

dividual kinetic variables of the process (the rate constants and the activation energies and entropies) and: composition, X, of the anionic solutions, concentration,  $MX_2$ , of the salts used, and the nature of the central ion, M. The reaction was found to be of the first order with respect to both the pheophytins and the salts. A brief discussion of the correlations based on the results of this study is included.

#### Relationship Between Electronic Structure of Cobalt-Nickel Catalysts and Their Catalytic Properties

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The experimentally-determined data of catalytic properties of cobalt-nickel alloys show that specific catalytic activities, electron work functions, and numbers of the unpaired *d*-electrons change with changes in the chemical composition of these alloys.

#### Kinetics of Benzene Hydrogenation Over a Nickel Catalyst: Reactions in the Kinetic Region

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A review of the literature on hydrogenation of benzene reveals contradictory results. Possible reasons for the contradictions were examined. The hydrogenation kinetics were determined experimentally in a recycle-continuous unit at widely-different operating conditions. The results show that the reaction order changes with operating temperature due to changes in the adsorption equilibria. Analysis of the information obtained by substitution of pertinent experimental data into the kinetic equations for the feasible reaction mechanisms, resulted in selection of the most satisfactory scheme of the reaction course. The calculations to select the optimum scheme were carried with the aid of linear programming methods and electronic computers.

#### Catalytic Properties of NiO in Homomolecular Oxygen Exchange Reactions

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The homomolecular isotopic oxygen exchange reaction,  $O_2^{16} + O_2^{18} = 2O^{16}O^{18}$ , was investigated over "pure" NiO and over the NiO containing

admixed Li and In at temperatures of 25° and 275°–400° and oxygen pressures of 10–160 mm Hg. The results show that at the temperatures studied NiO is catalytically active and that the additives used materially alter its catalytic properties. The initial rate of the exchange reaction is significantly greater at a room temperature than at the elevated temperatures.

#### Kinetics of Cyclohexane Dehydrogenation Over Chromic Oxide in a Non-Gradient System

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The results of a study of kinetics of cyclohexane dehydrogenation over chromic oxide in a recycle-continuous unit show that the reaction is of the first order and that its activation energy is 41.5 kcal/mol. The results obtained are discussed on the basis of a two-step scheme proposed for the process.

#### Effect of System pH on Kinetics of Hydrogenation Reactions Over a Palladium Catalyst

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The information supplied by the Pd/BaSO<sub>4</sub> (5% Pd) "charge" curves at pH of 1.2 and 13.0, leads to the conclusion that energy of the Pd—H bond increases with increasing pH of the reaction system. Compared to Pd-black, the catalyst studied contains a greater amount of adsorbed hydrogen and a smaller amount of dissolved hydrogen.

The rates of hydrogenation of hexene-1 and of cyclohexene reactants, which alter but little the catalyst potential, are at the maximum in an acidic media, the hydrogenation being realized via the weakly-bonded hydrogen.

In hydrogenation of phenylacetylene and nitrobenzene, which strongly displace the catalyst potential, the system pH has no effect on the reaction rates.

#### Homomolecular and Isotopic Oxygen Exchange on Gadolinium Oxide

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Catalytic activity of gadolinium oxide in isotopic and homomolecular oxygen exchange

reactions was determined at widely different temperatures. At high temperatures, the rates of the two reactions are approximately the same and their energies of activation are equal. This finding indicates that at high temperatures the limiting step is identical for both reactions.

Calcination of the catalyst in vacuum at a temperature of 700° imparts to it high catalytic activity—even at -78°—in the homomolecular exchange; however, subsequent heating of the catalyst in oxygen at temperatures of over 200° completely deactivates the catalyst. At low temperatures, the exchange reactions occur in two temperature regions, which are characterized by different activation energies.

#### Effect of Surface Acidity of Catalysts on Rate of Polymerization of Three-Membered Heterocyclics

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Polymerization of ethylene oxide, propylene oxide, and ethylenimine in gaseous phase was determined gravimetrically over several  $\text{Al}_2\text{O}_3$ — and  $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ —based heterogeneous catalysts at temperatures of 0°–95°. Pretreatment of the  $\text{Al}_2\text{O}_3$  base with HCl and  $\text{BF}_3$  decreases activity of the  $\text{Al}_2\text{O}_3$ -based catalysts in polymerization of the olefin oxides and increases it in polymerization of ethylenimine. Silica-alumina is less active catalytically than aluminum oxide in polymerization of the olefin oxides. Calcination of this support at 800°–900° increases its activity in these reactions. Replacement of the  $\text{H}^+$  ions on the silica-alumina surface with  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ , and  $\text{Sr}^{+2}$  increases activity of this support in polymerization of the olefin oxides but decreases it in polymerization of ethylenimine. The results obtained in the catalytic polymerization of the olefin oxides are attributed to progress of the reaction by the coordination mechanism and those in the polymerization of ethylenimine, to progress by the proton-acidic mechanism.

#### Mechanism and Kinetics of Catalytic Conversion of Acetylene: Kinetics of Acetonitrile Synthesis from Acetylene and Ammonia Over a $\text{ZnO}/\text{Al}_2\text{O}_3$ Catalyst

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A study of kinetics of acetonitrile synthesis from acetylene and ammonia was carried out in a

nongradient reaction system, using a zinc oxide catalyst at temperatures of 340°–435°. The kinetic equation based on the experimental data satisfactorily describes the reaction at the conditions studied. Analysis of the experimental data and of the kinetic equation validates the assumption that the limiting step of the process is dehydrogenation of the adsorbed intermediate product, ethylideneimine, which is formed by the interaction of acetylene with ammonia.

#### Kinetics of Cyclohexane Splitting by Steam Over Nickel Catalysts

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Activity of a Ni/C and a Ni/SiO<sub>2</sub> catalysts was investigated in cyclohexane-water reaction at temperatures of 400°–460°. Despite the near-equal activity of the two catalysts in dehydrogenation of cyclohexane, the Ni/C catalyst—unlike to the Ni/SiO<sub>2</sub> catalyst—is totally inactive in the presence of water. Over the Ni/SiO<sub>2</sub> catalyst, the reaction is of the zero order with respect to the cyclohexane; with respect to the water, the order of the reaction changes with increasing water concentration from that of the first to that of the zero. Activation energy of the cyclohexane-water reaction over the Ni/SiO<sub>2</sub> catalyst is 22–24 kcal/mol.

#### Kinetics of Copolymerization Reactions in Continuous Flow Systems at Conditions of Ideal Mixing

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The kinetics of copolymerization reactions in continuous flow systems were analyzed at the conditions of ideal mixing in the reactor. The equations derived on the basis of the data of the batch-type studies are adequate to calculate conversion, composition of the copolymer, and the degree of polymerization at each specified set of conditions. These equations also aid in determining the parameters of the processing variables to obtain the copolymers with properties desired. The sample calculations are shown for copolymerization of styrene with methylmethacrylate in the presence of azoisobutyric acid at temperatures of 60°–80°.