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NOTE

Low-Temperature Superacid Catalysis: Reactions of *n*-Butane Catalyzed by Iron- and Manganese-Promoted Sulfated Zirconia

Environmental concerns are leading to the replacement of aromatic hydrocarbons in gasoline with high-octane-number branched paraffins and oxygenated compounds such as methyl *t*-butyl ether, which is produced from methanol and isobutylene. The latter can be formed from *n*-butane by isomerization followed by dehydrogenation. To meet the need for improved catalysts for isomerization of *n*-butane and other paraffins, researchers identified solid acids that are noncorrosive and active at low temperatures. Sulfated zirconia catalyzes the isomerization of *n*-butane even at 25°C (1), and the addition of Fe and Mn promoters increases its activity by three orders of magnitude (2–4). Little is known about this new catalyst. Here we provide evidence of its performance for *n*-butane conversion, demonstrating that isomerization is accompanied by disproportionation and other, less well understood, acid-catalyzed reactions and undergoes rapid deactivation associated with deposition of carbonaceous material.

The catalyst was prepared by incipient wetness impregnation of sulfated zirconium hydroxide (125.5 g, Magnesium Elektron, Inc.) with 43 ml of a 0.62 *M* solution of Fe(III) nitrate nonahydrate (Aldrich, 98%) in an amount corresponding to 0.34 ml of solution per gram of zirconium hydroxide. The material was dried at 120°C for 5 h, impregnated with 43 ml of a 0.21 *M* solution of Mn(II) nitrate hexahydrate (Aldrich, 98%), and dried. It was then calcined in static air as the temperature was raised at a rate of 2.7°C/min from 20 to 500°C and held for 3 h. The weight percentages of Fe, Mn, and S were 1.0, 0.5, and 1.8, respectively, as determined by inductively coupled plasma emission spectroscopy. The surface area was 90 m^2/g; the catalyst was rust colored.

Before each reaction experiment, the catalyst in flowing N_2[30 ml(NTP)/min] was heated from 20 to 450°C at a rate of 7.1°C/min, and the temperature was then held at 450°C for 1.5 h. After this pretreatment, the catalyst was cooled to the desired reaction temperature in N_2 flowing at 30 ml/min. Reactions were carried out in a quartz tubular flow reactor with an inner diameter of 1.3 cm; the finely ground catalyst particles were supported on a porous frit. Typically, 1.5 g of catalyst was used for each experiment, except when the space velocity was varied by changing the mass of the catalyst. In catalysis experiments, 1.0 mol% *n*-butane in N_2 (containing <0.0002 mol% isobutane) was mixed with N_2 (99.998%). Reactions were carried out at 1 atm and at temperatures in the range 40–225($\pm$1)°C. The *n*-butane inlet partial pressure was varied from 0.0025 to 0.01 atm; the total volumetric flow rate was 80 ± 1 ml(NTP)/min. Products were analyzed with an online gas chromatograph. The first injection was made after 5 min on stream, and the subsequent injections were made every 20 min.

In the absence of a catalyst, no *n*-butane conversion was observed. The promoted sulfated zirconia catalyzed the formation of propane, isobutane, *n*-pentane, and isopentane (with traces of methane, ethane, and hexanes) at temperatures of 40–225°C. The selectivity for formation of isobutane was $>85\%$ for conversions $<60\%$. At times on stream <1 h, the carbon balance closed within $\pm10\%$; at longer times on stream it closed within $\pm5\%$. *n*-Butane conversion data are shown as a function of time on stream in Fig. 1. The plots are characterized by two distinct regimes, represented as a break-in period followed by a deactivation period. At the lowest reaction temperature (40°C), the conversion of *n*-butane was still increasing even after 4 h on stream. In contrast, at 75°C and 100°C, the maximum conversion was observed after less than 1 h. At 75°C, the maximum conversion of *n*-butane was observed at approximately the same time on stream when the inverse space velocity varied from 7.33×10^6 to 1.47×10^7 (g of catalyst · s)/(mol of *n*-butane); however, the maximum shifted to longer times on stream when the contact time decreased.

A linear correlation was observed between the maximum *n*-butane conversion and the inverse space velocity in experiments carried out at 40–100°C (Fig. 2). Thus the data demonstrate that these conversions are approximately differential, providing estimates of reaction rates for the undeactivated catalyst. However, catalyst deactivation was so fast at the higher temperatures that the maxima in conversion vs inverse space velocity plots could not be discerned, and estimates of rates are lacking.

