mechanism is proposed for the oxidation and an equation is derived to calculate the reaction rate of the process.

The Kinetics of Para-Ortho Conversion of Hydrogen Over Various Metallic Catalysts

S. L. Keeperman

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

The kinetics of para-ortho conversion of hydrogen were analyzed in operation over the catalysts with non-homogeneous surface. The kinetic equations derived are for a two-stage reaction scheme, assuming that the dissociated adsorbed particles form the surface-based intermediates at small, intermediate, and high surface coverages. The kinetic relationships obtained are compared with published kinetic data for the para-ortho conversion of hydrogen over various metallic catalysts.

Polymerization of Ethylene in the Presence of $VOCl_3$ — Al $(iso\text{-}C_4H_9)_3$ Catalyst

N. D. Zavorokheen, P. E. Matkovsky,
and N. M. Tcheerkov

Institute for Chemistry of Petroleum and Natural Salts of the Academy of Sciences of the Kazahsk SSR.

Institute of Chemical Physics of the Academy of Sciences of USSR

Polymerization of ethylene was studied at a temperature of —50°, using a $VOCl_3$ — Al(iso-$C_4H_9)_3$ catalyst dissolved in n-heptane. The results show (a) a linear relationship between the reaction rate and the monomer concentration at the p_{C_2H} of 100–400 mm Hg and (b) a non-linear relationship between the polymer yields and the catalyst concentration. Activity of the catalyst is a function of the molal ratio of its components. Activation energy of the reaction at temperatures of —80° to 0° is 3.8 kcal/mol. Activity of the catalyst decreases with the on-stream time due to deactivating interaction of the active centers.

Effect of Poisons on Selectivity of Aluminum Oxide in Decomposition of n-Butyl Alcohol

V. A. Dzees'ko, M. Kolov'yortnova,
T. S. Veenneekova, and
Yu. O. Boolgakova

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

Regardless of the preparation method and of the heat treatment temperatures, the maximum value of the acid function, H_0, of the aluminum oxide samples tested is less than —8.2. Concentration of the acidic centers on the surface of the γ- and θ-alumina samples is approximately equal. The number of the centers on the surface is about 2.5 μ-equivalents/m^2 — as determined by the indicator method, and 1.2 μ-equivalents/m^2 — by a poisoning technique. Increasing the extent of decomposition of n-butyl alcohol, results in increased isomerization of α-butylene. At like conversion levels, the product distribution is independent of the NaOH content of the samples. The active sites on the surface of the aluminas are of equal acidic strength. The dehydration of the alcohol and the isomerization of α-butylene take place on the same acidic centers.

Investigation of Catalytic Properties of Organic Semiconductors Prepared by Thermal Dehydrochlorination of Polyvinylchloride

E. S. Dokookeena, O. A. Goloveena,
M. M. Sakharov, and
R. M. Asei'yeva

Institute of Chemical Physics of the Academy of Sciences of USSR

Catalytic activity of a thermally dehydrochlorinated polyvinylchloride was determined at temperatures of 400°, 500°, and 700°. The data of catalytic decomposition of hydrazine, formic acid, and hydrogen peroxide served to construct a model for the reactions of this type. A clear-cut correlation was not uncovered between catalytic activity of polyenes and concentrations of the paramagnetic particles.

Kinetics of CO Oxidation Over a Modified Zinc Oxide Catalyst

G. I. Tcheejeekova

Institute of Chemical Physics of the Academy of Sciences of USSR

Oxidation of CO over "pure" and a modified zinc oxide catalysts was studied at temperatures of 300°–500° and the conditions precluding poisoning of the catalysts during the operations. The kinetics and activation energies of the reactions were determined.

A Mechanism of Decomposition of Vaporized Formic Acid Over Metallic Palladium

A. A. Khom'yenko, L. O. Apel'ba'oom,
and M. I. T'yomkeen

L. Ya. Karpov Physico-Chemical Institute

A study of dehydrocyclization of formic acid was carried out on the surface of a palladium metal membrane at temperatures of 225°–275° and the HCOOH partial pressures of 0.01–0.1 atm., using a recycle-continuous unit. The reaction rate is proportional to $p^{0.66}_{HCOOH}$ and the energy of activation is 16.2 kcal/mol. The data of volatility of the hydrogen on the palladium surface and of the hydrogen delivery rates through the palladium membrane, preclude the possibility of the reaction course via a chain mechanism.

