

**Non-Equilibrium Kinetics in Ammonia Synthesis**

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Based on experimental data, a generalized equation was derived to express kinetics of ammonia synthesis at any partial pressure of  $\text{NH}_3$  (Ref. 38). This equation is based on the concept that chemisorption of nitrogen and addition of molecular hydrogen to the chemisorbed nitrogen are the slowest steps in the reaction. At normal reaction conditions this generalized kinetic equation becomes identical with that proposed earlier (Ref. 1).

The value of calculated activation energy, including the effects of the two controlling stages of the process, remains constant at a wide temperature range of 325° to 550°.

**Duration of Induction Periods in Homogeneous Catalytic Reactions in Presence of Hydrogen Peroxide**

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Homogeneous catalytic reactions were studied to correlate the length of their induction periods with the catalyst, hydrogen peroxide and iodide, concentrations and with acidity of the reacting mixtures.

Equations are proposed to describe kinetics of activation of tungstate and molybdate catalysts by the interaction of hydrogen peroxide and iodide in an acidic medium. Calculated values of the catalyst activation constant are also presented.

**Reactions of  $\alpha$ -Oxides: Kinetics of Secondary Reactions in Ethylene Oxide-Acetic Acid Interaction**

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The results of a study of secondary reaction kinetics—comprising the interaction of ethylene oxide and acetic acid, the primary reactants, with monoacetate glycol, the primary product—enabled to determine similarities and differences of the acid-base mechanisms of the two parallel processes, to compare their reaction rates and activation energies, and to describe in detail the reaction steps and their sequence in each process.

**Kinetic Principles and Mechanism of Dimerization of Styrene in Aqueous Solutions of Sulfuric Acid**

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Kinetics of acid-catalyzed dimerization of styrene in aqueous sulfuric acid solutions was studied to produce a linear dimer, 1,3-diphenyl butene-1. The results show that this reaction is practically irreversible and that the interaction between molecular styrene and the carbonium ions is the rate-limiting step of the process.

Lack of agreement between the anticipated and the experimentally-determined relationship of the reaction rates to acidity of the medium is attributed to the participation of the reacting particles in the complex protolytic equilibrium of the process. These observations are supported by the data on ionization of styrene in this reaction system. An estimated value of true activation energy of dimerization of styrene is given.

**Kinetics of Cracking of Cumene Over Aluminum Oxide Activated by Boron Fluoride**

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The effects of varying the amounts of  $\text{BF}_3$  chemisorbed on a commercial-grade  $\text{Al}_2\text{O}_3$  and of the chemisorption temperature upon catalytic activity were investigated in cumene cracking reaction. The results of this study show that catalytic activity is a function of the  $\text{BF}_3$  content and that it is practically independent of the chemisorption temperature.

This study of cumene cracking reaction kinetics was carried out in a continuous-flow reactor at temperatures of 371°–492° over two  $\text{BF}_3/\text{Al}_2\text{O}_3$  samples differing in activity. The activation energy and a range of conditions valid for the reaction were also determined.

**Effect of Regeneration Conditions on Activity and Composition of Aluminochromate Catalysts**

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The effects of various regeneration conditions on activity of an aluminochromate catalyst were investigated in dehydrogenation of butane. A

correlation between catalytic activity and the chromium trioxide content is shown and possible reaction mechanism is described.

### Kinetics of Liquid Phase Dehydrogenation of Isopropyl Alcohol

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Experimental data are presented covering kinetics of liquid phase dehydrogenation of isopropyl alcohol over a skeletal nickel catalyst in presence of an outside diffusion-retarding agent. The results over the diffusion-limited catalyst are compared with the earlier-published data on the unretarded catalyst.

### Hydration of Tertiary Amylenes Over Cationite KY-2 and Nature of Concurrent Reactions

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The results of this investigation demonstrate that hydration, polymerization, and isomerization of tertiary amylenes do take place simultaneously in presence of the H-type cationite KY-2.

Polymerization of amylenes, a side-reaction over the hydrated cationite, is the primary reaction over the dehydrated resin.

Various sulfocationites selectively catalyze hydration of tertiary amylenes in multicomponent mixtures of  $C_7$  hydrocarbons, a fact advantageous in production of tertiary amyl alcohol. Prolonged use of KY-2 resin (288 hrs at 75°) to catalyze this reaction results in insignificant irreversible decrease of its exchange capacity (2.5%) and reduction in particle size.

### Effect of Conditions of Preparation of Zinc Oxide Catalysts with and without Added Indium and Gallium Upon Catalytic Properties in Homomolecular Isotopic Oxygen Exchange Reaction

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The effect of conditions of preparation of zinc oxide-based catalysts upon catalytic activity were

determined in the reaction,  $^{16}O_2 + ^{18}O_2 = 2 ^{16}O^{18}O$ . The results show that increasing of ZnO calcination temperature increases its catalytic activity, apparently, as a result of increasing concentration of interstitial zinc.

Addition of indium in 0.25 and 0.5 atom per cent, followed by a 30-hour calcination at 850° decreases the homomolecular oxygen exchange rate. Addition of gallium in the like amounts has the same effect.

Raising the catalyst (ZnO + 0.5 at.% Ga) calcination temperature from 850° to 1200° decreases the apparent activation energy of the reaction from 40.1 to 24.5 kcal/mole.

### Vapor Phase Catalytic Conversion of Acetylene: Mechanism and Kinetics of Catalytic Vapor Phase Hydrochlorination of Acetylene Over Supported Chlorides of Hg(II), Cd, Zn, Bi

By A. I. GELBSHTEIN, G. G. SHCHEGLOVA,  
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Kinetics of vapor phase catalytic hydrochlorination of acetylene was studied in a recycle-continuous unit. The catalysts used in this study were  $MeCl_n$  salts [ $Me = Hg(II)$ , or Cd, or Zn, or Bi] supported on activated AP-3 carbon and, also, the activated carbon containing  $HCl$  adsorbed on its surface.

The results of this kinetic study and published thermodynamic data on the formation of  $MeCl_n - C_2H_2 - HCl$  complexes (1,2), provided a basis to formulate a mechanism for catalytic hydrochlorination of acetylene and to explain the deviations from the basic mechanism due to the differences in the catalytic activity of the added salts.

### Yield Curve Equation of Continuous Equilibrium Sorption of Adsorbates by Adsorbent Beds

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An equation was derived and critically checked to express processing yields as linear isotherms in an equilibrium sorptive-chromatographic process, employing the frontal analytical technique.

To derive the equation a variant of a layer-to-