Approximate rates of formation of the various products

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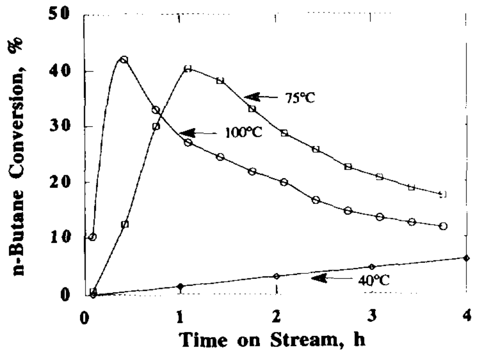

FIG. 1. The effect of reaction temperature on *n*-butane conversion catalyzed by Fe- and Mn-promoted sulfated zirconia. Feed *n*-butane partial pressure = 0.0025 atm at 75 and 100°C and 0.005 atm at 40°C. Total feed flow rate = 80 ml(NTP)/min. Catalyst mass = 1.5 g.

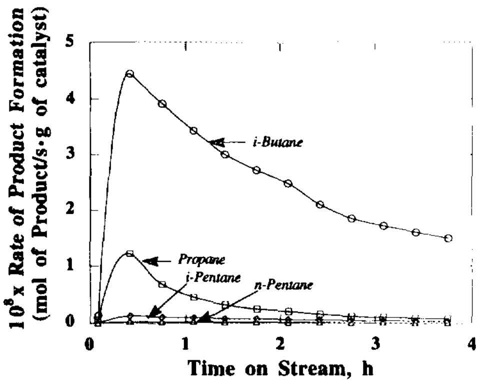

FIG. 3. Approximate rates of product formation from *n*-butane catalyzed by Fe- and Mn-promoted sulfated zirconia. Feed *n*-butane partial pressure = 0.0025 atm, temperature = 100°C. Total feed flow rate = 80 ml(NTP)/min. Catalyst mass = 1.5 g.

at 100°C are summarized in Fig. 3; no other products were observed in these experiments except for traces of methane, ethane, and occasionally hexanes. Because the predominant product was isobutane, it is concluded that the principal reaction was the isomerization of *n*-butane. The observation of propane and pentanes suggests that disproportionation also occurred. The molar C_3/C_5 ratio approached a value of 1.10 ± 0.05 at the lowest temperature investigated (40°C), after about 25 h onstream. Thus these data suggest that stoichiometric disproportionation and isomerization were virtually the only catalytic reactions taking place under these conditions. However, this simple result was not generally observed. Typically, the molar C_3/C_5 ratio was greater than unity. For example, after 3 h on stream at temperatures of 75 to 150°C, the ratio was in the approximate range 1.5–1.7. The samples taken at the shortest times on stream (0.08 h) were characterized by an absence of C_5 products, which suggests that these were held up in the catalyst bed. During the first hour on stream at temperatures from 75 to 150°C, the C_3/C_5 ratio decreased by a factor of 3–4. Variation of space velocity did not lead to significant changes in this ratio, and this result suggests that the products were primary.

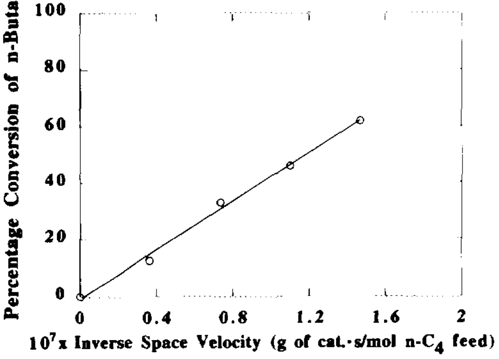

FIG. 2. Differential conversion of *n*-butane in a flow reactor. The values reported are for maximum activity at 75°C. Feed *n*-butane partial pressure = 0.0025 atm. Total flow rate = 80 ml(NTP)/min. Catalyst mass = 0.5–1.5 g.

At short times on stream, C_3/C_5 ratios > 1 were observed at all temperatures, suggesting that C_5 cracking occurred with the olefinic products being rapidly converted or that disproportionation of C_5 occurred (which is consistent with the observations of C_6 at the higher conversions). Thus the product C_3/i-C_4 ratio is taken as only an approximate measure of the selectivity for disproportionation relative to isomerization. For example, with a feed *n*-butane partial pressure of 0.005 atm at 40°C and a conversion of 11%, the C_3/i-C_4 ratio was 0.03; with the same feed composition at 100°C, this ratio at a conversion of 50% was 0.1. This ratio varied with temperature and time on stream. The maxima in the C_3/i-C_4 ratios were observed at times on stream corresponding to the maxima in *n*-butane conversion at the lower temperatures, i.e., those at which the maxima could be observed.

