

with the hydrocarbon. In inert solvents, all of the oxygen consumed in oxidizing the cyanisopropyl radical is found in the reaction products. The product radical from oxidation of the cyanisopropyl radical is more active in splitting off atomic hydrogen from the hydrocarbon than the peroxide radical of the hydrocarbon. With the aid of the chemiluminescence technique, evaluations were made of the decomposition rate constant of AIBN, the probability of escape of the primary radicals from the "cage," and the activation energy of AIBN decomposition.

Heterogeneous Recombination of Free Radicals and Their Interaction With Adsorbed Layer

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Heterogeneous recombination of free methyl radicals over different surfaces (glass, quartz, metals, metal oxides) was studied with the aid of a semiconductor sounding technique. The results show that the recombination obeys the first order reaction law. Based on these data, a hypothesis is proposed that in the recombination process the free radicals interact with the radicals adsorbed on the surface. The rate constant of the interaction process is proportional to that of the heterogeneous recombination.

The techniques developed in the course of this work can be utilized to study important processes, such as interaction of free active particles with any adsorbed layer. These processes play an important role in heterogeneous radiation and catalytic reactions, involving participation of free radicals.

Kinetics of Radiation Isotopic Exchange of Deuterium With Hydroxyl Groups of Silica Gel

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A study was made of the kinetics of radiation isotopic exchange of D₂ with the OH groups of silica gel. A kinetic equation developed is in good agreement with the experimental data. Solution of the equation involves numerical integration by the method of terminal differences. The number of exchangeable hydroxyl groups on the surface is 1.2×10^{14} cm⁻². A mechanism is proposed to describe the radiation isotopic exchange reaction.

Kinetics of Dehydration of Formic Acid Over Nickel Catalysts

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Kinetic data were obtained for dehydration of formic acid over nickel catalysts in non-gradient and in continuous-flow systems. At volumetric space velocities of 1,075–33,500 hr⁻¹, partial pressures of 40–400 mm Hg, and temperatures of 77°–110°, the reaction in the non-gradient systems proceeds according to the equation for the zero order reactions. In the continuous-flow systems and at somewhat higher temperatures, the reaction rate obeys the equation for the half-order reactions.

Based on the results obtained and on published data, a mechanism is considered for the reaction. The results of determination of the isotopic kinetic effect in the HCOOH-to-HCOOD exchange validate the assumptions used to develop the reaction mechanism.

Changes in Emanation Capacity of Oxide Catalysts in Chemisorption and Catalysis

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The changes in emanation capacity of different oxide catalysts (TiO₂; ZrO₂; MgO; ZnO; ZnO + 0.22% Na₂O; ZnO + 2% ZnSO₄) tagged with radioactive thorium were determined in chemisorption of the gases and vapors from decomposition of isopropyl alcohol. Concurrently, changes in emanation were determined in decomposition of the alcohol over a TiO₂ catalyst. The changes in emanation in chemisorption of acetone and of water on the surface of the oxide catalysts are associated with formation of surface chemical compounds. The results with the zinc oxide samples show that incorporation of modifiers into ZnO, which alter catalytic selectivity and the rates of chemisorption and desorption of acetone, changes its emanation capacity.

Mechanism and Kinetics of Oxidative Ammonolysis Reactions and of Partial Oxidation of Propylene Over Bismuth-Molybdenum Catalysts

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