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

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ABSTRACT

The primary goal of this project is to evaluate the potential value of solid superacid catalysts of the sulfated zirconia type for light hydrocarbon conversion. The key experiments catalytic testing of the performance of such catalysts in a flow reactor fed with streams containing, for example, *n*-butane or propane.

Fe- and Mn-promoted sulfated zirconia was used to catalyze the conversion of *n*-butane at atmospheric pressure, 225-450°C, 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; 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 3×10^{-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 1×10^{-8} mol/(g of catalyst · s) [as determined by extrapolation of the data of Krannila *et al.*, *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 acidic sites responsible for the low-temperature catalytic performance of (promoted) sulfated zirconia do not exist at the higher

temperatures; alternatively, the low-temperature reactions may involve catalyst functions other than the acidic function.

Iron- and manganese-promoted sulfated zirconia was also tested for conversion of propane at 1 atm, 200-300°C and propane partial pressures in the range of 0.01-0.05 atm. At 250°C, catalysis was demonstrated, as the number of propane molecules converted was at least 1 per sulfate group after 16 days of operation in a continuos flow reactor. Propane was converted in high yield to butanes, but the conversions were low, for example being only a fraction of a percent at a space velocity of 9.1×10^{-7} mol/(g of catalyst · s) and 250°C. Coke formation was rapid. The observation of butanes, pentanes, and methane as products is consistent with Olah superacid chemistry, whereby propane is first protonated by a very strong acid to form a carbonium ion. The carbonium ion then decomposes into methane and an ethyl cation which undergoes oligocondensation reactions with propane to form higher molecular weight alkanes. The results are consistent with the identification of iron- and manganese-promoted sulfated zirconia as a superacid.

INTRODUCTION

Solid superacids offer the prospect of practical new catalysts for paraffin conversion at low temperatures, at which the equilibria favor branched products. Most reports 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_2 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 non-halide 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*).

One 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. Another objective was to test the performance of this catalyst for propane conversion.

EXPERIMENTAL METHODS

Materials. Gases (Liquid Carbonic) included diluent N_2 (99.998%) and a mixture consisting, for example, of 1.0 mol% *n*-butane in N_2, which was found by gas chromatography 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^2/g; it contained 1.0 wt% Fe, 0.5 wt% Mn, and 1.8 wt% S.

Catalytic Reaction Experiments. The butane conversion experiments were carried out with 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_2. 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.

Experiments were done similarly for propane conversion. The reaction conditions were as follows: temperature, 200, 250, or 300°C; pressure, 1 atm; mass of catalyst, 0.5-2.0 g; inverse space velocity, (1-6) x 10^6 (g of catalyst · s)/(mole of propane fed); propane partial pressure, 0.01, 0025, and 0.05 bar; and run length, 4 h to 16 days.

RESULTS

Butane Conversion. 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 products (based on the gas-phase products only) was about 80% or greater, and the molar C_3/C_5 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_{5+} 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 temp. 25 to 225°C	Intermediate temp. 225 to 275°C	High temp. 350 to 450°C
isomerization + disproportionation	disproportionation + isomerization + cracking	cracking + isomerization

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 product was 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 are 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 divided by 4. The fact that the conversions do not total one 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°C at each of the observed space velocities [6.8×10^{-8} to 2.7×10^{-7} (mol of *n*-C_4)/(s · g of catalyst)]. At 150°C, no methane was observed. At 225°C, methane was detected only for 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_2 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 of 275-450°C.

Small amounts of C_4 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_4 olefinic products increased as a function of time on stream. Isobutylene was the first C_4 olefin observed as a function of time on stream (at approximately 0.5 h). Subsequent injections contained the other C_4 products, formed at conversions 2- to 3-fold less than 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 selectivity 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. 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 3), consistent 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_3 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 1.2×10^{7} (g of catalyst · s)/(mol of n-C_4 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 a *n*-butane partial pressure of 0.0025 atm are about 3.0×10^{-8}, 3.5×10^{-8}, and 1.9×10^{-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 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 4). The estimates are rough because of the uncertainty of the extrapolation caused by the rapid deactivation.

