moters in this case were due to simple additive catalytic efficiencies of the individual oxides of the mixtures.

In the case of the catalysts made from nitrates, the two *p*-type catalysts (IV and V) were similar in performance, whereas the three catalysts with zirconium promoter [including (VI), the *n*-type] showed a drastic change in catalytic performance, giving sharp increases in the rates of formation of styrene, benzene, and off-gas. The composition of the off-gas was not determined quantitatively, but qualitatively we found it was mainly hydrogen and carbon dioxide; the latter came from coking of the ethylbenzene and the concurrent water-gas reactions of the carbon with steam.

It has been shown that the semiconductor type of a solid changes the hydrogen chemisorption characteristics (*5*). The *n*-type semiconductors promote adsorptive dissociation of molecular hydrogen into atoms and/or protons. This leads to an enhancement of H_2–D_2 exchange rates, as shown by other authors (*6*). Presumably it is the relatively high free electron density of the *n*-type semiconductor that causes this property, which is similar to that of metals. It was thus concluded that the atomic/protonic hydrogen at the surface of the *n*-type iron oxide [sample (VI)] lead to dealkylation and cracking of the ethylbenzene, giving the increased rates to benzene and off-gas shown in Fig. 1(B). This property also gave an increased dehydrogenation rate, apparently by increasing the ease of dissociation of the ethylbenzene via loss of hydrogen.

Thus, semiconductor character is often a useful model for modifying metal oxide catalysts in reaction systems involving hydrogen. However, the complex atomic and electronic structure of the usual laboratory or industrial catalysts make it difficult to make more than qualitative correlations such as these shown here.

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The Use of Supported Solutions of Rhodium Trichloride for Homogeneous Catalysis

A practical limitation to performing homogeneously catalyzed reactions in the liquid phase is the difficulty of removing the product continuously. No equivalent problem arises with heterogeneously catalyzed reactions which are conveniently performed by causing the gaseous or liquid reagents to flow through a bed of the solid catalyst. With homogeneous catalysis we have, however, a number of potential advantages over the heterogeneous catalysis of the same reaction, in particular the possibility of greater selectivity and of more efficient use of the metal atoms. We have attempted to combine the desirable features of both systems by using catalytic solutions supported within a porous solid, after the manner of gas-liquid chromatography.

Alcoholic solutions of rhodium trichloride are known to catalyze double-bond migration in olefins (*1*), and this has been used as the test reaction. Rhodium trichloride dissolves readily in ethylene glycol and in related hydroxylic solvents of sufficiently low volatility for the present purpose. Preliminary experiments were conducted by passing a stream of 1-pentene at a partial pressure of 12.5 mm by means of nitrogen through a W-shaped column, 60 cm long, containing 7 g of catalyst at 60°C; the products were condensed and analyzed by gas-liquid chromatography. The catalyst was prepared by dissolving one part of $RhCl_3 \cdot 3H_2O$ in 12 parts (catalyst A) or 22 (catalyst B) parts by weight of ethylene glycol and adding one part of this solution to two parts by weight of 44–60 mesh Silocel suspended in methanol. The methanol was then evaporated by heating on a steam bath with continuous agitation; the product was a dry, free-flowing powder.

Figure 1 shows that with catalyst A the conversion decreases rapidly with decreasing contact time. *cis*-2-Pentene attains a concentration exceeding its equilibrium value. The mean ratio of *trans*-2-pentene/*cis*-2-pentene is 1.6 ± 0.1, which is much lower than the equilibrium value of about 4; this is a common phenomenon in olefin isomerizations (*2*). With catalyst A at 70°C and a contact time of 19 sec, only 37% of the 1-pentene remained unconverted. With catalyst B in a column 145 cm long at 60°C and a 1-pentene partial pressure of 0.8 mm, a conversion of 76% was obtained at a contact time of 35 sec.

