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Superacid Catalysis of Light Hydrocarbon Conversion

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SUMMARY

Transition metal promoters markedly increase the activity of sulfated zirconia for isomerization of butane. Data presented here demonstrate the effects of the promoters zinc, iron, and manganese; none of these is as effective as the iron/manganese combination. The effects of feed impurities (olefins and/or isobutane in n-butane) are consistent with those described in the preceding quarterly report: they lead to an improvement in catalytic activity. These observations are inferred to be of practical importance; they indicate the benefit of the impurities in increasing butane conversion. The product distribution data show that reactions accompanying isomerization and disproportionation are more important with some promoters (e.g., iron) than others (e.g., zinc). The data demonstrate that the iron- and manganese-promoted catalyst can be regenerated at least seven times with negligible loss of activity (within the experimental error). To apply this catalyst or a related catalyst industrially, it seems very likely to be necessary to reduce the rate of deactivation substantially and/or to regenerate the catalyst through many cycles.
INTRODUCTION

Butane conversion catalyzed by solid superacids is promoted by various transition metals, as summarized in earlier reports in this series. The earlier reports summarize the preparation of a number of these promoted catalysts. Here we report additional new catalytic results for butane isomerization. We report (1) new data for promotion of the reaction, (2) effects of impurity olefins and isobutane in the feed, (3) results concerning the product distributions in n-butane conversion, and (4) data characterizing the regeneration of the catalyst by burning of carbonaceous deposits.

EXPERIMENTAL

Materials and Preparation.

The details of the preparation of the iron- and manganese-promoted sulfated zirconia are stated in previous reports in this series. The usual calcining of the impregnated material at 500°C was done with once-through flow through a tube in a Lindberg furnace; however, the catalysts used in the regeneration experiments reported here were calcined at 650°C in a Fisher muffle furnace. The catalytic activity for n-butane isomerization of the variously treated promoted sulfated zirconia samples, one calcined in one furnace, the other in another, were nearly the same. Platinum-promoted sulfated zirconia, containing 2 wt% Pt, was made by incipient wetness impregnation of sulfated zirconium hydroxide.
with an aqueous H₂PtCl₆ solution followed by drying at 110°C and calcination at 650°C in the muffle furnace.

Catalytic Testing. The experimental setup and pretreatment have been described in previous reports in this series. The reaction conditions are stated in the captions of the figures, where the results are presented. Feeds with different purities were used, as follows:

Feed 1: 1% n-butane in N₂ (supplied by Liquid Carbonic) containing approximately 2 ppm isobutane.

Feed 2: 1% n-butane in N₂ (supplied by Puritan Bennett) containing approximately 0.8 ppm propane, 10 ppm isobutane, 11 ppm neopentane, and 3.5 ppm butenes. The impurities in this feed, especially the butenes, might be expected to be representative of some industrial feedstocks that had not been purified to remove olefins.

RESULTS AND DISCUSSION

Data reported previously demonstrate for the unpromoted sulfated zirconia that the feed impurities cause an increase in the activity of the catalyst. The results presented here show the promotion effects of zinc (Figure 1), cobalt (Figure 2), iron (Figure 3), and manganese (Figure 4). All these metals are
effective promoters, but they are not as effective as the iron-manganese combination, which has been chosen for the major emphasis in the research.

The data show that the effect of feed impurities demonstrated in the preceding report is quite general; it is illustrated for all four catalysts reported here, as shown in the results of Figures 1-4. The magnitude of the effect is different from one promoted catalyst to another, however. The data for all the promoted catalysts show an improvement in catalytic activity resulting from the presence of the feed impurities, indicated by an extended induction period and an increased activity, but the effects are much smaller for iron and manganese than for zinc and cobalt, and the zinc and cobalt seem not to be the promoters of choice.

Another important experimental observation is that the benefit of the manganese promoter is very short lived, whereas that of the iron lasts longer. These observations may provide a clue about why the combination of iron and manganese provides the most effective catalyst promotion yet observed for the sulfated zirconia catalyst.

Isomerization of \( n \)-butane is accompanied by disproportionation, giving \( C_3 \) and \( C_5 \) products. However, the disproportionation is not always stoichiometric; the value of the \( C_3/C_5 \) ratio gives evidence of whether it is stoichiometric or whether further reactions are significant.

The data are presented in Figures 5 and 6. They show that the \( C_3/C_5 \) ratio is approximately 1 for cobalt-, zinc-, and nickel-promoted sulfated zirconia.
Thus we infer that disproportionation is nearly stoichiometric for these catalysts. In contrast, the $C_3/C_5$ ratio observed for reaction catalyzed by the iron-promoted sulfated zirconia is slightly in excess of 2, suggesting that there was significant further reaction of pentanes in the presence of this catalyst but not in the presence of the others. The comparison suggests that there may be a more complex promoter role of iron than of the other metals tested; a redox character of the iron is a possibility.

The products observed for the iron- and manganese-promoted sulfated zirconia were isobutane (predominantly), propane, isopentane and $n$-pentane, as reported before. However, isobutane was the only product observed for the platinum-promoted sulfated zirconia for $n$-butane conversions < 1%. The conversion of $n$-butane for both sulfated zirconia-supported catalysts showed a break-in period followed by deactivation. The rate of deactivation for the platinum-promoted sulfated zirconia appeared to be less than that of the iron- and manganese-promoted sulfated zirconia, but the latter catalyst was much more active than the former. The rates of $n$-butane conversion, taken at the maximum in conversion vs. time on stream at 75°C and 0.0025 bar $n$-butane partial pressure for the fresh iron- and manganese-promoted sulfated zirconia and the platinum-promoted sulfated zirconia were $1.2 \times 10^{-8}$ and $5.5 \times 10^{-10}$ mol/(s · g of catalyst), respectively.