Propane Conversion. The definitions for propane conversion are analogous to those stated for butane. Carbonaceous deposits formed from propane on the surface of the promoted sulfated zirconia, but they were not accounted for in the calculations of conversion. These deposits formed on the surface of the material at all investigated temperatures, and the color changed from rust to gray or black.

The gas-phase products formed from propane at 200°C were methane, butanes, and pentanes. The conversion to gas-phase products increased for the first hour on stream (the induction period), followed by a period of declining conversion. At 250 and at 300°C, the products included ethane, ethylene, propylene, and the products observed at 200°C. The propane conversion at 300°C was at most 0.6%. A plot of propane conversion at 250°C at the end of the induction period as a function of inverse space velocity (figure 2) is nearly linear, suggesting that the conversion was differential. Thus the slope of the line is taken as an approximation of the reaction rate, i.e. 3×10^{-10} mol/(g of catalyst · s).

The change in product distribution with time on stream at 200°C is shown in figure 3. The initially formed gas-phase products were mostly methane and butanes. The selectivity to butanes initially increased with time on stream and then declined slowly as the selectivity to pentanes increased. Concomitantly, the selectivity to methane declined rapidly with time on stream. The selectivity to butanes was greatest at the lowest temperatures. After the induction period, typical selectivities to butanes at 200°C were about 85% and those at 300°C were about 15%.

The ratio of methane to ethylene in the gas-phase products at 250°C is shown in figure 4. This ratio was approximately 1 as the conversion approached zero; however, it deviated significantly from unity when the conversion was higher than 0.09%.

The flow reactor experiment at 250°C was continued with a constant feed flow rate for 16 days. The conversion profile as a function of time on stream was similar to that observed at 200°C, and conversion was proceeding when the experiment was terminated. If we assume that the number of catalytic sites is the same as the number of sulfate groups, then these data demonstrate that the number of turnovers (propane molecules converted per catalytic site) was 1.0 ± 0.1 and that the reaction was catalytic. However, the number of turnovers per site estimated in this way from the data obtained at 200°C was only 0.12 ± 0.02 when the experiment was terminated after 5 days of operation.

DISCUSSION

Butane Conversion. The data confirm the acidic character of the promoted sulfated zirconia catalyst. The product distributions are those of acid catalysis, and the occurrence of butane 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, 3×10^{-8} mol/(g of catalyst · s), is about the same as that observed by Krannila *et al.* (*1*) with HZSM-5 catalyst, 1×10^{-8} 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, or perhaps the catalytic sites responsible for low-temperature *n*-butane isomerization were destroyed by treatment at the higher temperatures. 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_2 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 are relatively more reactive and converted into secondary products. For example, the olefinic products are 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 relative 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 application of the test reaction would require successful extrapolation to determine the activities of the fresh catalysts.

Propane Conversion. Because the rates of reaction were so low, the data were sufficient to demonstrate catalysis only for propane conversion at 250°C after 16 days of operation. The data taken at 200°C may represent noncatalytic reactions. However, the estimate of the number of turnovers/site is regarded as conservative, because the number of sulfate groups is considered to be an upper limit of the number of active sites and the amount of propane converted into carbonaceous deposits is not included. Thus the data do not rule out the occurrence of catalysis at 200°C.

Olah et al. (*15*) investigated the conversion of alkanes, for example, propane in the temperature range of -78 to 150°C in the presence of excesses of liquid superacids in a Teflon-lined stainless steel bomb. The superacid was diluted with the weakly nucleophilic SO_2ClF. With propane, they observed protolysis of C-H and, predominantly, C-C bonds, leading to the formation of methane, ethane, H_2, and carbenium ions. Subsequent oligocondensation led to the formation of higher alkylcarbenium ions.

The products observed by Olah et al. (*15*) for propane conversion were also observed in the present work. The presumed analogy to Olah superacid chemistry implies that the solid superacid protonates propane to initiate its conversion. Thus the results are consistent with the earlier conclusion that the iron- and manganese-promoted sulfated zirconia is a superacid.

