

all-alumina samples (1). The two correlations (1, 6) based on the form of Eq. (1) yield the same general results here, although rather large volume assignments are required for samples II and IV, particularly for the Mingle and Smith correlation. It has also been shown that this correlation is not consistent for certain types of porous structures (1).

The present results, thus, affirm the applicability of the correlation reported by Butt to various types of porous structures and demonstrate that this correlation is valid for adsorption on substrates other than the aluminas employed for the original study.

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Effect of Solid-State Properties on Catalytic Selectivity

Decomposition of Isopropyl Iodide on a Cuprous Iodide Catalyst*

We wish to report briefly some evidence that the selectivity of a catalyst can be controlled by suitable adjustment of its solid-state properties. We have investigated the decomposition of isopropyl iodide on a cuprous iodide catalyst because it appeared feasible to modify the electronic properties of the catalyst by electrochemical means. By applying a voltage between an anode embedded close under the surface and a cathode in the interior of the solid catalyst, we changed the stoichiometric composition (Cu/I ratio), and thereby the electronic properties of the CuI, and observed the resulting changes in the distribution of reaction products, i.e., in the selectivity of the catalyst. A model mechanism for the catalytic reaction has

been developed to explain the role of solid-state properties.

EXPERIMENTAL

The solid catalyst consisted of cuprous iodide made from hydrogen-reduced 99.99% copper and resublimed iodine according to Wagner's procedure (1). A 3/4-inch diameter pellet was made by compression (vacuum, 4400 psi) around a central copper cathode and a cage-shaped platinum anode embedded just under the pellet surface; its geometric surface area was 11 cm². The reaction was carried out in a continuous stream of helium carrier gas. The partial pressure of the reactant isopropyl iodide (iso-PrI) was controlled by bubbling the carrier gas through a reservoir of iso-PrI kept at constant temperature. At intervals, samples of the gaseous reactor effluent were withdrawn, and analyzed for the decomposition products, C₃H₆ and

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C_3H_6 by gas chromatography on a column of 25% dimethylsulfolane on Chromosorb P.

The ratio of reaction products, $\Phi = C_3H_6/C_3H_8$, was determined as a function of flow rate, partial pressure of iso-PrI, and electronic solid-state properties of the catalyst pellet which were controlled by the application of a DC voltage. Experiments were done at 270°C and a total gas pres-

sure of 1 atm in a glass system of about 200 cm³. Total flow rate of gas was usually 68 cm³/min. "Blanks" run in the absence of catalyst amounted to less than 10% of the iso-PrI decomposition exhibited by catalytic experiments, and experimental data were corrected for the "blank" contribution.

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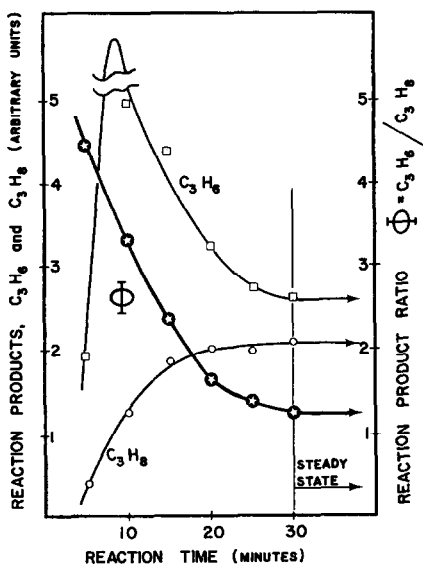


Fig. 1. Change of reaction product ratio Φ with time of exposure to iso-PrI (270°C; 60 torr iso-PrI).

