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 chemiluminscence 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 $D_2$ 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 $1.2 \times 10^{14}$ $cm^{-2}$. 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 ($TiO_2$; $ZrO_2$; MgO; ZnO; ZnO + 0.22% $Na_2O$; ZnO + 2% $ZnSO_4$) 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 $TiO_2$ 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 Ammonalysis Reactions and of Partial Oxidation of Propylene Over Bismuth-Molybdenum Catalysts

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Some of the governing principles were determined in oxidative ammonalysis of propylene to acrylonitrile (Reaction I) and in oxidation of propylene to acrolein (Reaction II), using a recycle-continuous unit and a bismuth-molybdenum catalyst. Kinetically, both reactions are of the first order with respect to propylene; with respect to oxygen, both are of the zero order, provided that the partial pressure of the oxygen is not below a specified minimum value. The results show that Reaction I is not retarded by the reaction products; Reaction II, on the other hand, is retarded by the acrolein product. The reaction rates of the two processes become practically identical, when the acrolein, produced in Reaction II, is continuously removed by freezing out. The effect of varying partial pressure of the ammonia on the product composition was determined for Reaction I. It is believed that formation of different nitriles in Reaction I is via formation of the corresponding aldehyde intermediates.

## Effect of Chemical Composition and of Methods of Preparation on Physico-Chemical Properties of Complex Oxide Catalysts: Silica-Magnesia Catalysts

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The structure and phase composition were determined for several samples of silica-magnesia catalysts. The investigation shows that during the preparation these catalysts form a specific silicate structure with the magnesium atoms in a lowered (quaternary) coordination relative to the oxygen.

The effects of chemical composition and of methods of preparation on catalytic activity were evaluated in dehydration of isopropyl alcohol. The greatest concentration of acidic centers was found in the catalyst samples with the highest content of the four-coordinated magnesium. Activity of a milliequivalent of the acid centers is not affected by the composition of the silica-magnesia catalysts tested.

## Catalytic Properties of the Oxides of Metals of Period IV of Periodic Table in Oxidation Reactions: Decomposition of Nitric Oxide

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Catalytic properties of different transition metal oxides ($TiO_2$; $V_2O_5$; $Cr_2O_3$; $MnO_2$; $Fe_2O_3$; $Co_3O_4$; NiO; CuO; ZnO) were determined by statistically evaluating the results of decomposition of nitric oxide in a recycle-continuous unit. The order of the reaction with respect to NO and the reaction rate-temperature relationship were determined.

## Effect of Platinum and Sodium Content on Aromatization Activity of $Pt/Al_2O_3$ Catalysts

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The effects of 0.01–1.2% (wt) Pt and 0.02–1.6% (wt) Na on properties of $Pt/Al_2O_3$ catalysts were determined in aromatization of n-hexane at atmospheric pressure and a temperature of 545°. In addition, conversion of n-hexene-1 was studied over an $Al_2O_3$ catalyst at the conditions above.

Various schemes of formation of alkyl aromatics from n-hexane were considered. A scheme for conversion of n-hexane over a $Pt/Al_2O_3$ is described, which assumes concurrent formation of alkyl aromatics on both the Pt and the acidic centers. The experimental data presented show that the optimum concentration of sodium is a function of the Pt content in the $Pt/Al_2O_3$ catalysts.

## Activity of Ferric Oxide-Molybdena Catalysts in Oxidation of Methanol to Formaldehyde: Specific Activity as a Function of Composition

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A study of the effect of chemical composition of ferric oxide-molybdena catalysts on specific catalytic activity in oxidation of methanol to formaldehyde demonstrates the non-additivity of the catalytic properties of the starting components and of individual catalysts in a mixture. The catalysts with the Mo/Fe ratio of about 1.7 have the greatest activity for conversion of methanol to formaldehyde. It is believed that the active component of this catalyst is a chemical compound of iron and molybdenum oxides, containing about 60% of Mo.

## Mechanism and Kinetics of Carbon Monoxide-Steam Reaction Over a Ferric Oxide-Chromia Catalyst