Oxidation of Naphthalene Over Vanadium Catalysts

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A comparison of catalytic activities, chemical compositions, and EPR spectra of different vanadium catalysts shows that selectivity of the so-called complex Vd—K—SO_4-silica gel catalyst for oxidation of naphthalene to phthalic anhydride is improved when in addition to the lower oxides of vanadium it also contains vanadyl sulfate. The latter may be present in the catalyst either as a solid dilute solution or as a distinct solid phase. The effect of either form on catalytic activity is practically the same. The roles of potassium sulfate and of different carriers were determined to optimize activity and selectivity of the catalysts.

Activity Change of an Aluminum-Chromium Catalyst in Dehydrogenation of Butane

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A study of activity of an aluminum-chromium catalyst to dehydrogenate butane was made in a recycle-continuous unit, using a moving pseudo-fluidized catalyst bed. Initially, activity of the catalyst increases, reaching the maximum after 3–12 minutes; thereafter, the activity decreases, the rate of decrease being proportional to the space velocity. The low activity during the initial few minutes of operation is due to the presence in the catalyst of CrO_3 and of oxygen-containing compounds, which are formed in the course of its reduction. The decrease in activity following the point of peak activity is due to accumulation of carbonaceous deposits. The rate of carbon laydown decreases with increasing rate of butane conversion.

A Combined Radio-Chromatographic Method to Investigate Mechanism of Heterogeneous Catalytic Reactions

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A combined radio-chromatographic analytical method is described to study the mechanism of heterogeneous catalytic reactions. The method includes the use of a microcatalytic synthesis of tagged and non-tagged compounds (in mg amounts) and of a pulsed method to inject them into the catalytic reactor.

The outstanding features of the method are its rapidity, requirement of relatively small amounts of catalysts and charge stocks, and convenience to obtain a large number of compounds. As is well known, synthesis of these compounds by usual techniques presents appreciable difficulties.

Usefulness of this novel method to determine reaction mechanisms is illustrated by the case of dehydrogenation and isomerization of butylenes to divinyl.

BRIEF COMMUNICATIONS

Kinetics of Destruction of Free Radicals by Ionizing Radiation

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EPR studies were made of the kinetics of decrease of paramagnetic particles in irradiation with fast electrons of stable radicals, such as 2,2,6,6-tetramethylpiperidine of nitric oxide. The results show that the destruction of the radicals is a first order reaction, with the reaction rate proportional to the dosage. At temperatures of 100°–300°K, the values of k increase with increase in the activation energy of 0.4 kcal/mol.

Multi-Step Super-Fast Reactions of Amines with Chloroanhydrides

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Thermometric measurements in continuous flow systems were employed to study the kinetics of interaction of different mono- and bifunctional amines with chloroanhydrides. These studies covered reactions at a temperature of 20° in homogeneous (heptane) and in near-heterogeneous (heptane-water) phases. The results show that the reactions studied occur in several steps. The rate constant values of the final, the slowest, reaction steps are 10^4–10^5 l/mol × sec.

Kinetics of Heterogeneous Catalytic Reactions Retarded by Side-Reaction Intermediates

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This paper describes a study of kinetics of heterogeneous catalytic reactions which are being