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Abstracts from Shokubai (Catalyst)

The Catalyst for the Dehydrogenation of Cyclohexanol

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The Raney-type Cu catalyst for the vapor-phase dehydrogenation of cyclohexanol has been investigated. It has been observed that the Raney Cu-Cd catalyst, as well as the other well-known Raney-type Cu catalysts, is active at low temperatures and can be regenerated after deactivation; moreover, the life of the Raney Cu-Cd catalyst is longer than the other well-known Raney-type Cu catalysts. With an eye to obtaining information concerning the difference between the life of these catalysts, the surface area, the pore distribution, and the X-ray diffraction have been measured, and the influence of the high-boiling by-products on the catalytic activity has been examined.

The Relation between the Catalytic Hydrogenation and the Deuterium Exchange Reaction of Propene by Metal Catalysts

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The distributions of all the isotopic isomers of propene produced by its exchange reaction with deuterium oxide (A)

$$C_3H_6 + xD_2O \rightarrow C_3H_{6-x}D_x + xHDO \qquad (A)$$

and by its hydrogenation reaction with deuterium (B)

$$C_3H_6 + D_2 \rightarrow C_3H_{6-x}D_x + C_3H_{8-y}D_y \qquad (B)$$

have been investigated by means of the microwave absorption technique; the following conclusions have been obtained, on the assumption that propane is produced via the half-hydrogenated state, C_3H_7, on nickel and palladium:

(1) In both reactions, (A) and (B), catalyzed by nickel, the methine hydrogen of propene is the most easily exchangeable. Propene may be chemisorbed mostly as the undissociated state, C_3H_6 (ads), and it may subsequently produce the half-hydrogenated state, C_3H_7(ads). However, the nickel supported on γ alumina shows a different catalytic activity from the nickel in reaction (A).

(2) On palladium, however, all the hydrogen atoms of the methyl group are the most easily exchangeable in propene, and some dissociated species, C_3H_5(ads), may exist in addition to the above chemisorbed species.

(3) The exchange reaction can be regarded as a part of the hydrogenation from the standpoint of the reaction scheme.

(4) Since water does not poison the formation of the half-hydrogenated state, it can supply the chemisorbed hydrogen on the surface, though its concentration is too small to produce propane.

The Polymerization of Acetaldehyde

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Our recent studies of the polymerization of acetaldehyde will be summarized. A new method of preparing the amorphous acetaldehyde polymer by an alumina catalyst has confirmed the possibility of the catalyzed polymerization of acetaldehyde without using a frozen monomer (Chapter 2). Then the stereoregular (isotactic) polymerization with metal alkyl and alkoxide catalysts has been described, and the polymerization mechanism has been discussed in connection with several organic reactions involving metal alkoxide and carbonyl compound (Chapter 3). The preparation of the stereoblock polymer of acetaldehyde, consisting of isotactic and atactic blocks, has then been presented; in this preparation partially hydrolyzed aluminum alkoxide and the alumina-diethylzinc system acted as catalysts. The so-called "coordination polymerization" mechanism has then been discussed. When the acetaldehyde monomer was subjected to contact with three aluminum compound catalysts, i.e., alumina, aluminum alkoxide, and partially hydrolyzed aluminum alkoxide, a shift of the carbonyl band in the infrared spectra of acetaldehyde was observed. This finding has been taken to indicate the coordination of acetaldehyde upon the aluminum catalyst site in the so-called "coordination polymeriza-