

# Cracking of *n*-Butane Catalyzed by Iron- and Manganese-Promoted Sulfated Zirconia

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Fe- and Mn-promoted sulfated zirconia was used to catalyze the conversion of *n*-butane at atmospheric pressure and *n*-butane partial pressures in the range of 0.0025–0.01 atm. At temperatures <225°C, the significant reactions were isomerization and disproportionation; in the range of 225–300°C, these reactions were accompanied by cracking, and at temperatures >350°C, cracking and isomerization occurred. Catalyst deactivation, resulting at least in part from coke formation, was rapid. The primary cracking products were methane, ethane, ethylene, and propylene. The observation of these products along with an ethane/ethylene molar ratio of nearly 1 at 450°C is consistent with cracking occurring, at least in part, by the Haag–Dessau mechanism, whereby the strongly acidic catalyst protonates *n*-butane to give carbonium ions. The rate of methane formation from *n*-butane cracking catalyzed by Fe- and Mn-promoted sulfated zirconia at 450°C was about  $3 \times 10^{-8}$  mol/(g of catalyst · s); for comparison, the rate of cracking of *n*-butane catalyzed by HZSM-5 under these conditions was estimated to be  $4 \times 10^{-9}$  mol/(g of catalyst · s) [as determined by extrapolation of the data of H. Krannila, W. O. Haag, and B. C. Gates (*J. Catal.* 135, 115, 1992)]. This comparison suggests that the catalytic activity of the promoted sulfated zirconia at 450°C is about the same as that of the zeolite, although its activity for *n*-butane isomerization and disproportionation at temperatures <100°C is orders of magnitude greater than those of zeolites. Thus the indication of superacidity of the promoted sulfated zirconia does not extend to high temperatures. The results raise questions about the nature of the presumed superacidity: perhaps the low-temperature reactions may involve catalyst functions other than the acidic function responsible for high-temperature cracking reactions or perhaps superacidic sites may be very rapidly poisoned at cracking temperatures. © 1995 Academic Press, Inc.

## INTRODUCTION

Solid superacids offer the prospect of practical new catalysts for paraffin conversion at low temperatures, at which the equilibria favor branched products. Most re-

ports of paraffin conversion catalyzed by solid acids concern high-temperature reactions, e.g., cracking. Cracking of *n*-butane and of isobutane are good test reactions for strong-acid catalysts because they require strong acidity and give simple product distributions (1–3). The product distributions provide mechanistic information about reactions proceeding through carbocation intermediates. For example, the cracking of *n*-butane at low conversions catalyzed by HZSM-5 at about 500°C gives methane, propylene, ethane, ethylene, butenes, and H<sub>2</sub> in nearly equimolar amounts, implying the occurrence of the Haag–Dessau carbonium ion cracking mechanism (1, 4). At higher conversions, the product distribution is more complex, including high yields of propane and indicating classical carbenium ion cracking (1, 4, 5).

Sulfated zirconia is a sufficiently strong acid to catalyze the conversion of *n*-butane at temperatures as low as room temperature (6). Promotion of this catalyst with Fe and Mn increases the activity by 2–3 orders of magnitude; promoted sulfated zirconia has been referred to as the most strongly acidic nonhalide solid acid (7). At temperatures <100°C, this promoted catalyst is selective (>90%) for isomerization, also giving disproportionation products (7–9); however, deactivation is rapid. Addition of platinum to sulfated zirconia catalysts reduces the rate of deactivation (10).

The objective of the research reported here was to use *n*-butane conversion to characterize Fe- and Mn-promoted sulfated zirconia catalysts over a wide range of temperatures to allow a comparison of its performance with that of conventional solid acid catalysts such as zeolites. This work is the first characterization of promoted sulfated zirconia as a cracking catalyst.

## EXPERIMENTAL METHODS

**Materials.** Gases (Liquid Carbonic) included diluent N<sub>2</sub> (99.998%) and a mixture consisting of 1.0 mol% *n*-butane in N<sub>2</sub>, which was found by gas chromatography

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to contain <0.0002 mol% isobutane impurity. The catalyst preparation is described elsewhere (8). Briefly, the catalyst was made by incipient wetness impregnation of sulfated zirconium hydroxide (Magnesium Elektron, Inc.) with nitrates of iron and manganese, followed by calcination in static air as the temperature was increased from 30 to 500°C at 2.7°C/min and then held at 500°C for 3 h. The catalyst surface area was 90 m<sup>2</sup>/g; it contained 1.0 wt% Fe, 0.5 wt% Mn, and 1.8 wt% S.

