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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)

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

and by its hydrogenation reaction with deuterium (B)

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

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 polymerization" (Chapter 4). Then the mechanism of stereoregulation in the polymerization with a metal alkoxide catalyst has been studied. Some observations presented here support the assumption that the stereoregulation is performed by the steric hindrance around the catalyst sites, which are controlled primarily by the bulkiness of the alkoxy group and by the degree of catalyst aggregation (Chapters 5 and 6). Polymerization by $Al(C_2H_5)_3$–H_2O systems (Chapter 7) with varying $H_2O/Al(C_2H_5)_3$ ratios and the alternating copolymerization of acetaldehyde with trichloroacetaldehyde by the $Al(C_2H_5)_3$ catalyst (Chapter 8) have also been described.

Abstracts of Articles in Russian Journal, "Kinetics and Catalysis," Volume 6, Number 2, pages 185–195; Published by Siberian Division of the Academy of Sciences of USSR

Chemiluminescence in Slow Chemical Reactions: Application to Studies of Kinetics of Gaseous Phase Oxidation Reactions

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Studies show that the chemiluminescence in oxidation of different organic compounds is quenched by oxygen. Since, here, oxygen functions as a reactant and a quenching agent, the kinetic curves of the chemiluminescent reactions at small concentrations of oxygen typically pass through a maximum point. In oxidative decomposition of tertiary butyl peroxide (TBP) and in oxidation of acetaldehyde, the time to reach the respective maximum points was utilized to determine kinetic parameters of the two reactions.

The results of determination of kinetics of chemiluminescence in oxidation of propane over hydrogen bromide as the catalyst show that, here, the chemiluminescence reflects the kinetics of formation and consumption of an unstable intermediate reaction product.

Reactivity of Phosphoric and Thiosulfuric Acid Esters with Cholineesterase and Hydroxyl Ions

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Reactivity of phosphoric and thiosulfuric acid esters ("POS") was studied in inhibited cholineesterase (CE) and hydrolysis reactions. For these reactions the rate constants were determined and the pre-exponential factors were calculated. It was found that the kinetic constants vary with changes in the structure of "POS."

Nature of Intermediate Radicals Formed in Inhibited Radical Polymerization Reactions

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Pictures were taken of the EPR spectra of the radicals produced in polymerization of styrene in presence of the reaction-inhibiting compounds resulting from addition of a macro-radical to certain aromatic nitroso-compounds.

The basic characteristic of the spectra of the intermediate radicals, in which a nitroso-group is attached to the benzene nucleous, is the triplet of 1:1:1 intensity ratio, involving splitting of 10–12 electrons. The triplet is formed by interaction of the unpaired electron with the nitrogen-containing nucleous. With the radical concentration measurements as the basis, correlations between some of the constants were evaluated for the elementary reactions.

Mechanism and Kinetics of Bromination of Vinylphosphinic Acids

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The mechanism of bromination of derivatives of vinylphosphinic acids was studied, using the