are derived. These are based on experimental data at small surface coverages.

Infrared Spectra of Ethylene and of Some Aliphatic Alcohols Adsorbed on Titanium Dioxide

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The infrared spectra of CH_3OH, CH_3OD, C_2H_5OH, n-C_3H_7OH, iso-C_3H_7OH, and C_2H_4 were obtained by adsorption at 20°–300° on TiO_2—alone and with admixed WO_3. The spectra of these compounds in the adsorbed state are clearly similar. The possibility of formation of two types of ethers on the TiO_2 surface is discussed. These ethers are regarded as the intermediates in the alcohol dehydration reactions.

Investigation of Homomolecular Oxygen Exchange Over ZnO at Low Temperatures

By V. J. Gorgorakey, G. K. Bor'yeskov, L. A. Kasatkeena, and V. D. Sokolovsky

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The homomolecular isotopic oxygen exchange, $^{16}O_2 + {}^{18}O_2 \rightarrow 2{}^{16}O{}^{18}O$, was studied at temperatures of 25°, −63°, and −194° over a ZnO, which was first calcined in air at 850° and then rapidly cooled to the reaction temperatures, above.

At the reaction temperatures of −63° and −164°, the isotopic oxygen exchange rates approximate that at 425°. In this temperature range, the catalyst is stable in activity. The apparent activation energy of this reaction is 0.18 kcal/mol. This was calculated from the exchange rates at −63° and −194°. The exchange rate with ZnO at 25° is initially many times greater than at 425° to 500°. But in oxygen atmosphere at 25°, the catalyst rapidly (5–6 hrs) loses its activity.

Activity of ZnO, deactivated by contact with air at elevated temperatures, can be restored by contacting with vaporized zinc.

A Mechanism of C_5-Dehydrocyclization

By A. L. Leeberman

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The proposed mechanisms for dehydrocyclization of pentane and for the reverse reaction of hydrogenolysis of the C_5 ring are based on the assumed participation of atoms, of the catalyst in a transition state at the active surface, the geometry of the transition state, and the concept of cyclical electron transfer within the transitory system.

Kinetics of Catalytic Oxidation of Propylene into Acrolein—in Presence of Steam

By Ya. B. Gorokhovatsky and E. N. Popova

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The kinetics of oxidation of propylene over a copper catalyst with unlimited diffusion characteristic were investigated at temperatures of 380°–420° in presence of large amounts of steam. The kinetic equations, as proposed below for the conversion of propylene into acrolein and carbon dioxide, are valid at the following concentrations (vol. %) of the components in the reaction mixture: H_2O, 3–60; O_2, 3–15; C_3H_6, 16–60; C_3H_4O, 0.25–1.25.

$$W_1 = k_1 \frac{C_{O_2}{}^{0.8} \times C_{C_3H_6}}{1 + b' C_{acrol}} \cdot \frac{(1 + C_{H_2O})^{0.5}}{1 + b_1 C_{H_2O}}$$

$$W_2 = k_2 \frac{C_{O_2} \times C_{C_3H_6}}{1 + b'' C_{acrol}} \cdot \frac{1}{1 + b_2 C_{H_2O}}$$

The heats of activation to form acrolein and CO_2 were determined.

The action mechanism of steam at the reaction conditions is explained. The improvement in selectivity of the copper catalyst in presence of steam is believed to be due to the inhibiting action of steam to prevent complete oxidation of the product acrolein.

Catalyzed Reactions of Acetylene in Vapor Phase: Kinetics and Mechanism of Vapor Phase Synthesis of Vinyl Acetate Over Various Metal Acetate Catalysts

By I. B. Vasil'yeva, A. J. Gelbshtein, I. N. Tolsteekova, and Dao Van T'yong

L. Ya Karpov Physico-Chemical Institute

The study of kinetics of vapor phase synthesis of vinyl acetate from acetylene and acetic acid was carried out, using Zn, Cd, Hg, and Bi acetates on activated carbon as the catalysts. Activity of other metal (Be, Mg, Ca, Ba, Fe, Co, Ni) acetates as catalysts for the reaction was also evaluated. The schemes proposed describe the acetylene-acetic acid reaction mechanisms over the catalysts used. Reasons are given to explain the experimentally-observed differences in the kinetics due to changes in the reaction conditions, i.e., nature of the cationic salt, reaction temperature, partial pressures of the reactants.

A Novel Method of Investigation of Heterogeneous Catalytic Reactions: Decomposition of Ammonia on Platinum

By YA. M. FOGEL, B. T. NADIKTO, V. F. RIBALKO, R. P. SLABOSPEETZKY, I. E. KOROBCHANSKAYA, AND V. I. SHVACHKO
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A novel method of investigation of heterogeneous catalytic reactions is proposed. This consists of simultaneously observing the course of the I(T) curves for the ions produced by ionization of the gas around a catalyst and for the secondary ions being knocked out from the catalyst surface by a beam of the primary ions (I is the intensity of certain lines in mass spectra; T is a catalyst temperature).

This method was used in studying the mechanism of catalytic decomposition of ammonia over platinum. The mechanism of poisoning and reactivation of the plantinum catalyst was determined. The experimental data show that decomposition of ammonia involves two stages: during the first stage, adsorbed NH_3 molecules are decomposed into NH and H_2; during the second stage, pairs of adsorbed NH particles react to form N_2 and H_2.

Abstracts from Shokubai (Catalyst)

Shokubai (Catalyst) publishes both original articles and reviews or translations of articles appearing originally in languages other than Japanese. The following abstracts are of original Japanese language articles only.

Acidity and Activity of Silica-Alumina Catalysts

By TADAO SHIBA, TAKAMASA AONUMA, KAZUAKI YOSHIDA, HIDESHI HATTORI, AND MASAO SATŌ
From Tokyo Institute of Technology, Meguro-ku, Tokyo, Japan

The activities of gel-mixed, co-gelated, and co-precipitated silica-alumina and alumina catalysts for such reactions as the polymerization of olefins, the cracking of cumene, and the decomposition of isobutane were measured, and their dependence upon the acidity of the catalyst surfaces was examined.

For the polymerization and the cracking of cumene, a correlation between the catalytic activities and the protonic acidity has been established, though not directly parallel. The activity for the decomposition of isobutane, on the other hand, revealed to be approximately proportional to the nonprotonic acidity. The change in the catalytic activity for isobutane cracking with reaction time and the reaction products in isobutane conversion were studied. The role of the nonprotonic sites in the cracking of paraffins has been discussed.

The Decomposition of Hydrogen Peroxide by Hydroxyl Ion in Homogeneous Aqueous Solution

By SYOICHI OKI AND YOSHIHISA KANEKO
From the Faculty of Liberal Arts, Utsunomiya University, Utsunomiya, Japan

The reaction rate of hydrogen peroxide decomposition has been determined near room temperatures in a pH range from 11.5 to 15.0, by means of titration with potassium permanganate solution. The following results were obtained: The specific reaction rate increases linearly with the concentration of hydroxyl ion until the pH reaches 13.4, above which the rate suddenly begins to decrease; it again increases above pH 14.0 linearly with the square of hydroxyl ion concentration. The pH range in which the N-shape variation of the rate has been observed is nearly independent of the reaction temperature and the type of positive ion in the solution, i.e., sodium or potassium. The activation energy decreases with an increase in pH below 13.6 but increases with pH above 13.7.

These results suggest that the mechanism of this reaction is different on both sides of the pH range at which the N-shape variation takes place.