The iron- and manganese-promoted sulfated zirconia was repeatedly almost fully regenerated by treatment in air. The data characterizing seven
cycles of regeneration are shown in Fig. 7. The conversion versus time-on-stream profiles for the fresh and regenerated catalysts are virtually indistinguishable from each other. The variations in the curves are evidently more an indication of scatter in the data than of any trend in the activity resulting from regeneration. The catalytic performance for the regenerated catalysts at 75°C and 0.0025 bar n-butane partial pressure could be recovered to within ±15% of that of the fresh promoted sulfated zirconia.

These results demonstrate that the promoted catalyst has sufficient regenerability (combined with high activity and selectivity to isomerization products) to indicate its potential value in practice. Further work will be needed to more fully evaluate this potential. We anticipate that further improvements can be made by incorporation of platinum in the catalyst and by inclusion of H2 in the feed stream.

CONCLUSIONS

1. First-row transition metals were tested as promoters of sulfated zirconia for the isomerization of n-butane in a flow reactor at 100°C and 0.005 bar n-butane partial pressure. The activity of each of the sulfated zirconia samples increased through a maximum and then decreased with time on stream. In order of increasing activity measured at the maximum, the effect of the promoters increased from right to left in the periodic table: zinc, nickel, cobalt, iron, and manganese. Iron and manganese, used in combination, increased the activity
by 2-3 orders of magnitude. The most active catalyst tested for \textit{n}-butane isomerization is the iron- and manganese-promoted sulfated zirconia.

2. The data demonstrate that the iron- and manganese-promoted catalyst can be regenerated by burning of carbonaceous deposits. The catalyst can be regenerated at least seven times with negligible loss of activity (within the experimental error).

3. The effects of feed impurities (olefins and/or isobutane in \textit{n}-butane) lead to an improvement in catalytic activity of the iron- and manganese-promoted sulfated zirconia. The observations indicate a practical benefit of the impurities in increasing butane conversion.

4. Isomerization of \textit{n}-butane is accompanied by disproportionation, giving C\textsubscript{3} and C\textsubscript{5} products. The C\textsubscript{3}/C\textsubscript{5} ratio is approximately 1 for cobalt-, zinc-, and nickel-promoted sulfated zirconia, showing that disproportionation is nearly stoichiometric for these catalysts. In contrast, the C\textsubscript{3}/C\textsubscript{5} ratio observed for reaction catalyzed by the iron-promoted sulfated zirconia is in excess of 2, suggesting that there was further reaction of pentanes in the presence of this catalyst.
FIGURE CAPTIONS

Fig. 1. Promotion by zinc of the conversion of \( n \)-butane to gas-phase products at 100°C and 1 bar; other conditions are stated in the text. ZnSZ stands for zinc-promoted sulfated zirconia.

Fig. 2. \( n \)-Butane conversion catalyzed by cobalt-promoted sulfated zirconia under conditions stated in the caption of Fig. 1.

Fig. 3. \( n \)-Butane conversion catalyzed by iron-promoted sulfated zirconia under conditions stated in the caption of Fig. 1.

Fig. 4. \( n \)-Butane conversion catalyzed by manganese-promoted sulfated zirconia under conditions stated in the caption of Fig. 1.

Fig. 5. Conversion of \( n \)-butane to gas-phase products catalyzed by cobalt-promoted sulfated zirconia and propane:pentane molar ratios in the products.

Fig. 6. Propane:pentane molar ratios in the products in \( n \)-butane conversion catalyzed by sulfated zirconia and iron-, nickel-, and zinc-promoted sulfated zirconia at 100°C.

Fig. 7. Conversion of \( n \)-butane to isobutane in a flow reactor. Effects of regeneration of the iron- and manganese-promoted sulfated zirconia catalyst. Reg. refers to the regeneration. Reaction conditions: temperature, 75°C; pressure, 1 bar; \( n \)-butane partial pressure, 0.0025 bar; mass of catalyst, 1.0 g; total feed flow rate, 80 ml(NTP)/min.
Influence of impurities in the feed on the performance of Zinc-promoted sulfated zirconia

![Graph showing conversion vs time on stream for ZnSZ feed 1 and ZnSZ feed 2.](image-url)
Influence of impurities in the feed on the performance of Cobalt-promoted sulfated zirconia

Fig. 2
Influence of impurities in the feed on the performance of Iron-promoted sulfated zirconia

![Graph showing conversion over time on stream for FeSZ, feed 1 and FeSZ, feed 2.](image)

**Fig. 3**
Influence of impurities in the feed on the performance of Manganese-promoted sulfated zirconia
propane/pentanes ratio during n-butane conversion by CoSZ

![Graph showing propane/pentanes ratio during n-butane conversion by CoSZ. The graph includes lines for conversion at 373K and 348K, and for C3/C5 ratio at 373K and 348K.](image)

*Figure 5*
propane/pentane ratio during n-butane conversion for SZ, FeSZ, NiSZ, ZnSZ

![Graph showing the propane/pentane ratio over time for different catalysts. The x-axis represents time on stream (hours) ranging from 0.00 to 6.00, and the y-axis represents the C3/C5 ratio ranging from 0.00 to 3.00. Different catalysts are represented by different line styles: FeSZ (solid line with diamonds), SZ (dashed line), NiSZ (dotted line with stars), and ZnSZ (dashed-dotted line with crosses).]