**Catalytic Reaction Experiments.** The reaction experiments were carried out with an apparatus and methods described in the earlier report (8). The reaction took place in a tubular flow reactor packed with catalyst particles, and products were analyzed with an on-line gas chromatograph. Experiments were done with a feed of *n*-butane diluted with N<sub>2</sub>. The *n*-butane partial pressures were low (0.0025 to 0.01 atm) to minimize catalyst deactivation. Conversions were typically low, as a major goal was to measure primary products of cracking and estimates of reaction rates. The temperature was varied from 225–450°C. The pressure was atmospheric.

RESULTS

At reaction temperatures <225°C, only few products were formed from *n*-butane, predominantly isobutane, in agreement with earlier observations (7–9). In the temperature range 225–275°C, both isomerization and disproportionation occurred, and the selectivity to isomerization product (based on the gas-phase products only) was about 80% or greater, and the molar C<sub>3</sub>/C<sub>5</sub> ratio was always >1. Low selectivities for formation of cracking products were observed under these conditions. At temperatures >350°C, the products were methane, ethane, ethylene, propane, propylene, isobutane, and traces of isobutylene, *trans*-2-butene, *cis*-2-butene, and 1-butene. At these temperatures, the cracking products predominated, and no C<sub>5+</sub> products were observed by the gas chromatographic analysis. A summary of the conversions of *n*-butane to individual products at 400°C is given in Table 1. The selectivity for isomerization decreased with increasing temperature. Reaction was accompanied by rapid formation of carbonaceous deposits, as evidenced by the change in catalyst color from rust to black.

Thus, the following classification summarizes the reactions observed, except for formation of carbonaceous deposits:

Low temperature 25 to 225°C	Intermediate temperature 225 to 275°C	High temperature 350 to 450°C
isomerization + disproportionation	disproportionation + isomerization + cracking	cracking + isomerization

TABLE 1

Distribution of Products in Cracking of *n*-Butane Catalyzed by Fe- and Mn-Promoted Sulfated Zirconia at 400°C<sup>a</sup>

Product	Conversion of <i>n</i> -butane to product (%)		
	Extrapolated to zero time on stream <sup>b</sup>	1 h on stream <sup>c</sup>	2 h on stream <sup>d</sup>
Methane	18	1.3	1.2
Ethane	19	2.4	1.5
Ethylene	8.2	2.4	1.5
Propane	15	1.5	0.74
Propylene	0.15	0.18	0.27
Isobutane	1.8	0.38	0.28

<sup>a</sup> Mass of catalyst, 1.5 g; feed *n*-butane partial pressure, 0.0025 atm; total feed flow rate, 80 ml (NTP)/min.

<sup>b</sup> Total conversion, 95%.

<sup>c</sup> Total conversion, 8%.

<sup>d</sup> Total conversion, 6%.

Rapid catalyst deactivation characterized the high-temperature *n*-butane reactions catalyzed by Fe- and Mn-promoted sulfated zirconia. As shown in Fig. 1, the overall conversion of *n*-butane at temperatures in the range 350–450°C decreased rapidly with time on stream. The major products were carbonaceous deposits. We infer that these deposits were responsible for at least part of the catalyst deactivation. The lack of steady-state operation with the deactivating catalyst complicates the interpretation of these data.