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Regardless of experimental conditions, all experiments yielded a certain typical time curve. On admission of iso-PrI to the carrier gas (t_0), the product ratio $\Phi = C_3H_6/C_3H_8$ started out at a very high value (often > 10) and decreased sharply to approach a steady state, Φ_{ss} , within half an hour or more (Fig. 1). Measurements of current and voltage indicated that the conductance increased by a factor of 3

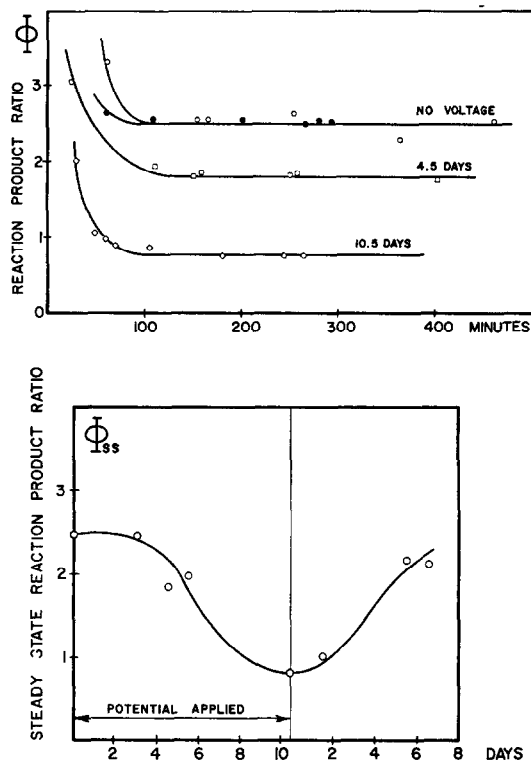


Fig. 2. Effect of a DC potential of 0.4 V on the catalytic reaction: (a) individual experiments, decrease of reaction product ratio Φ with time of exposure to iso-PrI; (b) steady-state product ratio Φ_{ss} as a function of time that the DC potential was applied (270°C; 18 torr iso-PrI).

after removing the potential the ratio increased again with a comparable time constant (Fig. 2b).

The partial pressure of iso-PrI was also found to affect the steady-state product ratio Φ_{ss} . In experiments performed at partial pressures of 18, 60, and 150 torr iso-PrI, the corresponding values of the product ratio Φ_{ss} in the steady state were 2.5, 1.2, and about 0.9, respectively.

The influence of contact time on the product ratio was studied by varying the total flow rate of gas through the system. It is interesting to note that the steady-state production of propylene appears to be relatively independent of contact time, whereas the production of propane increases with contact time (Fig. 3).

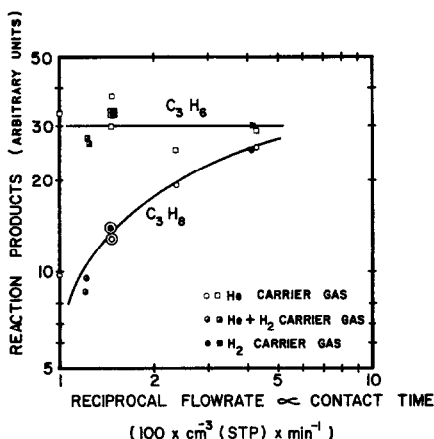


Fig. 3. Steady-state product ratio $\Phi_{s,s}$ as a function of contact time (270°C; 18 torr iso-PrI).

Experiments performed in mixtures of hydrogen and helium carrier gas, or in hydrogen carrier gas alone, gave no significant differences in product amounts and ratios from those run in helium (filled, or partially filled symbols, respectively, in Fig. 3).

DISCUSSION

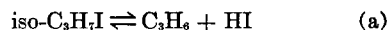
Our experimental results indicate that the solid-state properties of the CuI catalyst affect the catalytic decomposition of iso-PrI occurring on its surface. The application of an electric potential to the catalyst causes Cu^+ ions to migrate to the central Cu cathode where they are deposited. The resulting Cu^+ concentration gradient creates a driving force for Cu^+ diffusion in the opposite direction, i.e., towards the surface. In the steady state ionic Cu^+ transport in both directions balances out, and the measured current is entirely due to an electronic hole-transfer mechanism (1). From our measurements of conductivity and the known hole mobil-

ity in CuI (2-4), we calculate the stoichiometric iodine excess to be about 10^{-6} when the catalyst is subjected to the potential of 0.4 V, and assuming that $\text{I} = \text{I}^- + \text{p}$.

