Possible Mechanisms of Some Homogeneous Catalytic Oxidation-Reduction Reactions

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The action mechanisms of different catalysts in oxidation-reduction reactions are examined, including the formation of a complex to effect transfer of electrical charge. In complexes of this type, an electron is transferred from a filled d-orbital of a catalyst to an anti-bonding orbital of the reactant ($d \rightarrow \rho\delta^*$). This step is followed by rupture of the δ-bond of the reacting molecule.

An electron can also be transferred to a d-orbital of a catalyst either from the π-orbital of the reactant (the $\pi \rightarrow d^*$ mechanism) or, else, from one of the non-bonding orbitals of the reactant (the $\delta \rightarrow d^*$ mechanism).

Realization of any one of the three mechanisms, above, requires appropriate orientation of the atomic orbitals of the catalyst and of the reactant. The substances which can facilitate these orientations, are also the ones which accelerate the reactions examined in this study.

The Essential Changes and Refinements in Classification of Reactions of Thermal Decomposition of Solids

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(No abstract.)

Radiolysis of Water Vapor Over Semiconductor Oxides, ZnO and V_2O_5

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In radiolysis of pure water vapor, the yields of molecular products can be significantly increased in presence of an electronic semiconductor, such as zinc oxide. It is believed that in the case of zinc oxide, the sensibilization reaction occurs via (a) capture of the excited electrons of the semiconductor by the adsorbed molecules of water, and (b) photodecomposition of the water molecules due to thermoluminescence.

Hydrogenation of Carbon Monoxide and Carbon Dioxide Over a Nickel Catalyst

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The results of hydrogenation of the oxides of carbon in small concentrations show that (a) CO_2 (in the reaction system) has no effect on the conversion of CO; (b) hydrogenation of CO_2 is retarded by presence of CO; (c) initiation of CO_2 hydrogenation is observed in the course of transitory hydrogenation of CO on the catalyst surface; (d) the CO_2 hydrogenation rate increases with increasing effect of the CO diffusing from the surface, on the rate of CO methanation; (e) During hydrogenation of CO in the outer zone of free diffusion, the rate of CO_2 hydrogenation should approximate its rate of hydrogenation in the absence of CO.

The Problem of Modification of Ziegler Catalysts

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The effect of modifiers on activity of α-$TiCl_3$ + $(C_2H_5)_3Al$ catalyst (Ti:Al ratio, 1:5 to 1:10) was studied in polymerization of propylene with aromatics and their derivatives benzene, toluene, ethyl benzene, chlorobenzene, naphthalene, tetrahydronaphthalene) at a temperature of 45°. The modifiers used with the α-$TiCl_3$ + $(C_2H_5)_3Al$ catalyst were nucleophylic $(C_2H_5)_3N$ and electrophylic $(iso\text{-}C_4H_9)_3Al$ and $(C_2H_5)_3Al$. The modifying effect of the $(C_2H_5)_3H \cdot\cdot (C_2H_5)_3Al$ complex on α-$TiCl_3$, alone, was also determined.

The results show that the polymerization rate varies with the concentration of each modifier used. In general, the action mechanism of the additives on catalysts of Ziegler-Natta type can be explained in terms of the concepts of heterogeneous catalysis.

Nature of Oxidation of Individual n-Butenes and of Their Mixtures Over Copper Catalysts

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Oxidation of mixtures of n-butenes over copper catalysts was investigated in a continuous-flow unit. The gaseous- and liquid chromatographic analyses show that oxidation of butene-1, butene-2, and of mixtures of isomeric n-butenes proceeds