To summarize, the data show that conversion of *n*-butane catalyzed by Fe- and Mn-promoted sulfated zirconia at 40°C gives propane, isobutane, and pentanes as the principal products, along with traces of methane, ethane, and hexanes. The predominant product was isobutane. The same principal product has been observed for *n*-butane conversion catalyzed by unpromoted sulfated zirconia at 25°C; it was formed along with propane and traces of isopentane (1). In the presence of a H-mordenite catalyst at 400°C, *n*-butane was also converted into isobutane and propane along with some C_5 products, methane, and ethane (5–7). When unpromoted sulfated zirconia was used as a catalyst for *n*-butane conversion at 300°C, a high selectivity to isobutane was observed, with only traces of other products being formed (8). Thus the general pattern indicates that *n*-butane isomerization is accompanied by the formation of higher- and lower-molecular-weight products.

The product distribution in all these examples is that of acid catalysis. The differences from one catalyst to another evidently reflect their different activities, and presumably their different acid strengths. The catalysis of *n*-butane conversion at such low temperatures confirms the identification of the promoted sulfated zirconia as a superacid (2, 4). Our results (not shown), consistent with the published result (2), show that the activity of this promoted catalyst is two orders of magnitude greater than that of unpromoted sulfated zirconia.

The simplest product distribution observed in this work (at the lowest reaction temperature, 40°C, following the break-in period) is consistent with a reaction network including only isomerization and stoichiometric disproportionation. The only other demonstration of a nearly stoichiometric paraffin disproportionation reaction was reported for *n*-butane conversion catalyzed by aluminum chloride supported on sulfonic acid resin at 100°C; the principal reaction was isomerization, which was much faster than disproportionation (9). The products, in addition to those formed by isomerization and disproportionation, indicate the occurrence of other reactions, including coke formation; the networks are thus complex and not fully resolved.

The observation of disproportionation products suggests that a C_8 intermediate might have formed. This same suggestion was made by Bearez *et al.* (5–7, 10), who proposed a bimolecular pathway for isobutane conversions catalyzed by H-mordenite at about 350°C. According to their proposal, both the isomerization and disproportionation products could be formed from the C_8 intermediate. Reactions involving C_8 intermediates might be energetically favored over monomolecular isomerization because they would be expected to involve secondary and tertiary carbenium ions, whereas the monomolecular isomerization of *n*-butane requires the formation of a primary carbenium ion, which is highly unstable.

The performance of the catalyst as a function of time on stream in the flow reactor indicates an induction period followed by a period of deactivation (Fig. 1). The deactivation is fast, and any application of the catalyst would be likely to require frequent regeneration and/or addition of components such as Pt to minimize coke formation. The causes of the break-in period are not known. It appears unlikely that it is a consequence of holdup in the reactor, because as inverse space velocity was varied in the range of 7.3×10^6 to 1.5×10^7 (g of catalyst · s)/mol of *n*-butane), the time of the maximum did not change. At the lowest inverse space velocity [3.7×10^6 (g of catalyst · s)/mol], the maximum was shifted to 1.8 h. This shift to a longer time on stream with a smaller inverse space velocity demonstrates that the maximum should not be attributed to a holdup of material in the catalyst bed, as the opposite trend would be expected if the holdup were dominant. The break-in may be an indication of changes in the chemical properties of the catalyst, such as the oxidation state of the sulfur or promoter components. The break-in period might also be related to the formation of an intermediate in the reaction pathway.

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REFERENCES

1. Hino, M., and Arata, K., *J. Chem. Soc. Chem. Commun.*, 851 (1980).
2. Hsu, C-Y., Heimbuch, C. R., Armes, C. T., and Gates, G. C., *J. Chem. Soc. Chem. Commun.*, 1645 (1992).
3. Jatia, A., Chang, C., MacLeod, J. D., Okubo, T., and Davis, M. E., *Catal. Lett.* **25,** 21 (1994).
4. Lin, C-H., and Hsu, C-Y., *J. Chem. Soc., Chem. Commun.*, 1479 (1992).
5. Bearez, C., Chevalier, F., and Guisnet, M., *React. Kinet. Catal. Lett.* **22,** 405 (1983).
6. Guisnet, M., Avendano, F., Bearez, C., and Chevalier, F., *J. Chem. Soc. Chem. Commun.*, 336 (1985).
7. Bearez, C., Avendano, F., Chevalier, F., and Guisnet, F., *Bull. Soc. Chim. Fr.* 346 (1985).
8. Mukaida, K., Miyoshi, T., and Satoh, T. *in* "Acid Base Catalysis" (K. Tanabe, H. Hattori, Y. Yamaguchi, and T. Tanaka, Eds.), p. 363. VCH, Weinheim, 1989.
9. Fuentes, G. A., and Gates, B. C., *J. Catal.* **76,** 440 (1982).
10. Zarkalis, A. S., Hsu, C.-Y., and Gates, B. C., *Catal. Lett.* **29,** 235 (1994).

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