Further experiments were performed in a small pulsed-flow reactor containing 8 g of catalyst A, the carrier gas again being nitrogen; products were conveyed directly to the analytical column and in each injection of 1-pentene there was 2.5 μl. These experiments showed that no reaction occurred below 60°C with a contact time of 9 sec but that conversion increased rapidly between 60° and 70°C. It also appeared that the activity of the catalyst decreased with increasing number of injections, and this was further examined using 16 g of catalyst B and 68°C with a contact time of 30 sec; the results are shown in Fig. 2. The probable cause of this deactivation is the slow reduction of the rhodium trichloride (or the active species formed therefrom) by

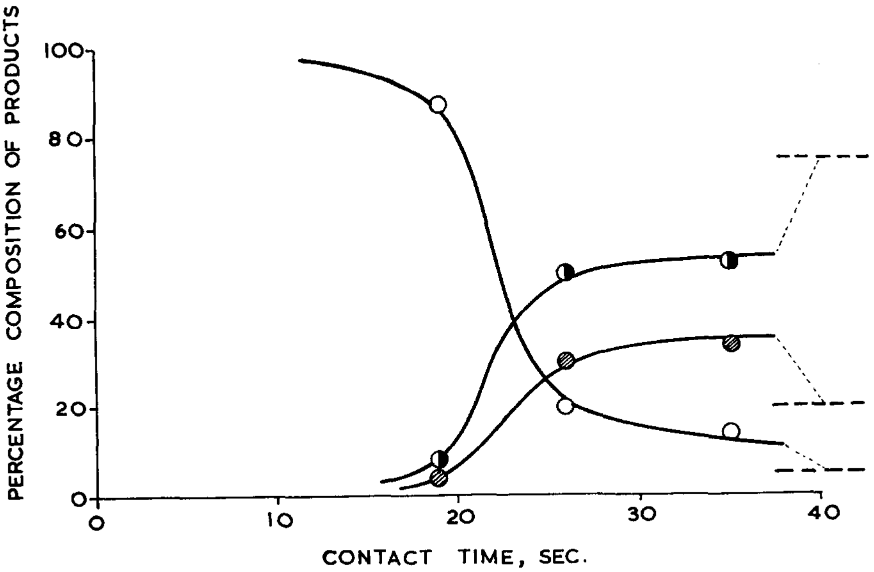

FIG. 1. Variation of product composition with contact time: continuous-flow reactor at 60°C: ⊙, 1-pentene; ◍, *cis*-2-pentene; ◑, *trans*-2-pentene. The broken lines indicate the equilibrium composition.

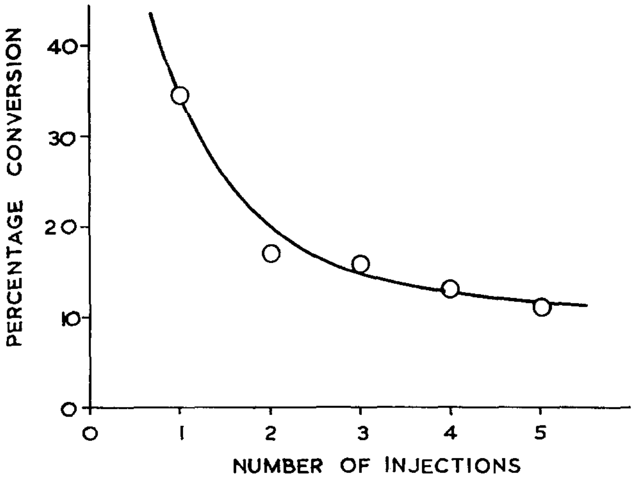

FIG. 2. Decrease in conversion of 1-pentene with increasing number of injections: pulsed-flow reactor at 68°C; 2.5 μl 1-pentene in each injection.

either the solvent or the olefin; further evidence on this will be reported later. It would seem, however, that the results obtained in the continuous-flow reactor may refer to a substantially deactivated catalyst.

Our views on the mechanism of the reaction will be discussed in a later paper.

The application of this method to other possibly more amenable and commercially important systems will readily be conceived.* We have established that many noble metal salts are sufficiently soluble in thermally stable organic compounds of low volatility, such as are commonly used as stationary phases in gas-liquid chromatography, to make their examination seem profitable.

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[*] Patent protection for this technique has been sought; inquiries for further information will be welcomed.

Lack of Dependence of Conversion on Flow Rate in Catalytic Studies*

In studies of solid catalysts, it is imperative to ascertain the possible influence of temperature and concentration gradients on the rate of reaction. For heat and mass transfer to the external surface of catalytic particles packed in a fixed bed, an easy

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