

line solid being decomposed. The effect of different factors, including that of heterophase additives, on thermal decomposition of solids is considered from the above point of view. The results by the authors and by other investigators are discussed in the light of the concepts presented.

#### Effect of Ionizing Radiation and of Other Factors on Rate of Topochemical Decomposition of Various Inorganic Compounds

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Ionizing radiation and composition of a gaseous reactant affect differently the decomposition rates of hydroxides of magnesium and aluminum as compared to the effect of these factors on the rates of decomposition of oxalates of copper and nickel. Decomposition of magnesium and aluminum hydroxides is characterized by the presence of apparent induction periods and by the oxidation-reduction insensitivity of the gaseous media. Preirradiation of the hydroxides with  $\gamma$ - and  $\beta$ -rays has practically no effect on the subsequent course of their thermal decomposition. The decomposition of oxalates of copper and nickel is also characterized by noticeable induction periods and, in addition, by sensitivity to the oxidation-reduction properties of the gaseous media. Preirradiation of the oxalates shortens the induction periods and markedly increases the subsequent thermal decomposition rates.

Electronic (donor-acceptor) properties of the copper and nickel oxalates in the decomposition reactions are hypothesized on the basis of the experimental data of this study.

#### Activity and Electronic Properties of Complex Catalysts Used in Oxidation of Hydrocarbons

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Electroconductivities and electron work functions of certain mixed vanadia-molybdena catalysts were determined. Electro-physical and structural properties of these catalysts are listed alongside their selectivity characteristics in hydrocarbon oxidation reactions. The optimum component concentrations of the mixed catalysts are functions of the composition and preparation history of each system. Thus, selectivity of the mixed catalysts can be controlled by changing

electronic properties of the surface via incorporation of additives with different electronegativity properties. Selectivity of the catalytic systems produced by chemical combination of the two oxides depends upon relative distribution of the metallic and oxygen ions on the catalytic surface. Finally, with the multiphase-type systems, each of the above two factors bears importantly on the catalytic selectivity.

#### Effect of Reactant Mixtures on Catalytic Properties of Copper Catalysts in Oxidation of Propylene

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Catalytic properties of metallic copper and of copper oxides were determined by studying the mechanism of formation of catalytically active surfaces in oxidation of propylene and acrolein. The results show that with the copper oxides, a catalytically active surface is formed by the process involving transition of  $\text{CuO}$  to  $\text{Cu}_2\text{O}$ . As a result, productivity of the catalyst increases with respect to acrolein and decreases with respect to carbon dioxide. Stabilization of catalytic activity of the copper oxide catalyst occurs faster than equilibration of its chemical composition. Selectivity of the catalyst with respect to carbonyl compounds decreases with increasing oxygen content, i.e. with increasing degree of copper oxidation.

#### Investigation of Nature of Irreversible Chemisorption on Semiconductors

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Interaction of chemisorbates with the additives dispersed in semi-conductive adsorbents is being investigated to determine effects of the additives on kinetics and partial irreversibility of the chemisorption reactions.

#### Relationship between Catalytic Properties and Electronic Structure of Iron-Cobalt Catalysts

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A relationship was established between electronic structure of iron-cobalt alloys and their

catalytic activity in decomposition of ammonia. The best structure is characterized by the presence of 2.37-2.40 unpaired d-electrons per atom of the catalyst. Formation of chemical compounds (superstructures) in the alloys results in sharp deactivation of the catalyst.

#### Catalytic Activity of Manganese Dioxide in Isotopic Exchange of Molecular Oxygen

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A study of kinetics of isotopic exchange in molecular oxygen over manganese dioxide was carried out at temperatures of  $-196^{\circ}$  to  $+360^{\circ}$  and oxygen pressures of 2-240 mm Hg. With the catalyst pretreated in vacuum at temperatures of  $350^{\circ}$  and  $550^{\circ}$ , the exchange reaction takes place in a wide temperature range of  $-78^{\circ}$  to  $+360^{\circ}$ . At temperatures of  $25^{\circ}$ - $50^{\circ}$ , and higher, activity of the catalyst in oxygen decreases with the on-stream time; at temperatures upwards of  $200^{\circ}$ - $250^{\circ}$ , stabilization of its activity is attained very quickly. At low temperatures, activation energy of the isotopic exchange is 3.7 kcal/mol and the order of the reaction with respect to the oxygen is 0.64. At high temperatures, activation energy of the exchange reaction over the catalyst with stationary activity is 18 kcal/mol.

At low temperatures, the exchange in molecular oxygen is not accompanied by isotopic exchange with the oxygen of the manganese dioxide. At high temperatures, the homomolecular exchange reaction takes place via exchange with the lattice oxygen.

#### Calculation of Reaction Rate Constants in Ammonia Synthesis Over a Reversibly Steam-Poisoned Catalyst in Continuous Flow Reactors

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The equation to describe kinetics of ammonia synthesis over a reversibly steam-poisoned catalyst was integrated for continuous operation at low and high pressures. Convenient calculation methods are described to obtain approximated numerical data. The published experimental data for operation in continuous-flow systems validate reliability of the subject equation at operating pressures up to 350 atm. Based on the kinetic equation, a discussion is presented regarding the

effect of steam concentration in a reaction mixture on the extent of the catalyst poisoning.

#### Dealkylation of n-Amylbenzene Over a Silica-Alumina Catalyst

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The results of cracking of n-amylbenzene over a commercial Houdry-type silica-alumina catalyst show that two side-reactions: dehydrocyclization and splitting of the carbon-carbon bond, occur concurrently with the principal reaction of splitting off of the alkyl group from the benzene ring. Apparent activation energy of the dealkylation reaction is 32 kcal/mol.

#### Kinetics of Dehydrogenation of Cyclohexane in a Non-gradient System

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Dehydrogenation of cyclohexane at low conversion levels was investigated in a recycle-continuous operation, using a nickel/zinc oxide catalyst at temperatures of  $263^{\circ}$  and  $275^{\circ}$  and cyclohexane partial pressures of 100-110 mm Hg, based on the concentration of this component in the cyclohexane-benzene-hydrogen charge mixture.

The reaction rate,  $w$ , is not decreased by addition of the outside hydrogen. At the conditions employed, the rate is expressed by the equation for reactions of the zero order and also by the equation,  $w = kP_{C_6H_{12}}^{0.5}$ . On the other hand, the reaction rate is retarded by addition of benzene to the cyclohexane feed. During the initial period of operation at the  $C_6H_6$  partial pressures of 42-210 mm Hg, the reaction rate is expressed by the equation,  $w = P_{C_6H_{12}}/P_{C_6H_6}^{0.5}$ . At temperatures of  $246^{\circ}$ - $275^{\circ}$ , the added hydrogen does not affect the reaction rate-temperature correlation.

The mechanism of the reaction is considered in the light of the experimental results and of the concepts as to the reaction course over a non-homogeneous catalytic surface. From the latter viewpoint, the reaction is regarded to proceed via two slow stages, with the alteration of the reaction mechanism occurring upon addition of sufficient amounts of benzene.