Furthermore, the ratio of methane to ethylene, which approaches 1 in the limit of zero conversion at 250°C, is consistent with protonation of propane as an initial reaction step to give carbonium ions (presumably transition states) that collapse into methane and ethyl cations (or into H_2 and *s*-propyl cations), so that the primary cracking products methane and ethylene are formed in equimolar amounts. The lack of data for H_2 leaves open the question of the ratio of H_2 to propylene, which would also be expected to approach 1 in the limit of zero conversion.

Cracking and dehydrogenation of alkanes via protonation has been demonstrated by Haag et al. catalyzed by zeolites at temperatures of 400-550°C (as mentioned above). For example, Krannila et al. (*1*) observed equimolar yields of ethane and ethylene formed from *n*-butane in the limit of zero conversion. The observation of a comparable cracking product distribution (with a much less reactive molecule) in our work at a temperature as low as 250°C is consistent with the suggestion that the promoted sulfated zirconia is a much stronger acid than the zeolites.

The observed formation of butanes and pentanes from propane at the lower reaction temperatures is consistent with oligocondensation chemistry proceeding via carbocation intermediates. Olah et al. (*15*) pointed out that almost all low-molecular-weight alkanes are converted with increasing temperature into stable carbocations, e.g. *t*-butyl cations, in the presence of a superacid. Our observation of butanes as products is consistent with the formation of *t*-butyl cations and hydride abstraction to form isobutane; isomerization would give *n*-butane. At longer times on stream, pentanes were observed, and these can also be accounted for by oligocondensation reactions. The data are explained by the reaction network of Fig. 9, which is based on Olah chemistry.

The similarities in the product distributions observed in this work and in the work of Olah et al. (*15*) with reactions in superacid solutions lead to the postulate that the chemistry on the surface was analogous to that in superacid solutions. But the differences in the experimental conditions were significant, leaving the fundamental issues distinguishing solution and solid superacid chemistry and catalysis largely unresolved.

CONCLUSIONS

Fe- and Mn-promoted sulfated zirconia is an active catalysts for the cracking of *n*-butane. At 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 relative rate at which these reactions occur is highly dependent on temperature greatly complicates unraveling the mechanism of cracking. Catalyst deactivation is rapid.

Propane is converted into butanes and pentanes in the presence of iron- and manganese-promoted sulfated zirconia at temperatures of 200-300°C. The observation of these products accompanied by methane suggests that the reactions are initiated by protonation of propane to form a carbonium ion which collapses into methane and ethyl cation, followed by oligocondensation of the ethyl cation with propane. The product distribution is consistent with Olah superacid chemistry; the chemistry has been demonstrated to be catalytic at 250°C, but it may not be catalytic at lower temperature.

PLANS

In the future, this investigation will emphasize the reactions of *n*-butane and of isobutane catalyzed by iron- and manganese-promoted sulfated zirconia, as the *n*-butane isomerization is evidently the reaction for which this class of catalyst holds the most promise of practical application, motivated by the need for isobutane and from that isobutylene for MTBE synthesis for high-octane clean-burning gasoline. The promoted catalyst is evidently the best in prospect for this reaction. Future experiments with emphasize higher pressures of reactant than have been investigated so far, and the data will include those of practical value, including measures of kinetics and catalyst stability and regenerability.

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TABLE 1

Distribution of Products in Cracking of *n*-Butane Catalyzed by Fe- and Mn-Promoted Sulfated Zirconia at 400°C[a]

Product	Conversion of *n*-butane to product (%)		
	Extrapolated to zero time on stream[b]	1 h on stream[c]	2 h on stream[d]
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

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

[b] Total conversion, 95%.

[c] Total conversion, 8%.

[d] Total conversion, 6%.

TABLE 2

Product Molar Ratios from *n*-Butane Cracking Catalyzed by Fe- and Mn- Promoted Sulfated Zirconia[a]

Temperature (°C)	Molar Ratio in Product	
	$CH_4/(C_3H_8 + C_3H_6)$[b]	CH_4/C_2H_6[c]
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

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

[b] Taken at 3 h time on stream.