The conversions to propane, propylene, and isobutane expressed as a function of time on stream are illustrated in Figs. 2–4. The conversions are normalized to represent butane equivalents, so that the conversion to each product is multiplied by the number of carbon atoms in the product

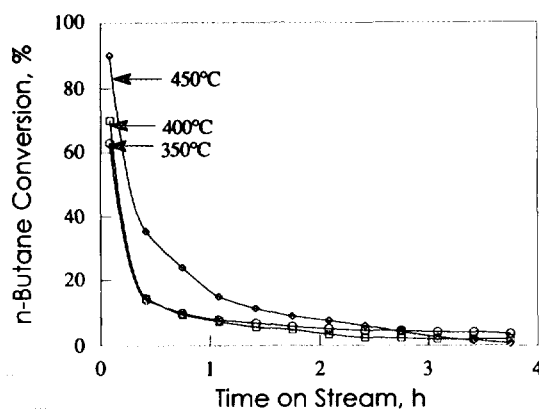


FIG. 1. Effect of reaction temperature on *n*-butane conversion to gas-phase products and coke catalyzed by Fe- and Mn-promoted sulfated zirconia. Feed *n*-butane partial pressure, 0.0025 atm; total feed flow rate, 80 ml (NTP)/min; catalyst mass, 1.5 g.

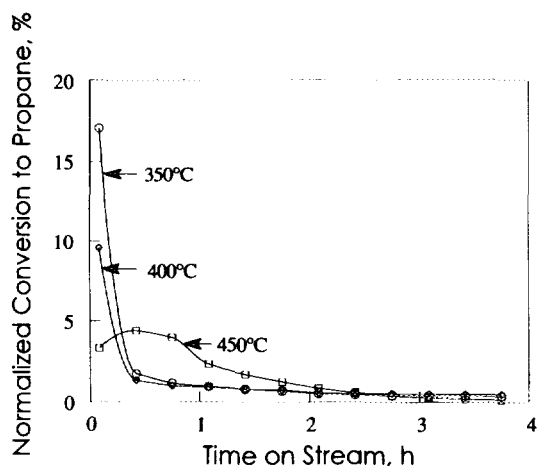


FIG. 2. Effect of reaction temperature on conversion to propane from *n*-butane reaction catalyzed by Fe- and Mn-promoted sulfated zirconia. Feed *n*-butane partial pressure, 0.0025 atm; total feed flow rate, 80 ml (NTP)/min; catalyst mass, 1.5 g.

divided by 4. The fact that the conversions do not total 1 is an indication of the formation of carbonaceous deposits. These data indicate how the product distribution changed with reaction temperature. The onstream time profile representing the conversion of *n*-butane to methane (not shown) is similar in shape to that characterizing the total conversion (Fig. 1). These conversions at each temperature decreased rapidly with time on stream as a consequence of catalyst deactivation. However, conversion of *n*-butane to methane, extrapolated to zero on stream time, increased with increasing temperatures  $>225^{\circ}\text{C}$  at each of the observed space velocities [ $6.8 \times 10^{-8}$  to  $2.7 \times 10^{-7}$  (mol of *n*-C<sub>4</sub>)/(s · g of catalyst)]. At 150°C, no methane was observed. At 225°C, methane was detected only for

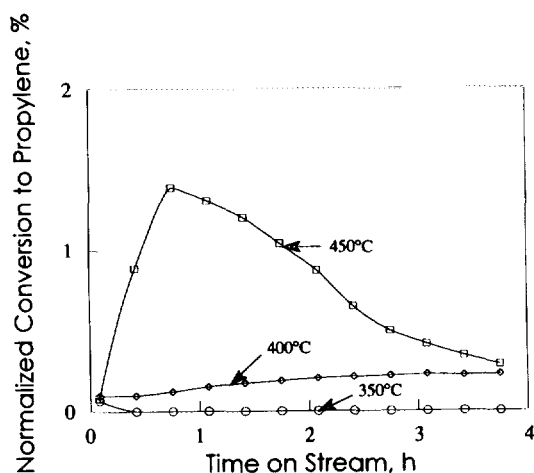


FIG. 3. Effect of reaction temperature on conversion to propylene from *n*-butane reaction catalyzed by Fe- and Mn-promoted sulfated zirconia. Feed *n*-butane partial pressure, 0.0025 atm; total feed flow rate, 80 ml (NTP)/min; catalyst mass, 1.5 g.

