tions of their strength and structural properties. Determinations of the nature of the acids dissolved in amines leads to the conclusion that in different cases the catalytic action may be due to any, or all, of the following acid forms: free acids; complexes having hydrogen bonds and/or proton donor characteristics; ammonia-substituting ions. It appears that catalytic activity of the first three forms varies with the nature of the acid.

A mechanism is proposed to explain acceleration of the reaction by use of added acids and hydroxyl-containing compounds.

Praseodymium Oxide as Catalyst for Dehydration of Alcohols and Dehydrogenation of Alcohols and Tetralin

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Catalytic activity of praseodymium oxide is greater in dehydrogenation than dehydration of ethyl, n-propyl, isobutyl, and secondary isopropyl alcohols. With the primary alcohols, its dehydrogenation activity increases with increasing molecular weight.

Compared to allylic substituents at a β-carbon atom, those at an α-carbon have greater effect on the activation energies of dehydrogenation and dehydration of alcohols and on the energies of C, H, and O bonding with praseodymium oxide.

Study of Kinetics of Heterogeneous Catalytic Reactions in a Recycle-Continuous Process: Cracking of Cumene Over Aluminosilicate Catalysts

By K. V. Topcheeyeva, B. V. Romanovsky, V. I. Teemoshenko

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A study was made of cracking cumene over two samples of aluminosilicate catalysts which were prepared by different methods. The results show that kinetic parameters of the process investigated depend substantially on the "biography" of the catalysts.

Effect of Manganese Dioxide Pretreatment Temperatures on Rate of Isotopic Oxygen Exchange

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Catalytic activity of several samples of manganese dioxide pretreated in vacuum at temperatures of 350°, 450°, and 550° was determined in the following reactions: isotopic exchange of the catalytic oxygen with molecular oxygen; homomolecular oxygen exchange; oxidation of CO at a pressure of 10 mm Hg and temperatures of 25° to 350°.

Increasing the catalyst pretreating temperature increases its activity in the isotopic oxygen exchange reaction and improves its homogeneity. Within a monolayer, the rate of isotopic oxygen exchange with the oxide oxygen falls off exponentially with the degree of completion. At temperatures below 300°, the oxygen exchange rates are smaller—and the corresponding activation energies are larger—than those of CO oxidation.

The homomolecular exchange of oxygen occurs in a high and a near-room temperature regions. Over freshly-pretreated samples of the catalyst, the rates of homomolecular exchange are greater at 25°–34° than at 200°. The near-room temperature homomolecular rates decrease with increasing time of contact with oxygen and are comparable to the CO oxidation rate.

Adsorption of Krypton on Thermally-Treated Platinum Films

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A study of the effect of thermal pretreatment of platinum films at temperatures of 100°–740° on their adsorptive properties shows that the overall film surface is either increased or remains unchanged. However, the pretreatment improves homogeneity of the surface.

Thermal pretreatment of platinum films on glass at a temperature of 630° increases the surface area; however, subsequent cooling to below a room temperature decreases the area—possibly, due to the competing effects of formation and disappearance of the surface defects, particularly, of the microcracks.

Effect of Non-Stoichiometric Amounts of Sulfur on Activity of Sulfide Catalysts

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Comparisons of the product compositions from hydrogenation of benzene over MoS_2/activated carbon and WS_2 catalysts show that the excess sulfur in these catalysts primarily affects the ionic reactions of isomerization and cracking.

The sulfur content of the catalysts studied was varied either by changing the preparation conditions or by varying the degree of reduction of the sulfur in the fresh catalysts.

A portion (5–10%) of the non-stoichiometric sulfur is very difficult—or altogether impossible—to remove by a reducing treatment. However, this is exchangeable with radioactive sulfur, when the latter is added to the raw materials. It is believed that this portion of the sulfur is relatively permanently bonded to the catalyst surface and functions as an added acceptor to increase the proportion of positively-charged surface elements which accelerate the ionic reactions.

Oxidation of Xylols in Vapor Phase Over Copper Catalysts Containing Added Heavy Metal Oxides

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The results of oxidation of o-, p-, and m-xylols over copper catalysts containing added heavy metal oxides show that these reactions involve oxidation of the methyl groups only, resulting in the formation of o-, p-, and m-toluyl aldehydes. A study of the kinetics of oxidation of xylols in a continuous processing unit shows close proximity of the activation energy values for formation of carbonyl compounds (9–12 kcal/mol) and for CO_2 (20–30 kcal/mol).

Some of the principles are compared which are equally applicable to the reactions of oxidation of hydrocarbons to carbonyl compounds over copper catalysts, to autooxidation processes to form hydroperoxides, and to oxidation of hydrocarbons in liquid phase.

Dehydrogenation of Isopropyl Alcohol and of Formic Acid Over Germanium Metal

By V. M. Frolov, E. K. Radjablee

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Dehydrogenation of isopropyl alcohol and of formic acid was studied over a finely divided surface of germanium metal made by grinding the metal in contact with the vaporized hydrocarbon feeds.

The results of the study show that the catalyst samples differing in conductivity property have about the same activity. This finding differs from the results of the earlier studies using samples of germanium metal which had been pretreated at high temperatures.

The paper lists the experimental values of specific catalytic activity of germanium metal.

Kinetics of Reactions Complicated by Autocatalysis

By L. M. Leetveen'yenko, A. F. Popov, V. I. Tokar'yev

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Different methods to treat the results of kinetic measurements were investigated in second order reactions which are complicated by autocatalytic effects. Based on an analysis of the results, several best methods were chosen.

A parameter is proposed to characterize quantitatively the extent of the autocatalysis. Within stated limits, the parameter defines with satisfactory accuracy the constants of catalytic and non-catalytic processes.

Diffusion Kinetics of Bimolecular Solid Phase Reactions: Reactions of Immobil Centers With Mobil Components of a Heterophase

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With the aid of electronic computers, a system of kinetic equations was developed to describe bimolecular reactions between the immobile centers and a gas diffusing into a solid body (in this study, a cylinder of infinite height). Based on precise calculation of the effective reaction times, different limiting conditions are examined and simple correlations are derived to analyze certain experimental data.

The correlations derived are also used to analyze some of the experimentally-determined kinetic data for the reactions of free radicals from irradiated polymers with molecules from the gaseous phase.

Mass Spectra of Dissociated CH_4^+, CH_3^+, and CH_2^+ Ions and of Some Radicals

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The dissociation spectra of CH_2^+ and CH_3^+ ions can be determined from that of CH_4^+ ion. Similarly, the mass spectra of CH_3, CH_2, and CH radicals can be calculated from the mass spectrum of methane.