

### Rare-Earth Oxides as Catalysts for the Oxidation of Propylene

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Oxides of lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, terbium, dysprosium, holmium, and erbium catalyze the oxidation of propylene to CO<sub>2</sub> and H<sub>2</sub>O plus small quantities of acrolein. The authors have determined the activation energies for this complete oxidation of propylene on oxides of Nd, Sm, Gd, Dy, Ho, and Er. Comparison of these results with data on isotopic exchange (of oxygen) between O<sub>2</sub> and the rare earth oxides leads to the conclusion that the activity of these oxides in both of the above reactions is governed by the energy of the bond between the O<sub>2</sub> and the catalytic surface.

### Catalysis of Decomposition of Formic Acid by Heat-Treated Polyvinyl Ketone

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The authors have studied the kinetics of dehydrogenation and dehydration of formic acid over PVK which had been heat-treated at 400°–870°C. If the heat-treatment takes place under N<sub>2</sub>, then the activation energy for dehydrogenation is 28 ± 1 kcal/mole. There was no direct relationship between changes in electronic characteristics of the heat-treated PVK (such as electric conductivity, work function, and concentration of paramagnetic sites) and the activity. Nevertheless, the data on the effect of the atmosphere surrounding the PVK during the heat treatment allow some conclusion about the electronic mechanism of formic acid dehydration.

### Effect of the Nature of the Promoter on the Activity of the Chromia-Alumina Catalyst for Isopentane Dehydrogenation

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The authors have studied the dehydrogenation of isopentane to isopentenes (550°C; atmospheric pressure; space velocity of 1 hr<sup>-1</sup>; flow system)

over chromia-alumina catalysts promoted by elements of Groups I (Li, Na, K, Rb, Cs) and II (Be, Mg, Ca, Sr, Ba). Alkali promoters increase the dehydrogenation activity and decrease the activity for rearrangement and cracking. Beryllium and magnesium oxides have a smaller effect on the above reactions. The lithium-promoted catalyst proved to be active, selective, and to require low contact times. Its activity for rearrangement and cracking is low.

### Isomerization of Cyclenes on Aluminum Oxide. I. Isomerization of 1-Methyl-1-Cyclohexene

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The authors used flow and pulse chromatographic techniques to study conversions of 1-methyl-1-cyclohexene, varying the temperature and the contact time. The results obtained from the pulse unit were identical to those obtained in the flow system. Below 400°C, the main reaction is isomerization. At low temperatures most of the product consists of 1-methyl-3-cyclohexene. Above 220°C, molecular rearrangement takes place: the primary product is 1-ethyl-1-cyclopentene. As the temperature and contact time are increased, this reaction starts to yield dimethylcyclopentenes as the main products. From the kinetic curves obtained, the authors surmise that 1-ethyl-1-cyclopentene and 1-methyl-3-cyclohexene are intermediates in the isomerization of the starting 1-methyl-1-cyclohexene.

### Kinetics of SO<sub>2</sub> Oxidation on Vanadium Catalysts

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The authors used a flow-recycle technique to study the oxidation of SO<sub>2</sub> on a BAV catalyst at 485°C. The applicability of known kinetic equations was confirmed, and the deviations from them were noted. An equation describing the process under the above conditions is given.

### The Mechanism of Cumene Oxidation on Copper Phthalocyanine

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Kinetics of decomposition of cumene hydroperoxide on copper phthalocyanine were studied.

Between 40° and 70°C, the decomposition is unimolecular:

$$k_{\text{specific}} = 1.5 \times 10^8 \exp -(13200/RT) \text{ sec}^{-1}\text{m}^2.$$

Between 90° and 110°C, the biomolecular mechanism takes over:

$$k_{\text{specific}} = 3.6 \times 10^{10} \exp -(24600/RT) \text{ liters/mole-sec-m}^2.$$

Data on products and changes of catalytic activity with time are given. The authors also compared data obtained by the inhibitor technique with those obtained by the direct decomposition of the hydroperoxide.

#### Modification of the Iron Catalyst for Ammonia Synthesis by Certain Metals

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The authors have studied the activities and work functions of industrial type GK catalysts for the ammonia synthesis. Various concentrations of Cu, Ni, and Co were introduced, and these caused changes in activity which could be correlated with changes in the work function. Addition of cobalt (0-4%) does not alter either the  $\Delta\phi$  or the  $\log k_{\text{specific}}$ , but Ni and Cu increase the  $\Delta\phi$  and decrease the  $k_{\text{specific}}$ .

#### Integrated Study of the Porosity of Catalysts. I. Some Questions on the Present Status of the Sorption Technique

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Analysis of the capillary condensation technique showed that its accuracy in determining the porosity of solids can be improved if one knows the shape of the pores; the latter can be found by electron microscopy. The author also analyzed the methods for selecting (for calculations) one branch of the capillary condensation hysteresis curve, as well as the selection of adsorbates. He shows that much better results are obtained by using the desorption data.

#### The Effect of Adsorption of Metal Vapor on the Conductivity of Zinc Oxide Films

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Vapors of Na, Zn, and In were adsorbed on thin zinc oxide films, and the conductivity of the latter was then measured. The kinetics of ZnO conductivity under the influence of metal vapors were studied, and it was shown that all metals act as donors on the ZnO surface. Their behavior is extremely complex. The thin ZnO film technique permits detection of very small concentrations (less than  $10^7$ - $10^8$  atoms/cm<sup>3</sup>) of metal atoms. By a probe technique the authors have measured the evaporation of these nonstoichiometric Na atoms from the ZnO surface, and have determined the heats of vaporization.

#### Supported Chromium Oxide Catalysts for Polymerization of Ethylene. The Reason for Stabilization of Hexavalent Chromium

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Spectral analysis of these catalysts shows that deposition of chromium trioxide on silica gel or an aluminum silicate with a low aluminum content leads to formation of bichromate ions on the surface, but that chromate ions are formed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. It is this formation of salts of chromic acids that stabilizes the hexavalent chromium upon the deposition of chromium trioxide on supports.

#### Effect of the Preparative Technique on the Porosity and Strength of Catalysts and Supports. I. Silica Gels of Uniform Porosity

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The authors have studied the porosity and strength of silica gels of uniform porosity as functions of the moisture content of the paste used as the starting material, the activation treatment and the calcining temperature. It was found that at lower moisture contents in the paste, the volume and radius of the pores decreases. The increase in strength accompanying this phenomenon is due to the increased number of contacts between individual globules, with no reduction in strength