with fresh samples of the catalyst, the thermo-EMF distribution is governed by the normal principles. On the other hand, the distribution on the aged samples is asymmetric in character. An equation is derived to calculate the thermo-EMF distributions and a correlation established between the distribution parameters and catalytic activity of the samples.

The Overlap Integral Method in Determining of Various Forms of Chemisorption on Metals: Dissociative Chemisorption

N. N. Boolgakov and Yu. A. Boreesov

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

The heats of hydrogen chemisorption on metals during the first transition period were calculated by the overlap integral method. In line with the experimental data, the calculations show that the heats decrease with the on-stream time. The calculated information predicts that at equilibrium conditions the bonding distance, M—H, decreases with the in-service time. The concept regarding the major role of the *d*-orbitals in the formation of the M—H bond was confirmed.

Hydrogenation of Olefins in the Presence of Complex Organometallic Catalysts

I. V. Kal'yetcheetz and F. K. Shmeedt

Institute for Petro- and Coal-Chemical Synthesis

Hydrogenation of cyclohexene and of heptene-1 was studied in the presence of organometallic catalysts, comprising mixtures of triethylaluminum with one of the following transition metal-containing compounds: $(C_5H_5)_2TiCl_2$; $VO(C_5H_7O_2)_2$; $Cr(C_5H_7O_2)_3$; $Mn(C_5H_7O_2)_2$; $Fe(C_5H_7O_2)_3$; $Co(C_5H_7O_2)_2$; $Ni(C_5H_7O_2)_2$.

In terms of the transition metal components of the catalysts with the Al/Me ratio of 10, catalytic activity of the preparations in hydrogenation of cyclohexene and of heptene-1 decreases in the following orders: $Co > Ni > Fe > Cr$ and $Co > Ni > Fe > Cr \geqslant Ti > Mn > V$, respectively.

Hydrogenation of heptene-1 is complicated by the concurrent isomerization of the reactant, involving the double bond shift.

Reactions of α-Oxides: The Mechanism and Kinetics of a Base-Catalyzed Reaction of Ethylene Oxide with Alcohols

N. N. L'yeb'yed'yev and Yu. I. Baranov

D. I. M'yend'yel'yeyev Chemico-Technological Institute

The reactions of ethylene oxide with alcohols of different acid strengths are of the first order with respect to both the oxide and the alcoholate; however, in terms of the alcohol concentration, kinetics of these reactions are complex. Here, with the weakly-acidic alcohols, the concentration -vs- rate constant curves pass through a minimum; on the other hand, with strongly-acidic alcohols, the correlation is linear in character. A clear-cut relationship was established between the acidity and reactivity of the alcohols.

The results of this study are interpreted as showing that the reaction passes through a transition stage, and that during this stage the alcoholate attacks carbon atoms of the ethylene oxide, while the free alcohol molecules attack oxygen atoms of the oxide.

The Mechanism and Kinetics of Catalytic Interaction of Isocyanates with Alcohols in the Presence of Organotin Compounds: The Reagent-Catalyst Complexes as the Reaction Intermediates

S. G. Ent'yelees, O. V. N'yest'yerov, and V. B. Zabrodeen

Institute of Chemical Physics of the Academy of Sciences of USSR

The results of n-chlorophenylisocyanate reaction with methyl alcohol dissolved in n-heptane show that in the presence of added dibutylallyllaurinate of tin, the active intermediate is the complex formed by interaction of the catalyst with an alcohol. This conclusion is supported by the observation that the reaction rates are proportional to concentrations of the activated complex. The equilibrium constants and the true interaction rates of the catalyst-alcohol complex with the isocyanate were determined at temperatures of 25°, 35°, and 45° with the aid of the kinetic data. The thermodynamic parameters were calculated for each stage of the reaction.

Catalytic Activity of Polychelates in the Liquid Phase Oxidation of Hydrocarbons

A. I. Meen'kov, G. M. Aleekeena, Yu. M. Greedn'yov, and N. P. Keyer

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

Certain kinetic relationships were established in oxidation of isopropylbenzene and ethylbenzene in the liquid phase in the presence of a catalyst on a polymeric chelate carrier. The results show that catalytic decomposition of the hydroperoxide is the fundamental source of the free radicals produced in the reactions studied. Based on the kinetic data obtained, a multi-stage reaction 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-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