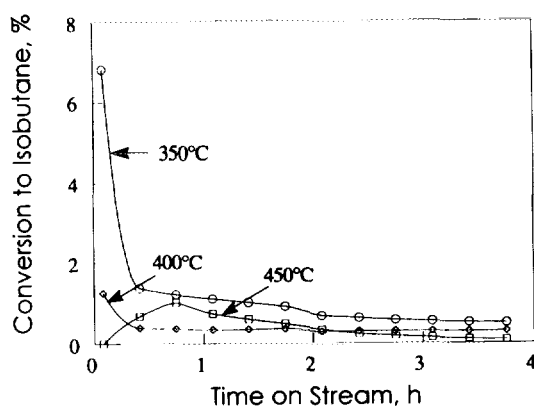


FIG. 4. Effect of reaction temperature on conversion to isobutane from *n*-butane reaction catalyzed by Fe- and Mn-promoted sulfated zirconia. Feed *n*-butane partial pressure, 0.0025 atm; total feed flow rate, 80 ml (NTP)/min; catalyst mass, 1.5 g.

the first 2 h on stream. At 275°C, methane was observed at 5 h on stream, and the selectivity for methane formation exceeded 5% of the gas-phase products.

The pattern of cracking to give ethane and ethylene in the temperature range 225–450°C was also similar to that characterizing the total conversion (Fig. 1). No C<sub>2</sub> products were observed at 150°C. At 225°C ethane was observed for 5 h, but ethylene was observed only at the shortest time on stream (5 min). Both ethane and ethylene were observed at temperatures in the range 275–450°C.

Small amounts of C<sub>4</sub> olefinic products (typically a few parts per million) were formed at a temperature of 450°C (data not shown). At the shortest time on stream (5 min), no isobutylene, 1-butene, *cis*-2-butene, or *trans*-2-butene was observed; however, the selectivities for formation of these C<sub>4</sub> olefinic products increased as a function of time on stream. Isobutylene was the first C<sub>4</sub> olefin observed as a function of time on stream (at approximately 0.5 h). Subsequent injections contained other C<sub>4</sub> products, formed at conversions two to threefold less than conversion to isobutylene.

Selectivities to individual products (based on gas-phase analyses only) are shown as a function of conversion in Fig. 5 for reaction at 225°C. These data represent variously deactivated catalysts, but there is little effect of the degree of deactivation on the selectivity–conversion plots. The data, extrapolated to zero conversion (Fig. 5), show that the selectivities for formation of methane and ethane exceeded zero at 225°C.

At 450°C, the conversion of *n*-butane extrapolated to zero onstream time was as much as almost 100%, and ethylene was formed. Similar selectivity vs conversion plots for reaction at 450°C (not shown) are consistent with the conclusion that methane, ethane, ethylene, and propylene are primary products, as the selectivities determined by extrapolation to zero conversion are nonzero.

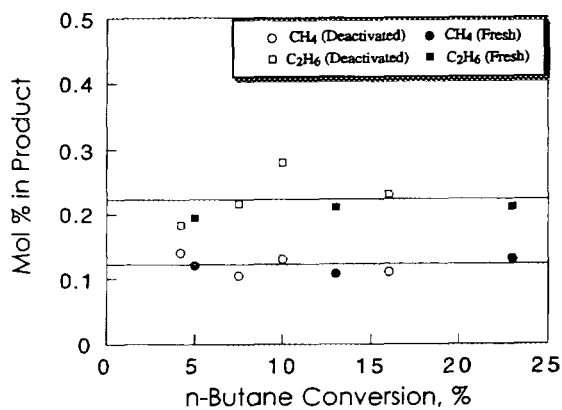


FIG. 5. Selectivity for formation of methane and ethane in *n*-butane reaction catalyzed by Fe- and Mn-promoted sulfated zirconia at 225°C. Data are based on analysis of the gas-phase products and do not account for carbonaceous deposits. Feed *n*-butane partial pressure, 0.01 atm; total feed flow rate, 80 ml (NTP)/min.

