Using as the model a bed of spherical particles which touch each other at one point only, the authors discuss the relationship between the strength of the particles and the degree of dispersion, porosity, nature of the surface contacts, and the internal arrangement. The authors emphasize that the hardness of granular catalysts—to meet industrial specifications—can be increased only at a sacrifice in the adsorptivity. Possible ways to increase physical hardness of particulated catalysts are discussed, such as vibro-compacting, use of crystallization methods to control the structural strength, and use of the carriers with skeletal structures making them inactive adsorption-wise to a specified environment.

Chelates of o-Quinone—With Cu(II) and Fe(III) Acting as Hydroxylators and Oxidators. Organic Catalysts: Catalytic Activity of o-Quinones

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A kinetic equation is given for catalytic oxidation of pyrocatechin in presence of Cu(II) and Fe(III) chelates. This equation is based on the kinetics, material balances, and spectrophotometric data. Comparative rates of separate steps of the process are shown. The catalytic oxidation mechanisms of the Cu(II) and Fe(III) chelates are different and involve different rate-determining steps.

The same substituents in position 8 of the moiety of 1,2-naphtoquinone exert different effect on the activity of the Cu(II) and Fe(III) chelates. The Fe(III) chelates are more selective and may be regarded as oxidases, i.e. they are oxidators. On the other hand, the Cu(II) chelates are less selective: along with the dehydrogenation activity, they also cause extensive oxidation of the substrate. Consequently, they may be regarded as hydroxylases, i.e. they are hydroxylators.

Electrochemical Methods to Determine the Mechanism of Catalytic Hydrogenation in Solutions

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In hydrogenation of unsaturated hydrocarbons in solutions, the relative concentrations of the reactants on a catalyst surface can be determined by electrochemical methods. The quantities of adsorbed hydrogen, the average energy of its bonding with a catalyst surface, and the magnitude of the surface, by itself—are determinable with the aid of a system of electrical charge curves, which are based on the results of determinations of anodic polarization of the catalysts by electric current, oxygen, or by use of a mixture of an unsaturated hydrocarbon and an inert gas. The method is particularly sensitive as a means to distinguish between the radical and ionic types of reactions.

Mechanism and Kinetics of Liquid Phase Oxidation of Metacrolein to Methacrylic Acid

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A study of kinetics of oxidation of metacrolein in liquid phase shows that in presence of salts of the metals with variable valence characteristics, the reaction proceeds chiefly via the radical-chain mechanism. The free radicals formed in the process initiate both the oxidation of the metacrolein and the subsequent polymerization of the methacrylic acid produced in the preceding step.

Over a silver catalyst, oxidation of metacrolein occurs by a different mechanism—mainly, of a non-radical type.

Kinetics of Oxidation of α-Naphthylamine by a Bromate in Presence of Molybdenum (VI) Catalyst

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Oxidation of α-naphthylamine by a bromate was studied in an acidic medium. The results show that the reaction is accelerated by the reaction product, quinoneimine. The reaction is catalyzed by molybdenum in very small concentrations, the catalysis occuring only in presence of the reaction product. Kinetic equations are derived for the non-catalyzed reaction.

Kinetic Parameters of Dehydrogenation of Isopropyl Alcohol and Tetralin and Dehydration of the Alcohol Over a Praseodymium Oxide Catalyst

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Over a praseodymium oxide catalyst, the values of the true activation energies of dehydrogenation of isopropyl alcohol and tetralin and of dehydration of alcohol approximate the corresponding apparent values. Qualitatively, the relationship of the bonding energies, which were evaluated, is as follows: $K_{Alc.App.} < K_{Napth.App.} < K_{Olef.App.}$

In dehydrogenation of tetralin and isopropyl alcohol and in dehydration of the alcohol, the relative adsorption coefficients of the reaction products vary with the temperature. Except for propylene, the reaction products are adsorbed more strongly than the feed components.

Of the reaction inhibitors tested, acetone and water are the strongest.

Kinetics of Hydrogenation of Carbon Monoxide Over a Nickel Catalyst

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A study of kinetics of hydrogenation of carbon monoxide over a nickel catalyst was carried out at atmospheric pressure. In the kinetic region, the reaction rate is defined by the equation for zero order reactions. The corresponding activation energy of the reaction is 16.2 kcal/mol and the coverage of the monomolecular layer of the active catalyst surface by carbon monoxide is 0.3.

The results show that the effect of the mass transfer processes on the reaction rates is a function of the CO concentration. For example, at the experimental conditions and the CO concentrations smaller than those specified, the hydrogenation process occurs at kinetically reversible conditions. The temperature-CO concentration correlations, which are given, define for the process the points of transition from the kinetically-controlling region to the internal diffusion-controlling region, and, finally, to the region where external diffusion controls. The assumption is made that the interaction of the chemisorbed hydrogen and CO is the limiting step of the process.

Oxidation of Hydrogen on Platinum Metal

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The mechanism of hydrogen oxidation on platinum was studied by measuring the kinetic isotopic effects and the reaction kinetics at static conditions and pressures of the order of 10^{-1} mm Hg. At a temperature of 20°, the reaction rate is proportional to the square root of the oxygen concentration and is not affected by the hydrogen concentration. These observations and the finding that the rates of individual H_2 and D_2 oxidation reactions are equal—demonstrate that the hydrogen does not participate in the over-all rate-determining step of the process. On the other hand, presence of the oxygen concentration term in the kinetic equation argues in favor of its participation in the rate-controlling step. The half-order of the reaction with respect to the oxygen is interpreted to be the result of the O_2 dissociation during adsorption on Pt.

Oxidation of Carbon Monoxide Over Titanium Dioxide and Over Its Solid Solutions With Tungsten and Iron Oxides

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Catalytic activity of titanium dioxide and of its solid solutions in oxidation of CO shows that the changes in the volumetric and electronic properties of these solids are paralleled by alterations in their catalytic properties.

With the aid of the kinetic data for oxidation of CO, of the earlier results of O_2 and CO chemisorption, and of the data on the electron work functions of these catalysts,—a multi-step CO oxidation mechanism is considered via the formation of an intermediate complex of CO_3 type.

Investigation of Adsorption Processes With Aid of Messbauer Effect

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Adsorption of $(CH_3)_4$ Sn by γ-Al_2O_3, silica gel, and other adsorbents was investigated with the aid of Messbauer effect. The results show that the surface of these adsorbents has active centers of at least two different types.

The kinetic principles governing the interaction of $(CH_3)_4$ Sn with the alumina surface were determined. The Messbauer spectra distinctly reflect changes in the adsorption temperatures as well as the donor-acceptor characteristics of the adsorption centers.

Adsorption Methods of Evaluation of Catalysts for Vinyl Acetate Synthesis in Vapor Phase

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The mechanisms of adsorption of acetylene and vaporized acetic acid were determined, using the