With the voltage applied to the catalyst, mass transport in the portion between the outer Pt anode and the central Cu electrode is driven by the electric field. The outermost layer of CuI, that between the Pt anode and the geometric surface of the pellet, however, is not affected by the potential. Transport of Cu across grain boundaries is slow, and only gradually, in the course of many days, will the chemical composition of the outer layer be equilibrated with the center of the pellet. When the voltage is removed, the same slow diffusion process causes equilibration of the solid in the reverse direction, and the original solid composition (Cu^+ , I^- , and p concentrations) is reached reversibly.

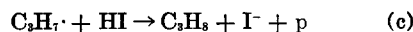
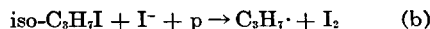
The following, tentative model for a reaction mechanism is consistent with all our experimental observations and suggests the effect of electronic properties on the selectivity of the catalyst.

The formation of propylene on the solid CuI catalyst is a rapid reaction as indicated by the apparent independence of C_3H_6 of the contact time, and by the large initial excess of C_3H_6 over C_3H_8 . This is in contrast to the homogeneous pyrolysis of iso-PrI where



was found to be rate-determining (5, 6). However, the rate of this reaction is also known to be greatly enhanced by solid surfaces, such as quartz wool (7).

The formation of propane is slow, as indicated by its decrease with flow rate, and by its slow increase on admission of iso-PrI. We propose a catalytic reaction involving holes (p) of the solid CuI catalyst:



An increase in partial iso-PrI pressure, or the application of a potential to inject holes into the surface, are expected to

produce a decrease in the reaction product ratio Φ , as confirmed by the experimental data.

The hole density is initially determined by the surface reaction itself, i.e., the pickup of electrons and resulting generation of holes by sorbed iodine. Complete coverage of grain surfaces throughout the pellet is reached when the conductivity attains a steady state value in about 6 min.

The equilibration of the chemical composition (stoichiometry) throughout the individual grains of the solid catalyst occurs more slowly and accounts for the time required (30 min or more) to reach a steady state in the reaction product ratio.

The absence of an effect of hydrogen on the reaction indicates that no rate-controlling step involving dissociation of hydrogen iodide, or hydrogen ion formation in the adsorbed phase is involved.

In summary, we have shown that the selectivity of a CuI catalyst is controlled by an electronic parameter. Our proposed model mechanism suggests that the hole density determines the reaction product distribution. In turn, the hole density is determined initially by the chemical reaction occurring on the catalyst surface,

and can be controlled in the steady state by an applied potential.

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Olefin Dimerization over Cobalt-Oxide-on-Carbon Catalysts

III. Oligomerization of Ethylene*

In 1932 Schuster (2) reported that a cobalt-oxide-on-carbon catalyst was able to dimerize ethylene to mixed *n*-butenes with a high degree of selectivity. Later studies on this dimerization (3) showed that typically the products were 77% butenes, 13.8% hexenes, 4.6% octenes, 2.3% decenes, and 2.3% higher oligomers. In this work Cheney *et al.* found that the butene isomer distribution in the product was dependent upon the contact time in their flow system.

At a flow rate (g/liter-hr) of 72 a 74% conversion to dimer (9% 1-butene and 91% 2-butene) was found while at a flow rate of 360 a 37% conversion to dimer (70% 1-butene and 30% 2-butene) was found. The hexene isomers consisted of 10% 1-hexene, 38% *cis*-2- and *cis*-3-hexenes, 38% *trans*-2- and *trans*-3-hexenes, and the balance (14%) mixed branched chain materials containing the 3-methylpentane skeleton. The dimerization rate of propylene was found to be one-fortieth that of ethylene and that of butene-1 correspondingly

* For Parts I and II see ref. (1).