the City of) Novosibirsk*

Mixing aqueous solutions of formylglycine, ethyl ester of glycine and n-toluene sulfonate cyclohexyl β -[N-(N-methyl morpholinium)] ethylcarbodiimide (CME-carbodiimide, for short) results in accumulation of a labile derivative which gives positive hydroxamic reaction with a neutral hydroxylamine. The fact that initial pH and concentration of the reactants affect the reaction kinetics, shows that this derivative is formed from formylglycine and CME-carbodiimide and that it is identical with the labile derivative when produced at the same reaction conditions except for the absence of ethyl ester of glycine.

Analyses of kinetic and direct experimental data show that the dipeptide ester is formed by interaction of the labile derivative with the glycine ester. The rate of this reaction increases sharply with the system pH.

Mechanism and Kinetics of Catalytic Oxidation of Ethylene in Contact with Aqueous Solutions of Palladium and Copper Salts

K. I. MATVEYEV, I. F. BOOKHTOYAROV,
N. N. SHULTZ, AND O. A. YEMEL'YANOVA

*Institute of Catalysis of Siberian Division
of the Academy of Sciences of USSR in
(the City of) Novosibirsk*

In contact with aqueous solutions of palladium and copper salts, ethylene is oxidized to acetaldehyde. The reaction is via the equilibrium formation of an ethylene-palladium chloride complex, with the Pd salt reacting along the following two independent routes: (1) equilibration with the copper ions, followed by an irreversible reaction with the hydroxyl ions; and (2) direct interaction with the hydroxyl ions. Although the reaction is

not complete by either route, the rate by Route (1) is greater.

Empirical and theoretical equations are proposed to calculate the reaction rates. The theoretical equation is based on the reaction mechanism proposed by the authors. The results calculated by use of these equations are in close agreement.

Decomposition of Monomethylamine Over Metallic Molybdenum and Nickel Catalysts

S. L. DOBICHEEN, V. V. FORSHEENA,
AND G. N. SMOLEENA

State University for Applied Chemistry

Interaction of monomethylamine (MMA) with molybdenum and nickel surfaces was studied at temperatures of 200°–1500° by a mass spectrometric method. The results show that MMA decomposition rates depend upon the rates of metal surface fouling with carbon formed in the reaction. With molybdenum, the extent of surface fouling—by carbide—depends on the extent of carbon diffusion into the metal; with nickel, the degree of fouling—by carbon—is, probably, a function of atomic carbon migration rates on the metal surface. In either case the products of MMA decomposition are N₂, H₂, C, NH₃, HCN, and CN. However, with Mo, the principal products are N₂, H₂, and C; but with Ni: HCN, H₂, NH₃, and C.

Catalytic Activity of Metal Oxides in Propylene Oxidation Reactions

M. YA. ROOBANEK, K. M. KHOL'YAVENKO,
A. V. GERSHEECOREENA, V. I. LAZOOKEEN

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

Specific rates of propylene oxidation over different metallic oxides were determined by a recycle—continuous method. The oxidation temperatures to attain constant specific oxidation rates with various fixed concentrations of the reactants were chosen as activity characterization factors. In descending order, catalytic activities of the metal oxides in partial and complete oxidation of propylene are, respectively: Cu > Co > Fe > Ni > V and Mn > Cu > C > Co > Fe > U > Cd > V > Ni > Mo > Zr > Pb > W. Depending on position of these metals in the Periodic Table the shapes of their activity curves in the subject, reaction resemble the shapes of the curves obtained in oxidation of hydrogen and in homomolecular and isotopic oxygen exchange reactions. The observed similarity of these curves is, apparently, due to oxygen participation in the formation of the activated complexes, the intermediate products in these processes.

Catalytic Dehydrogenation of 2,2-Dimethylbutane

E. A. TEEMOFEI'YEVA, N. I. SHOY'KEEN,
AND G. S. PETR'YAYEVA

N. D. Zelensky Institute of Organic Chemistry of the Academy of Sciences of USSR

Dehydrogenation of 2,2-dimethylbutane over a potassium aluminochromate catalyst at atmospheric pressure and a temperature of 500° results in 8.5 mole % (on charge) yield of 3,3-dimethylbutene-1. Addition of helium as an inert diluent increases the yield of neohexene to 10–11 mole % (on charge).

Effect of Chemical Composition and Methods of Preparation of Complex Oxide Catalysts Upon Their Physico-Chemical and Catalytic Properties: Silica-Zirconia Catalysts

V. A. DZESKO, M. S. BORESOVA, N. V.
AKEEMOVA, AND A. D. MAKAROV

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

A study was made of the effect of methods of preparation and thermal pretreatment upon activity of silica-zirconia catalysts. The results show that catalytic activity of the samples tested for dehydrogenation of isopropyl and ethyl alcohols is a direct function of the number of acid centers, but that the activity of the centers is not affected either by the SiO₂/ZrO₂ ratios, nor by the methods of preparation and thermal pretreatment of the samples. The following properties are affected by the catalyst preparation histories: pore structure, impurity content, extent of interaction among its components.

Effect of Chemical Composition and Methods of Preparation of Complex Oxide Catalysts Upon Their Physico-Chemical and Catalytic Properties: Alumino-silicate Catalysts

V. A. DZESKO, M. S. BORESOVA,
AND N. V. AKEEMOVA

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

The extent of interaction of aluminum oxide with silicic acid and the resulting number of acid centers in the catalyst samples vary with the composition and methods of their preparation. Of the catalysts with identical composition, those prepared by coprecipitation have the greatest number of surface acid centers. With increasing Al₂O₃