Activation and Ageing of a Chromium Oxide-Iron-Zinc Catalyst in a Full-Scale Commercial Reactor

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The authors have studied the activities and ageing of an industrial chromia-iron-zinc catalyst for the dehydrogenation of butylenes. They showed that 72% of the fresh catalyst consists of very fine spinel particles. Activation involves formation of a relatively stable crystalline lattice with high internal surface, while ageing involves crystallization with sintering, which results in lower specific surface.

The life and the required quantity of the catalyst depend on the specific surface which the catalyst retains following activation, and the rate at which this surface decreases during operation. The initial specific surface depends on the preparation technique, but after that it is a function of the activation and operating temperatures. Some recommendations for increasing the life of the catalyst are given.

Effect of Surface Conditions and Volume of TiO_2 on the Dissociation Adsorption of N_2O

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Partial reoxidation of reduced TiO_2 gives an "oxidized layer" on the surface; anionic holes in the latter affect the adsorption of N_2O. In samples with thermally induced defect structure, even an insignificant quantity of oxygen inhibits the adsorption of N_2O. This is apparently due to the fast disappearance of anionic holes from the surface. The latter are more active in N_2O adsorption than the interstitial Ti^{3+}.

Charging of Surfaces of Oxidation Catalysts during Adsorption of Mixtures of Propylene and Oxygen

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Studies of charging of surfaces of several oxidation catalysts during chemisorption of mixtures of propylene and oxygen revealed differences in the behavior of gases, depending on whether the catalyst is a mild one or whether it produces extensive oxidation. The authors suggest that the oxidation proceeds via oxygen-hydrocarbon complexes. These bear a positive change in the case of a mild catalyst, and a negative one in the case of extensive oxidation catalysts.

Comparison of Various Chromatographic Techniques for Determining the Specific Surfaces of Solids by Argon Adsorption

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The various presently used techniques have been compared. The calculations of the surface based on the retained volume or on the isotherm calculated from the distorted side of the chromatogram are useless at low temperatures because of poor accuracy. Both thermal desorption and frontal analysis allow measurement of surfaces by argon adsorption regardless of the porosity of a given solid. However, thermal desorption is preferable.

Preparation of Silica Gels with Predetermined Porous Structures

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The theory of formation of silica gel structures is presented. The factors governing the nature of the porous structure are characterized in terms of their influence on the size and packing density of particles constituting that structure. Based on the above, the authors show the various ways of obtaining silica gels of predetermined geometrical structure.

Internal Diffusion Effects in the Pulse-Chromatography Mode of Operation of a Reactor

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The authors analyze first-order heterogeneous catalytic reactions proceeding under conditions of pulse chromatography, where the gas diffuses into the pores. They show that this diffusion, operating in conjunction with the chemical reaction, reduces the average residence time of unreacted molecules in the reactor, as well as the width of the chromatographic peak. The authors studied the adsorption and diffusion of butane through the pores of a chromium-aluminum catalyst at 90°–154°C. In this range, chemisorption is not the rate-controlling step. The effective coefficient of diffusion of butane through the pores was also determined.

NOTES

Experimental Study of Dissociation of Excited Ions

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The authors ionized ethylene, ethane, *n*-hexane, and toluene by bombardment with 2 KeV electrons and measured the rates of decay of the resulting ions. Most of the excited ions decay in less than 10^{-9}–10^{-10} sec; however, several complex ions decay at lower rates. The authors conclude that the usual mass spectra are not always suitable for determining the mechanism of a complex radiation-chemical reaction.

Mechanism of Action of Elemento-Organic Antidetonating Substances

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It is suggested that the antidetonating properties of organic compounds of Pb, Tl, Co, Mn, Fe, Ni, Cu, Bi, Te, and Se are governed by the heat of formation of their oxides (Q). If Q is less than some critical value, then the unbranched $RO_2^{\cdot}$-annihilating oxidation: $R\cdot + O_2 \rightarrow RO_2^{\cdot}$; $RO_2^{\cdot} + M \rightarrow RO\cdot + MO$; $MO + R\cdot \rightarrow M + RO\cdot$ (where M is a metal or its lowest oxide) is energetically more favorable than the branched (degenerate) oxidation going via $RO_2^{\cdot}$. The elements whose organic compounds have antidetonating properties all have values of $Q \leqslant 69$ kcal/mole.

Radical Formation in Low-Temperature Radiolysis of Benzoyl Peroxide

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The low-temperature radiolysis of benzoyl peroxide was investigated by ESR and mass spectra. The primary gaseous radiolysis product is CO_2 (yield = 6.4 liters/100 eV). The hydrogen yield is 0.15 liter/100 eV. The main primary free radical is the phenyl. It undergoes a secondary reaction, adding to the benzoyl peroxide in a position *para* to the substituent. Radiolysis of one benzoyl peroxide molecule gives two radicals (because of liberation of CO_2). Free radical formation in azobenzene proceeds via the same path (because N_2 is liberated in this reaction).

Inhibition of Thermal Decomposition of Ammonium Perchlorate by the Products

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The authors studied the decomposition of ammonium perchlorate at 130°–190°C without removing the gaseous products, and measured the resulting pressures. Under these conditions, the decomposition does not go to completion. It stops after a definite gas quantity has been liberated, corresponding to a definite pressure for each temperature (for example, 1600 mm Hg at 150°C). In addition to the usual substances obtained upon decomposition of ammonium perchlorate, the products contain substantial amounts of perchloric acid hydrates. The results are interpreted by assuming that NH_4ClO_4 decomposes via a complex process which includes a reversible dissociation and a self-catalyzing decomposition of the starting salt, in which the products of decomposition of $HClO_4$ participate. The overall process is inhibited by the accumulation of stable hydrates of perchloric acid.

Chemisorption of H_2 and O_2 on Zinc and Aluminum Oxides in the Presence of Gamma Radiation

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The authors have studied the chemisorption of H_2 and O_2 on ZnO or α-Al_2O_3 with approximately the same specific surfaces (13–14 m^2/gm) in the presence of γ-irradiation. The temperature was 20°C. Given the same initial pressures, the rate of chemisorption of oxygen is higher; the oxygen-surface bond is also stronger. The results are interpreted in the light of possible chemical reactions of the chemisorbed gases with the oxides, as well as in the light of possible electronic structures.

Oxidation of Propylene over Silver. I. Unpromoted Catalyst

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The authors have studied the oxidation of a propylene-propane mixture over an unpromoted silver catalyst. In addition to propylene oxide, the