[c] At a given temperature, this ratio was nearly constant as a function of time on stream.

TABLE 3

Approximate Kinetics Parameters Characterizing *n*-Butane Cracking Catalyzed by Fe- and Mn-Promoted Sulfated Zirconia[a]

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

[a] 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.

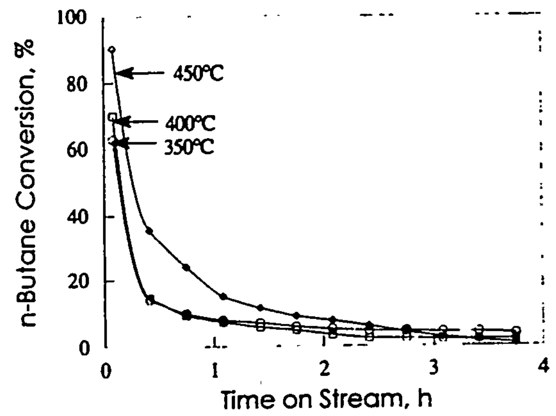

FIG. 1. Effect of reaction temperature on *n*-butane conversion to gas-phase products and coke catalyzed by Fe- and Mn-promoted sulfated zirconia. Feed *n*-butane partial pressure, 0.0025 atm; total feed flow rate, 80 ml (NTP)/min; catalyst mass, 1.5 g.

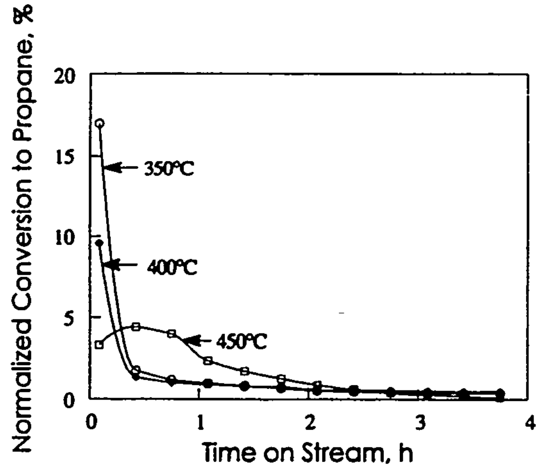

FIG. 2. Effect of reaction temperature on conversion to propane from *n*-butane reaction catalyzed by Fe- and Mn-promoted sulfated zirconia. Feed *n*-butane partial pressure, 0.0025 atm; total feed flow rate, 80 ml (NTP)/min; catalyst mass, 1.5 g.

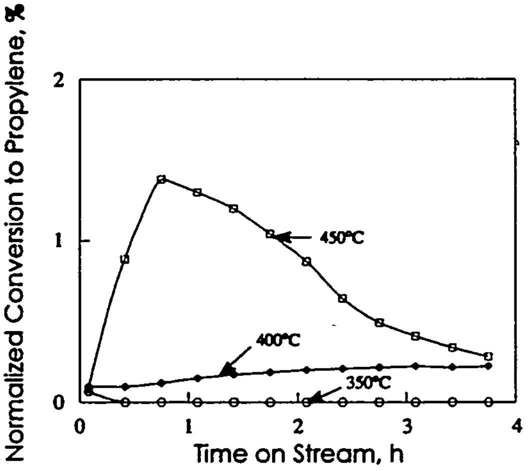

FIG. 3. Effect of reaction temperature on conversion to propylene from *n*-butane reaction catalyzed by Fe- and Mn-promoted sulfated zirconia. Feed *n*-butane partial pressure, 0.0025 atm; total feed flow rate, 80 ml (NTP)/min; catalyst mass, 1.5 g.

