Chemiluminescence in Slow Chemical Reactions. I. Regularity of Chemiluminescence in Catalytic Oxidation of Ethyl Benzene

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Oxidation of ethyl benzene catalyzed by cobalt acetate is accompanied by chemiluminescence of intensity which is proportional to the reaction rate. Both the intensity of chemiluminescence and the rate of oxidation vary with the temperature and concentrations of the catalyst and of the hydrocarbon.

A kinetic mechanism is proposed to explain basic regularity of chemiluminescence.

Effect of Reaction Components in Polymerization of Ethylene on the EPR Spectra of Chromoaluminosilicate Catalysts

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The change in the narrow line signal of the EPR spectra of a chromoaluminosilicate catalyst in polymerization of ethylene is due to adsorption of water, ethylene, heptane, and cyclohexane on the Cr^{+5} ions. Studies of the EPR spectra of the catalyst enriched with Cr^{53} isotope support the conclusion that the shape of the narrow line is affected by the Cr^{+5} ions.

Isotopic Exchange Between Molecular Oxygen and Carbon Dioxide Over Manganese Dioxide

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A study of isotopic exchange (a) between molecular oxygen and carbon dioxide over manganese dioxide, (b) between these two gases and the oxygen from MnO_2, and (c) in the reaction, $C^{16}O_2 + C^{18}O_2 = 2C^{16}O^{18}O$, leads to the following conclusions:

1. The rate of isotopic oxygen exchange in the oxygen-carbon dioxide system is many times smaller than in the $C^{16}O_2$—$C^{18}O_2$ system *and* is roughly equal to the exchange rate with the oxygen from MnO_2;

2. Isotopic oxygen exchange in an O_2—CO_2 system is believed to occur via the exchange with the oxygen from MnO_2 and that the exchange of molecular oxygen is the limiting step in the reaction.

Non-Equilibrium Kinetics in Ammonia Synthesis

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A study of the ammonia synthesis kinetics over a doubly-promoted iron catalyst was carried out in a recycle-continuous unit at atmospheric and sub-atmospheric pressures to obtain widely varying concentrations of NH_3 in the reaction products. At near-equilibrium concentrations of ammonia, the reaction rates are expressed by Equation (1). At ammonia concentrations well below the corresponding equilibrium values, Equation (7) gives the reaction rates. For the catalyst employed in this study $m = m' = 0.5$.

The results obtained are interpreted to mean that the limiting step concept applies only to near-equilibrium reaction conditions. Consequently, Horiuti and Takesawa's stoichiometric values for the limiting stage of ammonia synthesis are ill-founded.

Soluble Unsaturated Hydrocarbon—Metal Salt Complexes and Their Function in Catalytic Reactions. III. Soluble π-Complexes of Acetylene and Mercury

By O. N. Tiomkeena, R. M. Fleed, and
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The thermodynamics of acetylene-mercury sulfate complex formation in H_2SO_4 solutions was investigated at hydration-promoting conditions using a potentiometric analytical technique. The formation of π-complex, $HgC_2H_2^{2+}$, occurs at the optimum levels of catalytic activity, corresponding to the H_2SO_4 concentrations of 1.5–3.0 mol/l. The hydration process is realized via the π-complex formation and conversion steps. In presence of HgI^{2+} in the solution, conversion of the π-complex to acetaldehyde is the limiting step of the process.

Kinetics of Dimerization of Styrene in Aqueous Solution of Sulfuric Acid. I. Ionization of Styrene in H_2SO_4–H_2O System

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A spectrographic study to correlate process variables in ionization of styrene in aqueous sulfuric acid shows that the relationship is necessarily complex. To derive from the observed data the correlations essential for evaluating the heats of protonization and the basic constants for styrene and phenyl dimethyl carbinol—requires taking into account all of the protolytic equilibria possible in the reaction.

The constants obtained in this study for styrene are compared with the like constants for 1,1-diphenyl ethylene.

General applicability of the correlations established in this study is also discussed.

Effect of Pressure on Redistribution of Hydrogen in Cyclohexane

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The thermodynamic calculations based on experimental data show that at low pressures redistribution of hydrogen in cyclohexane is accompanied by separation of the hydrogen. At a pressure of 10 atm the redistribution temperature is higher than at one atm.

Oxidation-Reduction Effects Upon Activity of Aluminochromate Catalysts. II. Oxidation of Catalysts

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Investigation of methods of regeneration of aluminochromate catalysts shows that the activity of regenerated catalysts depends on their Cr^{+6} content and that the activity can be controlled by regulating the concentration of oxygen in a regeneration gas. The results also show that activity of the aluminochromate catalysts promoted by various oxides is also correlatable with their Cr^{+6} content.

Kinetics of Heterogeneous Catalytic Oxidation of Maleic Anhydride

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The kinetics of catalytic oxidation of maleic anhydride over a vanadium-molybdenum catalyst was investigated at a broad range of operating temperatures and reaction component concentrations. The rate of catalytic oxidation of maleic anhydride is given by a first order equation with respect to the anhydride. The relationship between the temperature and the reaction rate constant is expressed by the equation, $\ln k = 7.27 - (12{,}500/RT)$.

The data obtained for reactions of this type by use of requisite empirical equations are reasonably accurate as long as the phase changes in the catalyst crystals are taken into account.

Heats of Activation in Decomposition of Ammonia Over Catalysts Differing in Chemical Composition. II. Cobalt-, Nickel-, Copper-, and Zirconium-Based Catalysts

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Decomposition of ammonia was studied at atmospheric pressure over smooth-surfaced cobalt, nickel, copper, and zirconium catalysts in a recycle-continuous unit. The results show that specific activity of the Co, Ni, Cu, and Zr catalysts in this reaction decreases in the order mentioned; at the same time, the heats of activation over these catalysts also diminish in the following order: Zr, Co, Ni, Cu. Their specific activity changes with alteration of the interatomic distances, degree of the d-orbital saturation, and the "weight" of d-electrons in the orbitals.

Vapor Phase Catalytic Conversion of Acetylene: II. Thermodynamics of Formation of Complexes of Acetylene and Hydrogen Chloride with Chlorides of Mercury, Bismuth, Cadmium, and Zinc Supported on Activated Carbon

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The experimental data for adsorption of hydrogen chloride and acetylene on the activated carbon catalysts promoted with chlorides of Hg, Bi, Cd, and Zn—were utilized to evaluate the thermodynamic constants for formation of the C_2H_2 and HCl complexes with these salts. The equilibrium constants so obtained for the HCl-metal salt complexes are in good agreement with the constants calculated from the kinetic data for hydrochlorination of acetylene over these catalysts.