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NOTES

Effect of Matrix Promoters in Iron Oxide Catalysts for Dehydrogenation of Ethylbenzene

The literature in catalysis shows many efforts to correlate electronic properties of semiconductors and their performance as contact catalysts. We have found an apparent relation between semiconductor type and performance of promoted iron oxide catalysts for dehydrogenation of ethylbenzene in the presence of steam. An explanation is offered in terms of the free electron density of the catalysts which controls hydrogen chemisorption characteristics.

EXPERIMENTAL

Promoted iron oxide catalysts were first prepared by mixing the proper amounts of reagent grade, powdered metal oxides of iron, zinc, and zirconium to give compositions (I) and (III) shown in Fig. 1(A); a reference sample of pure iron oxide [sample (II)] was also prepared. The oxide powders were made into a paste with distilled water and mixed thoroughly with a mortar and pestle. The resulting pastes were oven-dried, then calcined in air for about 2 hr at 700°C. A second series of promoted catalysts was prepared by decomposing reagent grade nitrates of the metals. The object of this procedure was to introduce foreign cations into the crystalline matrix of the iron oxide; thus these additives are referred to as matrix promoters. The mixed nitrate powders were

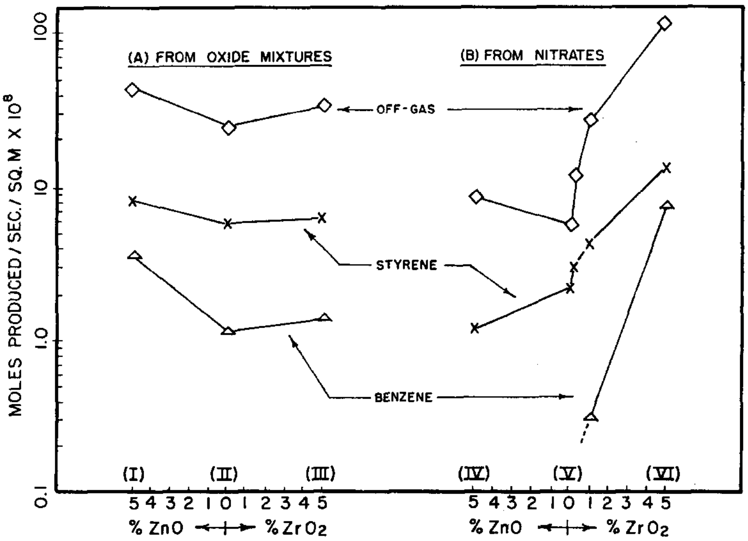

FIG. 1. Activity at 600°C of iron oxide catalysts promoted with zinc or zirconium oxides. Under (A) catalysts were prepared from metal oxides; under (B) catalysts were prepared from metal nitrates.

heated in an evaporating dish with constant stirring until decomposition of the nitrates occurred. The resulting dry mixtures were then calcined at 700° for 2 hr in air. Proper amounts of metal nitrates were used to give the compositions shown in Fig. 1(B); the three zirconium-containing samples had 0.1%, 1%, and 5% ZrO_2. A reference sample (V) was also prepared, using iron nitrate.

Specific surface areas of the catalysts were determined by nitrogen adsorption isotherms and the BET equation; the areas of the catalysts were in the range of 2–6 sq m/g. The semiconductor type of three of the catalysts, (IV), (V), and (VI) were determined by their thermoelectric power, Seebeck emf measurements [see ref. (3), for example] on compacted powders at 600°C in air. It would have been desirable to have made emf measurements on the catalysts in the reaction stream also. However, it was noted that the immediate initial and final performance of the catalysts was qualitatively the same during the 5-hr activity test; it was concluded that the catalysts retained their initial qualitative character throughout the test. The crystalline structures of samples (IV), (V), and (VI) were determined by X-ray diffraction (XRD) analyses.

The intrinsic catalyst activities, moles product/sec/sq m were determined with a differential flow reactor at 600°C and 1 atm, using 20 × 30 mesh catalyst granules. Ethylbenzene (99.7% purity) was fed with steam through the tubular quartz reactor, maintaining the mole ratio of H_2O/EB at 14/1. The condensed organic product was analyzed for styrene and benzene (the other expected product, toluene, was negligibly small in these tests). The noncondensable gases (at 0°C) were passed through a wet-test meter for volume measurement. The specific surface areas and activities of the catalysts decreased somewhat during the 5-hr tests. The data shown in Fig. 1 are based on final activities and surface areas of the catalysts. Products made by gas-phase reactions were subtracted from the totals to give net catalytic conversions to products. The reactor details and procedure for obtaining intrinsic catalyst activities [no diffusion limitations] were exactly the same as described in previous papers (*1*, *2*).

Results and Discussion

The sign of the Seebeck emf's at 600°C showed that samples (IV) and (V) were *p*-type semiconductors, and sample (VI) was an *n*-type semiconductor. No significance was attached to the absolute magnitudes of the emf's because of the inherent problems of interpretation of data on compacted powders (*3*). In addition, XRD measurements indicated that nearly all the zirconium in sample (VI) existed as zirconium oxide in a separate phase; the zinc in sample (IV) existed primarily as zinc ferrite in a separate phase (we found in later work that magnetic susceptibility was a sensitive measure of ferrite concentration in similar catalysts). Based on the crystallite size (from XRD) of the zinc ferrite and zirconium oxide phases, a solid–solid interface of about 2 sq m/g existed in samples (IV) and (VI). This interfacial network in the solids apparently contributed to the net semiconductor character as obtained by the Seebeck emf measurements.

Similar findings have been reported for modified iron oxides, where significant changes in semiconductor character were obtained in spite of separation of phases in the solids (*4*). In such complex cases one can only conclude by (the sign of) the Seebeck emf that the majority carriers are electrons (*n*-type) or holes (*p*-type).

As Figure 1 shows, the two methods of preparation of the catalysts gave entirely different results. Comparing the performance of samples (II) and (V) it is seen that the catalyst made from iron nitrate (V) was significantly less active for styrene, benzene, and off-gas production than the catalyst made from iron oxide (II). This could have resulted from the natural impurities in the reagent grade iron oxide that was used. The effects of adding zinc or zirconium oxide to the iron oxide were fairly insignificant, as shown in Fig. 1(A); the zinc may have increased the activity of the catalyst slightly. It was concluded that the small differences caused by the promoters 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