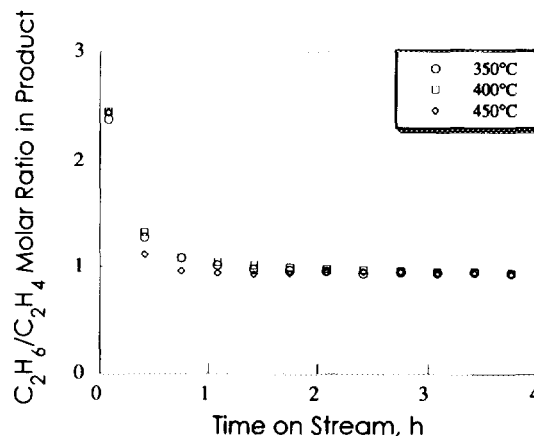


FIG. 7. Effect of reaction temperature on the ethane to ethylene ratio in the products of *n*-butane conversion. Feed *n*-butane partial pressure, 0.0025 atm; total feed flow rate, 80 ml (NTP)/min; catalyst mass, 1.5 g.

However, it is not clear from the data whether propane or isobutane is a primary product.

As a measure of the formation of carbonaceous deposits, the percentage of the carbon lost to non-gas-phase products is plotted as a function of *n*-butane conversion in Fig. 6. The percentage of carbon loss extrapolated to zero conversion of *n*-butane was approximately zero, indicating that the carbonaceous deposits were not primary products.

The data of Fig. 7 show that the ethane to ethylene molar ratio approached 1 after approximately 0.5 h on stream in the temperature range of 350 to 450°C. At shorter times on stream this ratio was greater than one, being about 2.5 at the first injection, taken at 0.08 h on stream.

Both the ratio of methane to ethane and the ratio of methane to (propane + propylene) increased with increasing temperature in the range 225–450°C (Table 2), consis-

tent with thermodynamics. The ratio of methane to ethane remained virtually constant as a function of time on stream, but the ratio of methane to C<sub>3</sub> products was higher at shorter times on stream (i.e., approximately 1–2 h).

The data presented in Fig. 8 represent conversions estimated by extrapolation to zero time on stream. Because the catalyst deactivation was rapid, the errors associated with the extrapolation are large, possibly as much as ±100%, especially at the highest temperatures. However, as shown in Fig. 8, a linear correlation was obtained for the conversion of *n*-butane into each of the products methane, ethane, and ethylene as a function of inverse space velocity in the range of 0 to 12 × 10<sup>7</sup> (g of catalyst · s)/(mol of *n*-C<sub>4</sub> feed). Thus, these data give rough estimates of differential conversions and hence reaction rates (slopes) for the undeactivated catalyst. The rates of methane, ethane, and ethylene formation at 450°C and an *n*-butane

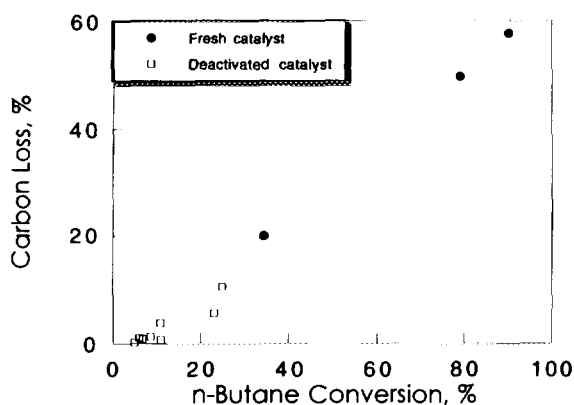


FIG. 6. Percentage of carbon loss in the gas phase effluent stream for *n*-butane reaction catalyzed by Fe- and Mn-promoted sulfated zirconia at 450°C. Feed *n*-butane partial pressure, 0.0025 atm; total feed flow rate, 80 ml (NTP)/min.

TABLE 2

Product Molar Ratios from *n*-Butane Cracking Catalyzed by Fe- and Mn- Promoted Sulfated Zirconia<sup>a</sup>

Temperature (°C)	Molar Ratio in Product	
	CH <sub>4</sub> /(C <sub>3</sub> H <sub>8</sub> + C <sub>3</sub> H <sub>6</sub> ) <sup>b</sup>	CH <sub>4</sub> /C <sub>2</sub> H <sub>6</sub> <sup>c</sup>
225	0.04	0.55
275	0.21	0.61
350	0.70	0.71
400	0.98	0.80
450	1.39	0.91

<sup>a</sup> Feed *n*-butane partial pressure, 0.0025 atm; total feed flow rate, 80 ml (NTP)/min.

