Possible Mechanisms of Some Homogeneous Catalytic Oxidation-Reduction Reactions

K. B. Yatzeemeersky

Institute of General and Inorganic Chemistry of the Academy of Sciences of USSR

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

V. V. Boldir'yev

Institute of Combustion and Chemical Kinetics of Siberian Division of the Academy of Sciences of USSR

(No abstract.)

Radiolysis of Water Vapor Over Semiconductor Oxides, ZnO and V_2O_5

N. S. Boobir'yeva, P. I. Doleen, A. I. Kononovitch, N. D. Rozenbl'yum

Institution—Not given

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

V. M. Vlas'yenko, G. E. Yuz'yefovitch, M. T. Roosov

L. V. Peesarjevsky Institute of Physical Chemistry of the Ukrainian SSR

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

G. A. Razoova'yev, R. P. Chernovskaya, K. A. Meensker

Institution—Not shown

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

N. N. Popova, F. A. Meel'man

Institute for Coal- and Petro-Chemical Synthesis

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 at about the same rate. The reaction products, too, differ but little in composition. Methyl-vinyl ketone is the principal product, with croton aldehyde being produced in a lesser amount. The yields of saturated carbonyl compounds and of olefin oxides are also significant—particularly, as compared to the product yields in oxidation of isobutylene over the same catalyst.

It is believed that the process of oxidation of *n*-butenes can be best understood from the properties and reactivity of the radicals and of the radical-catalyst complexes which are formed in chemisorption of these hydrocarbons.

Hydrogenation of Sodium Cinnamate Over Skeletal Nickel with Metallic Additives

D. B. Sokol'sky, A. M. Pa'k

Chemistry Department, S. M. Keerov State University in Kazahsk

Catalytic activity of certain skeletal nickel-aluminum alloys, containing added cobalt, rhenium, and molybdenum, was determined in hydrogenation of sodium cinnamate in 0.1 *N* NaOH solution. The results show that of the compositions tested, the alloy containing 10% of added Mo is the most active. Potentiometric measurements show that the bonding energy between hydrogen and the catalyst surface increases with increasing concentration of molybdenum.

Analysis of Kinetic Relationships of Isotopic Exchange in a Molecular Oxygen-Solid Oxide System

V. S. Moosikantov

Institute of Catalysis of Siberian Division of the Academy of Sciences of USSR

The kinetic equations for isotopic exchange in a molecular oxygen-solid oxide system are reduced to conveniently-tabulated forms. Subsequently, a comparison between the observed and calculated kinetic correlations enables to determine with the aid of the experimental data, the rates of isotopic exchanges of different types. The method proposed was used to determine the exchange rates in a molecular oxygen-vanadium pentoxide system.

LETTERS TO THE EDITOR:

Mechanism of Catalysis Over Complex Pd(II) Compounds

A. B. Fasman, V. A. Golodov

Chemistry Department, S. M. Keerov State University in Kazahsk