

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

By YU. M. TSHCHEKHOCHEKHEEN, V. N. FEELEMONOV, N. P. KEYER, AND A. N. TYERENEEN

Institute of Catalysis of Siberian Division of the Academy of Sciences of USSR. Scientific Research Institute of Physics at Leningrad State U.

The infrared spectra of CH_3OH , CH_3OD , $\text{C}_2\text{H}_5\text{OH}$, $n\text{-C}_3\text{H}_7\text{OH}$, $\text{iso-C}_3\text{H}_7\text{OH}$, and C_2H_4 were obtained by adsorption at $20^\circ\text{--}300^\circ$ 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. GORCORAKY, G. K. BOR'YESKOV, L. A. KASATKEENA, AND V. D. SOKOLOVSKY

D. I. Mend'elyevyev Chemico-Technological Institute in Moscow

The homomolecular isotopic oxygen exchange, $^{16}\text{O}_2 + ^{18}\text{O}_2 \rightarrow 2^{16}\text{O}^{18}\text{O}$, 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

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

The proposed mechanisms for dehydrocycliza-

tion 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

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

The kinetics of oxidation of propylene over a copper catalyst with unlimited diffusion characteristic were investigated at temperatures of $380^\circ\text{--}420^\circ$ 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; $\text{C}_3\text{H}_4\text{O}$, 0.25–1.25.

$$W_1 = k_1 \frac{\text{CO}_2^{0.8} \times \text{C}_{\text{C}_3\text{H}_6}}{1 + b'\text{C}_{\text{acrol}}} \cdot \frac{(1 + \text{C}_{\text{H}_2\text{O}})^{0.5}}{1 + b_1\text{C}_{\text{H}_2\text{O}}}$$

$$W_2 = k_2 \frac{\text{CO}_2 \times \text{C}_{\text{C}_3\text{H}_6}}{1 + b''\text{C}_{\text{acrol}}} \cdot \frac{1}{1 + b_2\text{C}_{\text{H}_2\text{O}}}$$

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