Determination of Kinetics of Heterogeneous Catalytic Reactions, Based on the Critical Ignition Conditions: Synthesis of Alcohols from Carbon Monoxide and Hydrogen

YU. B. KAGAN, A. T. PONAMAR'YENKO,
AND A. YA. ROZOVSKY

A. V. Topcheeyev Institute for
Petrochemical Synthesis of the
Academy of Sciences of USSR

A method, employing a differential-type reactor, was developed to determine the temperatures of the gases at the critical conditions of ignition. The kinetic parameters of the reactions of this type were determined with the aid of the method described in an earlier paper (1, 2), which correlates the critical parameters of strongly exothermal reactions with the critical conditions of ignition on the surface of a catalyst. The effectiveness of the latter method was demonstrated, by way of an example, in synthesizing alcohols from CO and H_2 over a fused iron catalyst.

Kinetics of Ammonia Synthesis at Non-Equilibrium Conditions

N. M. MOROZOV, E. N. SHAPATEENA,
L. I. LOO'K'YANOVA, AND
M. I. T'YOMKEEN

L. Ya. Karpov
Physico-Chemical Institute

An investigation of the kinetics of ammonia synthesis at near-equilibrium conditions and at conditions far-away from the equilibrium, was carried out in a recycle-continuous operation over nickel and cobalt catalysts at atmospheric and sub-atmospheric pressures. Two derived equations are shown to calculate the reaction rates: one of these is to be used when the NH_3 concentrations are close to the equilibrium values; the other one, when concentrations of the NH_3 are small relative to those at the equilibrium. The magnitudes of the exponent in the two equations are identical. The values of m and of m', (since $m = m'$) are 0.32 with the nickel catalyst and 0.22 with the cobalt catalyst. The equality of the m and m' values corroborates the theoretical interpretation of the kinetics of ammonia synthesis at the conditions far away from the equilibrium.

Mass-Spectrometric Determination of the Rate Constants of Elementary Reactions: Reaction of Atomic Hydrogen with Ethylene

V. P. STROONEEN, A. F. DODONOV,
G. K. LAVROVSKY, AND
V. L. TAL'ROZÉ

Institute of Chemical Physics of the
Academy of Sciences of USSR

The rate constant, k_1, of the addition of atomic hydrogen to ethylene was determined at continuous flow conditions, using the "diffusion flux" technique. At the P_{total} of 6.56 mm Hg and T of $(297 \pm 3)°K$, k_1 is $[8.8(\pm 20\%)](10^{-13})$ cm^3 molecule^{-1} sec^{-1}.

The atomic hydrogen was produced by passing a stream of helium with small amounts of admixed H_2 through a high-frequency electric discharge. The concentrations of the H and C_2H_4 atoms were determined mass-spectrometrically. The gas from the reactor was introduced into the ion generator in the form of a modulated molecular beam. The mass spectrometer was of known sensitivity for atomic hydrogen.

The Effect of Ammonia Preadsorption on Thin Coatings of Gold on the Visible-Region Adsorption Spectra of the Metal

V. D. YAGODOVSKY AND S. L. GREEGOROVEECH

Patrice Lamumba University of
Friendship of the Peoples

The absorption spectra in the visible region of very thin granular coatings of gold were studied before and after preadsorption of ammonia. The results obtained were analyzed in the light of the theory of plasmic oscillation of the electrons of a source-metal. The study shows that the preadsorbed ammonia increases concentration of the electrons due to the metal, decreases the electron relaxation time, and increases dielectric permeability of the medium around the metal granules. These findings are attributed to the electron transfer from the adsorbed molecules of ammonia to the metal. Other experimental data show that the preadsorbed ammonia alters the adsorption spectrum of atomic gold covering the quartz surface.