that either there is no attraction between the adsorbed cyclohexane molecules — in which case the reaction on the film surface must be of the order higher than the first, or that the molecular attraction is significant and, therefore, the surface reaction can be of the first order.

In dehydrogenation of cyclohexane over two palladium films with drastically different activities, the values of the activation energies and of the heats of adsorption — calculated by use of the experimental data in Hill's equation, agree satisfactorily with the experimental values calculated by Langmuir's equation.

Effects of Structure and Methods of Preparation on Catalytic Activity of Aluminum Oxide

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The effects of methods of preparation of crystalline aluminum hydroxides, their structural characteristics, and of the calcination temperatures were determined in decomposition of isopropyl and of n-butyl alcohols.

In decomposition of isopropyl alcohol, catalytic activity of the samples of γ-θ aluminas is proportional to the surface area. Specific activity of the finished samples remains approximately constant, regardless of the preparation history, crystal structure, and temperature of calcination of the alumina hydroxides.

In decomposition of n-butyl alcohol over these catalysts, the product composition varies with the degree of the alcohol conversion. In dehydration of n-butyl alcohol, the primary product is α-butylene.

The preparation history and crystal structure of the γ- and θ-aluminas have no effect on their specific activity and selectivity characteristics in processing n-butyl alcohol at a like degree of conversion in the region subject to the kinetic laws.

Infrared Spectroscopic Study of Photocatalyzed Oxidation of Vaporized Organic Compounds over Titanium Dioxide

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The character of photocatalyzed oxidation of vaporized isopropanol, methanol, n-heptane, and methane was studied by analyzing for composition the infrared adsorption spectra of the gas mixtures over the system TiO_2 and, also, by determining the changes in the infrared adsorption spectra due to the TiO_2 and of the spectra due to the adsorbed molecules. The results show that exposure to light of an isopropanol (or n-heptane)-TiO_2–O_2 reaction system results in formation of acetone, whereas the exposure of a methanol-TiO_2–O_2 system leads to formation of methylformate.

Kinetic correlations were determined for the photooxidation of isopropanol. A hypothesized mechanism of the reaction is described. This assumes that the isopropanol is oxidized by the TiO_2 oxygen, the resulting oxygen vacancies being filled by the oxygen atoms produced by dissociation of the gaseous O_2 molecules on the TiO_2 surface. The oxidation of the organic molecules is accompanied by the formation of stably-adsorbed compounds with ionic structure of acid carbonates.

Homomolecular and Isotopic Exchange of Oxygen on Cerium Dioxide

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A study of homomolecular oxygen exchange reaction was carried out over titanium dioxide at temperatures of 410°–545°; a study was also made of isotopic exchange of the oxygen in the gas phase with the oxygen of TiO_2 at temperatures of 365°–440°. The results show that the rate of the homomolecular exchange is 1.5 times greater than that of the isotopic exchange, although activation energies of the two reactions are practically equal (28 and 29 kcal/mol) and the orders of the two reactions with respect to the oxygen are identical (0.84). The results obtained lead to the conclusion that the limiting stages of the two processes are identical.

Pretreatment of the TiO_2 in vacuum at a temperature of 700°, followed by shock-cooling, yields a catalyst of high activity and poor stability in the operation at a room temperature.

Investigation of Catalysts for Oxidation of Ethylene to Ethylene Oxide

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A number of catalysts were evaluated to determine their effectiveness in oxidation of ethylene to ethylene oxide in pseudo-fluidized catalyst beds. The results show that silver on the surface of the corundum support is disposed in the form of discreet particles which occupy but a small portion of the carrier surface. Increasing the silver content of the catalyst results in the formation of comparatively larger aggregates of the metal within the voids of the carrier particles and in a decrease of specific surface of the silver. Relative to the unit surface of the silver, activity of the catalysts remains approximately constant, regardless of concentration of the silver component in them.

Heats of Oxygen Chemisorption on Silver

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The effects on differential heat, Q, of O_2 adsorption due to (a) simultaneous adsorption of oxygen and sulfur on a solid surface and (b) the degree of the surface coverage, θ, by the oxygen —were determined calorimetrically in adsorption of oxygen on silver at a temperature of 110°. Increasing the value of θ from 0 to 1, decreases the heat of the O_2 adsorption from $\sim$130 kcal/mol to $\sim$10 kcal/mol. Q is decreased by preadsorption of small amounts of sulfur.

The results of this study are discussed on the basis of the assumption that the oxygen adsorbed on the surface of silver is present in two forms.

Investigation of Kinetics of Heterogeneous Catalytic Reactions by a Non-Chromatographic Pulse Technique

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This study demonstrates that, in principle, kinetics of heterogeneous catalytic reactions in the gas phase can be determined, when the width of a pulse exceeds the catalyst bed height. At these conditions, chromatographic separation of substances practically does not occur.

BRIEF COMMUNICATIONS

Formation of Radicals in Radiolysis of Organic Solids: Yields of Radicals in Irradiation of Certain Sulfur-Containing Compounds

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The yields of radicals, G_R, were determined by an EPR technique in irradiation of various classes of sulfur-containing compounds: hexylmercaptan, hexyldisulfide, thiophenol, thiophene, and thiophene derivatives. A comparison of the G_R yields in the radiolysis of the sulfur compounds with those in the irradiation of saturated- and of oxygen-containing compounds of the analogous structures shows the following:

(1) G_R of the saturated sulfur-containing compounds is $0.4 \times 1/100$ ev, whereas G_R of the structurally-analogous saturated hydrocarbons and alcohols is $(4\text{–}8) \times 1/100$ ev;

(2) G_R of the sulfur-containing aromatics and of their derivatives of $(0.03\text{–}0.3) \times 1/100$ ev is identical with the G_R of the corresponding cyclic hydrocarbons.

Formation of Free Radicals in Ultraviolet Irradiation of Naphthalene Dissolved in Hydrocarbons at 77°K

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An EPR investigation of kinetics of the diquantum process of formation of alkyl radicals was carried out at a temperature of 77°K in intermittent irradiation by ultraviolet light of naphthalene dissolved in 3-methylpentane. For continuous and interrupted irradiation of the naphthalene generalized correlations were derived between the rates of the radicals formation and (a) the time, θ, of the exposure and the black-out periods; (b) τ_1, duration of the period of accumulation of the radicals in the triplet state produced by the action of UV light; and (c) τ_2, lifetimes of the radicals in the triplet state in the absence of the excitation light. The results obtained validate the concept that in the triplet state a molecule of naphthalene absorbs the second quantum of light. The results also show that the subject photochemical reaction can take place only by adsorption of the second quantum with energy, λ, of <370 mμ.

Catalytic Action of Nitrogen-Containing Compounds in Isomerization of Carbohydrates: Catalytic Activity of α-Aminoacids in α,β-Isomerization of d-Glucose

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In acidic α,β-isomerization of glucose, the greatest catalytic activity is exhibited by the aliphatic α-aminoacids containing carboxyl groups.