

tarded by the additives in the following order:  $Cd^{++} < Hg^{++} < Pb^{++}$ .

Compared to  $Cd^{++}$ ,  $Pb^{++}$  increases the loss of dielectric properties of silver oxalate to a lesser degree and alters its ionic conductivity to a greater degree. The most probable reason for the quantitatively different effects of these additives is their increasingly stronger ionic bonding ( $Cd^{++} \rightarrow Hg^{++} \rightarrow Pb^{++}$ ) with the charge-compensating cationic vacancies.

### Principles of Formation of High Melting Point Compounds of Desired Catalytic Properties

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Catalytic properties of the transition series metals and of their alloys and reaction products with non-metals (boron, carbon, nitrogen, and silicon) were examined from the standpoint of relative degree of fill up of the atomic d-electron shells of these metals and the fillage of the d-shells on forming alloys and compounds by combination with the electron-donating non-metallic elements.

The discussion also points out the role of different types of atomic chemical bonds due to combination of alloys and compounds with the non-metallic elements, and the role of isolated structural complexes which are formed by the nonmetallic atoms within crystalline lattices. The factors responsible for low catalytic activity of non-metallic compounds are cited.

### Effect of Adsorbed Oxygen on Changes in Zinc Oxide Conductivity with Temperature

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The results of simultaneous measurements of conductivity of zinc oxide and of oxygen gas pressure in a system at constant volume and at 20°–200° show that the anomalous decrease in conductivity of the oxide is accompanied by partial desorption of the oxygen. This phenomenon may be due to transition of the chemisorbed oxygen to a more highly charged state and to a simultaneous shift of the adsorption equilibrium toward desorption. The abnormally weak effect on the conductivity due to the oxygen adsorbed at temperatures of over 200°C is attributed to a gradual consumption of the system oxygen in oxidizing organic impurities.

### EPR Studies of Structure of Active Centers of Chromium Oxide Catalysts for Polymerization of Ethylene

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A structural model is proposed for active centers in chromium oxide on silica gel catalysts for use in extensive polymerization of ethylene. The active centers are the  $Cr^{+5}$  ions stabilized on the carrier surface. It is suggested that the  $Cr^{+5}$  ions partially displace the Si atoms of the silica oxide tetrahedra in the surface layer of silica gel. As a result, the tetrahedra are deformed, causing anisotropy of  $g$ -factor of the EPR signals. The parameters of the signals, which were calculated on the basis of the model proposed, are in good agreement with the experimental results. The model also serves to explain the changes in the EPR signals due to poisoning of the catalysts by alkalis.

### Electron Work Functions of Titanium Dioxide and of Its Solid Solutions in Chemisorption and Catalysis

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The work functions of  $TiO_2$  and of its solid solutions in  $WO_3$  and  $Fe_2O_3$  were determined in vacuum. Changes in the work function values were determined in chemisorbing gases of the electron-donor and electron-acceptor types, in oxidizing carbon monoxide, and in decomposing isopropyl alcohol. Based on the experimental results, feasible mechanisms are considered for the chemisorption and catalysis reactions over the catalysts studied.

### Reactions of $\alpha$ -Oxides: Acid- and Auto-Catalyses in Reactions of Ethylene Oxide with Amines

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This study of reaction kinetics of ethylene oxide with aniline and cyclohexylamine solvents demonstrates that these reactions are auto-catalyzed by the aminoalcohol and that they are accelerated by water and alcohols in proportion to their relative acidity.

Diverse catalytic effects of many acids, such as phenol and perchloric acid, are shown to be func-

tions of their strength and structural properties. Determinations of the nature of the acids dissolved in amines leads to the conclusion that in different cases the catalytic action may be due to any, or all, of the following acid forms: free acids; complexes having hydrogen bonds and/or proton donor characteristics; ammonia-substituting ions. It appears that catalytic activity of the first three forms varies with the nature of the acid.

A mechanism is proposed to explain acceleration of the reaction by use of added acids and hydroxyl-containing compounds.

#### Praseodymium Oxide as Catalyst for Dehydration of Alcohols and Dehydrogenation of Alcohols and Tetralin

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Catalytic activity of praseodymium oxide is greater in dehydrogenation than dehydration of ethyl, n-propyl, isobutyl, and secondary isopropyl alcohols. With the primary alcohols, its dehydrogenation activity increases with increasing molecular weight.

Compared to allylic substituents at a  $\beta$ -carbon atom, those at an  $\alpha$ -carbon have greater effect on the activation energies of dehydrogenation and dehydration of alcohols and on the energies of C, H, and O bonding with praseodymium oxide.

#### Study of Kinetics of Heterogeneous Catalytic Reactions in a Recycle-Continuous Process: Cracking of Cumene Over Aluminosilicate Catalysts

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A study was made of cracking cumene over two samples of aluminosilicate catalysts which were prepared by different methods. The results show that kinetic parameters of the process investigated depend substantially on the "biography" of the catalysts.

#### Effect of Manganese Dioxide Pretreatment Temperatures on Rate of Isotopic Oxygen Exchange

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Catalytic activity of several samples of manganese dioxide pretreated in vacuum at temperatures of 350°, 450°, and 550° was determined in

the following reactions: isotopic exchange of the catalytic oxygen with molecular oxygen; homomolecular oxygen exchange; oxidation of CO at a pressure of 10 mm Hg and temperatures of 25° to 350°.

Increasing the catalyst pretreating temperature increases its activity in the isotopic oxygen exchange reaction and improves its homogeneity. Within a monolayer, the rate of isotopic oxygen exchange with the oxide oxygen falls off exponentially with the degree of completion. At temperatures below 300°, the oxygen exchange rates are smaller—and the corresponding activation energies are larger—than those of CO oxidation.

The homomolecular exchange of oxygen occurs in a high and a near-room temperature regions. Over freshly-pretreated samples of the catalyst, the rates of homomolecular exchange are greater at 25°–34° than at 200°. The near-room temperature homomolecular rates decrease with increasing time of contact with oxygen and are comparable to the CO oxidation rate.

#### Adsorption of Krypton on Thermally-Treated Platinum Films

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A study of the effect of thermal pretreatment of platinum films at temperatures of 100°–740° on their adsorptive properties shows that the overall film surface is either increased or remains unchanged. However, the pretreatment improves homogeneity of the surface.

Thermal pretreatment of platinum films on glass at a temperature of 630° increases the surface area; however, subsequent cooling to below a room temperature decreases the area—possibly, due to the competing effects of formation and disappearance of the surface defects, particularly, of the microcracks.

#### Effect of Non-Stoichiometric Amounts of Sulfur on Activity of Sulfide Catalysts

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Comparisons of the product compositions from hydrogenation of benzene over MoS<sub>2</sub>/activated carbon and WS<sub>2</sub> catalysts show that the excess