<sup>b</sup> Taken at 3 h time on stream.

<sup>c</sup> At a given temperature, this ratio was nearly constant as a function of time on stream.

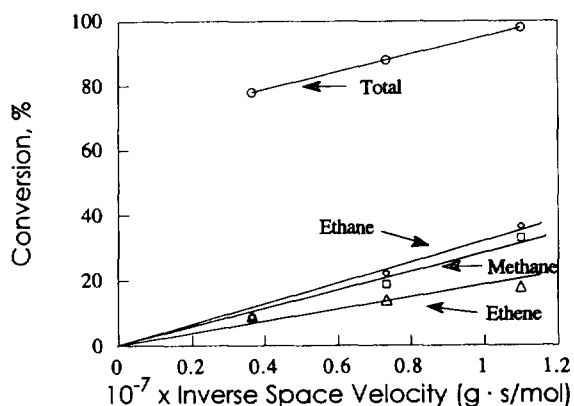


FIG. 8. Differential conversion of *n*-butane to methane, ethane, and ethylene at 450°C in a flow reactor. Values reported are from extrapolation to zero time on stream. Feed *n*-butane partial pressure, 0.0025 atm; total feed flow rate, 80 ml (NTP)/min.

partial pressure of 0.0025 atm are about  $3.0 \times 10^{-8}$ , and  $1.9 \times 10^{-8}$  mol/(g of catalyst · s), respectively.

Similarly, extrapolated conversions at various inverse space velocities (most data not shown) were used to make rough estimates of reaction rates for the formation of individual products. The estimates of rates of formation of methane and ethane show about the same pattern as shown by the *n*-butane conversion as a function of time on stream in the range 350–450°C. The same trend was also observed for ethylene, except for the sample taken at 5 min on stream.

The approximate rates of formation of methane, ethane, and ethylene increased with increasing temperature in the range of 350 to 450°C. The apparent activation energies, estimated from the temperature dependence of the rate data extrapolated to zero time on stream, were found to be 10–15 kcal/mol for each of these products (Table 3). The estimates are rough because of the uncertainty of the extrapolation caused by the rapid deactivation.

TABLE 3

Approximate Kinetics Parameters Characterizing *n*-Butane Cracking Catalyzed by Fe- and Mn-Promoted Sulfated Zirconia<sup>a</sup>

Product	$k_0$ preexponential factor (mol/(s · g of catalyst · atm))	$E_A$ apparent activation energy (kcal/mol)
Methane	0.13	13.3
Ethane	0.09	12.6
Ethylene	0.012	11.1

<sup>a</sup> Calculated on the basis of assumed first-order kinetics; feed *n*-butane partial pressure, 0.0025 atm; total feed flow rate, 80 ml (NTP)/min.

## DISCUSSION

The data confirm the acidic character of the promoted sulfated zirconia catalyst. The product distributions are those of acid catalysis, and the occurrence of reaction at temperatures <100°C and the onset of cracking at about 225°C indicate that the catalyst was strongly acidic. Low-temperature *n*-butane conversion data suggest that it is a superacid (7). The strong acidity was confirmed by temperature-programmed desorption of benzene from the catalyst (11).

This is, to our knowledge, the first observation and quantification of catalytic cracking of *n*-butane at temperatures as low as 225°C. The results demonstrate that the catalyst has a high activity for this reaction. However, the approximate rate of cracking to give methane at 450°C observed in this work with the promoted sulfated zirconia catalyst,  $3 \times 10^{-8}$  mol/(g of catalyst · s), is about the same as that observed by Krannila *et al.* (1) with HZSM-5 catalyst,  $4 \times 10^{-9}$  mol/(g of catalyst · s). This estimate of the methane formation rate for HZSM-5 was obtained by extrapolating the reported kinetics parameters (1) to the reaction conditions used for the Fe- and Mn-promoted sulfated zirconia.

Thus there is no evidence of unusually high activity of the promoted sulfated zirconia at the highest temperatures investigated. It has also been shown that the activity of the promoted sulfated zirconia for neopentane cracking at 450°C is not much higher than those of the unpromoted sulfated zirconia and USY zeolite (12). Perhaps the catalyst had been substantially deactivated before any measurements could be made at this temperature. Alternatively, we suggest that the catalytic properties at the lower temperature may be associated with properties other than just acidity. The roles of iron and manganese in the catalyst remain to be determined.

