Study of Mechanism of Cumene Oxidation in Liquid Phase by Inhibition Technique: Chain Initiation

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In oxidation of cumene, the rate of radical initiation is proportional to the hydroperoxide concentration of up to 0.5 mol/l. At more severe oxidation conditions, a degenerative branching occurs with participation not only of cumene but also of its oxidation products.

With pure cumene, chain initiation follows the reaction, $2RH + O_2 \rightarrow 2R + H_2O_2$. Its energy of activation is 15 ± 1 kcal/mol.

Effect of Additives on Physico-Chemical Properties of Silver Oxalate, Photolysis, Radiolysis and Thermal Decomposition of Silver Oxalate

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This investigation covered the effects of adding Cd^{++} and Pb^{++} ions on the rates of photolysis and radiolysis of silver oxalate. The results show that in thermolysis, photolysis, and radiolysis reactions, the initial effect of the additives to retard the reaction rates tends to change to the rate-accelerating effect. Quantitatively, the transition to the acceleration is greater in presence of the Pb^{++} than the Cd^{++} additive.

The effect of these additives on the course of the individual elementary stages of $Ag_2C_2O_4$ dissociation reaction is also considered, taking into account the results of this study and the earlier information on electrical and optical properties of the $Ag_2C_2O_4$ with added Cd^{++} and Pb^{++}.

The concepts advanced to explain the causes of the observed effects are supported by th EPR spectral analyses of the irradiated solid solutions.

Effect of Active Solids on Reaction Kinetics: Oxidation of Iron by Water

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The kinetics of oxidation of iron by water were studied, using three samples of fused iron catalysts which differed mainly in Al_2O_3 content.

Based on the earlier-described method to characterize the reaction kinetics of solid substances, the results of this study show that the three samples have practically the same oxidation reactivity. The only effect of the added Al_2O_3 is to increase the specific surface of the catalysts. As a result, the concentration of the product-generating surface defects increases.

The pretreatment with CO_2 of the catalysts containing small amounts of Al_2O_3 increases the activation energy of the Fe oxidation.

Properties of the Surface Defects in Irradiated Silica Gel: The Mechanism of Hydrogen Adsorption

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The structure of the surface centers of irradiated samples of silica gel was determined with the aid of optical and EPR spectral analyses, the distinctive coloration of the centers—due to admixed aluminum—facilitating their identification.

The centers are positively charged holes stabilized by the oxygen atoms adjacent to the atoms of the admixed aluminum. These defects are the centers responsible for irreversible adsorption of hydrogen.

Surface Ionization of Toluene Over Oxidized Molybdenum

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A study of surface ionization of toluene over a heated diode of oxidized molybdenum was carried in a continuous flow unit. The correlations obtained agree well with the hypothesis which explains surface ionization of organic molecules as a process of ionization of the radicals formed by chemical conversion of molecular reactants. The data on the surface ionization of organic molecules may be helpful in determining reaction kinetics.

Some of the Problems of the Physico-Chemical Theory of Ruggedness of Finely-Dispersed Porous Solids, Catalysts, and Sorbents

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Some of the fundamental problems are discussed to determine the mechanics of porous structures, the ruggedness of finely-dispersed solids —in terms of the physico-chemical theory, and the design of mechanical test methods.

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 dehydra-