

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  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{OD}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $n\text{-C}_3\text{H}_7\text{OH}$ ,  $\text{iso-C}_3\text{H}_7\text{OH}$ , and  $\text{C}_2\text{H}_4$  were obtained by adsorption at  $20^\circ\text{--}300^\circ$  on  $\text{TiO}_2$ —alone and with admixed  $\text{WO}_3$ . The spectra of these compounds in the adsorbed state are clearly similar. The possibility of formation of two types of ethers on the  $\text{TiO}_2$  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

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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  $25^\circ$ ,  $-63^\circ$ , and  $-194^\circ$  over a ZnO, which was first calcined in air at  $850^\circ$  and then rapidly cooled to the reaction temperatures, above.

At the reaction temperatures of  $-63^\circ$  and  $-164^\circ$ , the isotopic oxygen exchange rates approximate that at  $425^\circ$ . 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  $-63^\circ$  and  $-194^\circ$ . The exchange rate with ZnO at  $25^\circ$  is initially many times greater than at  $425^\circ$  to  $500^\circ$ . But in oxygen atmosphere at  $25^\circ$ , 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 $\text{C}_5$ -Dehydrocyclization

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The proposed mechanisms for dehydrocycliza-

tion of pentane and for the reverse reaction of hydrogenolysis of the  $\text{C}_5$  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

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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:  $\text{H}_2\text{O}$ , 3–60;  $\text{O}_2$ , 3–15;  $\text{C}_3\text{H}_6$ , 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  $\text{CO}_2$  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

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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