The identification of methane, ethane, and ethylene as primary products of cracking, combined with the observation that ethane and ethylene were formed in equimolar amounts, leads to the suggestion that *n*-butane cracking catalyzed by the promoted sulfated zirconia proceeded via the Haag–Dessau mechanism (4). According to this mechanism, which predominates in the cracking of *n*-butane catalyzed by HZSM-5 at 426–523°C and at low conversions (1), the *n*-butane is protonated directly by the catalyst to give carbonium ions, which collapse to give equimolar amounts of methane and propylene, ethane and ethylene, and H<sub>2</sub> and butenes. The carbonium ions are regarded as transition states (1, 13). The product distribution observed in this work is not as simple as that predicted by the Haag–Dessau mechanism, but the observation of the primary products and of equimolar yields of ethane and ethylene suggests its occurrence.

We infer that secondary reactions also occurred. The

least reactive primary products were methane, ethane, and ethylene, and these are the ones that were observed to form as expected for the Haag–Dessau mechanism. In contrast, the other products were relatively more reactive and were converted into secondary products. For example, the olefinic products were readily protonated to give carbenium ions, which undergo a variety of hydride transfer and cracking reactions. Even in *n*-butane cracking at the lowest conversions catalyzed by HZSM-5, the product distribution was not quite that corresponding to the primary products formed by the Haag–Dessau mechanism (1); the deviations from this simple product distribution were attributed to secondary reactions, especially of propylene. At higher conversions, cracking via the classical carbenium ion mechanism also occurred, giving, for example, high selectivities to propane.

In summary, because the product distribution in *n*-butane conversion catalyzed by promoted sulfated zirconia at the higher temperatures was sufficiently different from that predicted for the simple Haag–Dessau mechanism, we are not able to resolve quantitatively the primary from the secondary reactions, nor are we able to determine the relative importance of cracking proceeding via carbonium ions compared to that proceeding simply through carbenium ions.

The HZSM-5 catalyst used by Krannila *et al.* (1) underwent negligible deactivation, whereas the catalyst used in this work deactivated rapidly, as is typical of cracking catalysts. The lack of deactivation of HZSM-5 is related to the lack of coke formation in the zeolite pores as a consequence of restricted transition state shape selectivity (14). The catalyst used in this work deactivated rapidly, and the carbonaceous deposits might have been responsible for almost all of the catalyst deactivation.

There is evidently no prospective practical advantage to using the promoted sulfated zirconia catalysts for cracking. However, the data indicating the occurrence of the Haag–Dessau mechanism of *n*-butane cracking catalyzed by the promoted sulfated zirconia as well as by HZSM-5 suggest that measurements of the rate of this reaction might provide a useful basis for comparison of various catalysts. Rastelli *et al.* (2) advocated this test reaction in 1982. The Haag–Dessau mechanism requires protonation of an extremely weak base by the catalyst. Thus, presuming that the rate of *n*-butane cracking is determined by the rate of protonation, we suggest that the rate of *n*-butane cracking under conditions of Haag–Dessau cracking might be an easily measured criterion of the acid strength of solid acids. Successful applica-

tion of the test reaction would require successful extrapolation to determine the activities of the fresh catalysts.

## CONCLUSIONS

Fe- and Mn-promoted sulfated zirconia is an active catalyst for cracking of *n*-butane at very low *n*-butane partial pressures. Primary cracking products, methane and ethane, were observed at temperatures as low as 225°C. The observation of these products along with an ethane/ethylene molar ratio of 1 at 450°C is consistent with cracking occurring by a Haag–Dessau carbonium ion cracking mechanism. High concentrations of propane indicate that cracking via a classical carbenium ion mechanism also occurs. The fact that this catalyst is active for isomerization, disproportionation, and cracking and the fact that the relative rates at which these reactions occur are highly dependent on temperature greatly complicate unraveling the mechanism of cracking. Catalyst deactivation is rapid.

## ACKNOWLEDGMENT

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