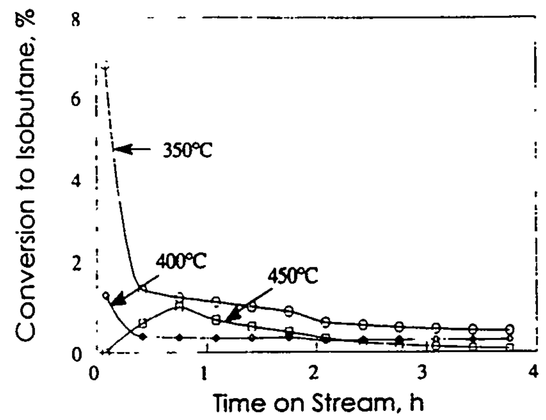

FIG. 4. Effect of reaction temperature on conversion to isobutane from *n*-butane reaction catalyzed by Fe- and Mn-promoted sulfated zirconia. Feed *n*-butane partial pressure, 0.0025 atm; total feed flow rate, 80 ml (NTP)/ min; catalyst mass, 1.5 g.

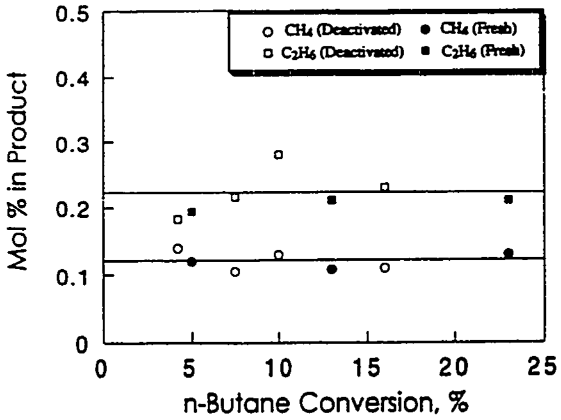

FIG. 5. Selectivity for formation of methane and ethane in *n*-butane reaction catalyzed by Fe- and Mn-promoted sulfated zirconia at 225°C. Data are based on analysis of the gas-phase products and do not account for carbonaceous deposits. Feed *n*-butane partial pressure, 0.01 atm; total feed flow rate,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

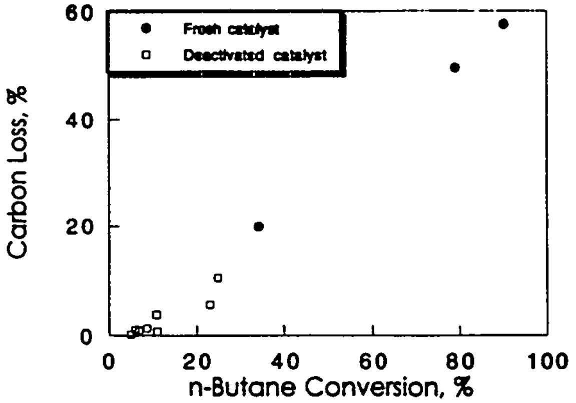

FIG. 6. Percentage of carbon loss in the gas phase effluent stream for *n*-butane reaction catalyzed by Fe- and Mn-promoted sulfated zirconia at 450°C. Feed *n*-butane partial pressure, 0.0025 atm; total feed flow rate, 80 ml (NTP)/min.

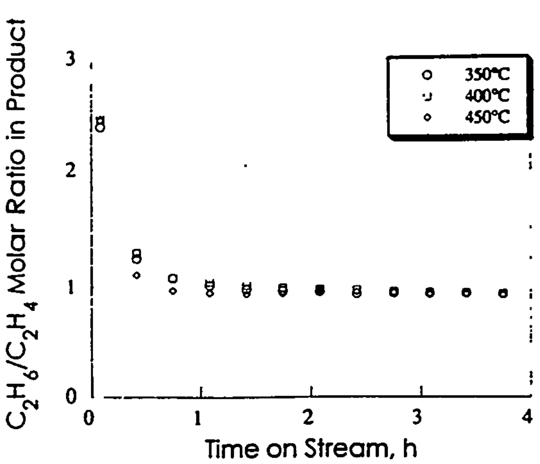

FIG. 7. Effect of reaction temperature on the ethane to ethylene ratio in the products of *n*-butane conversion. Feed *n*-butane partial pressure. 0.0025 atm; total feed flow rate, 80 ml (NTP)/min; catalyst mass, 1.5 g.

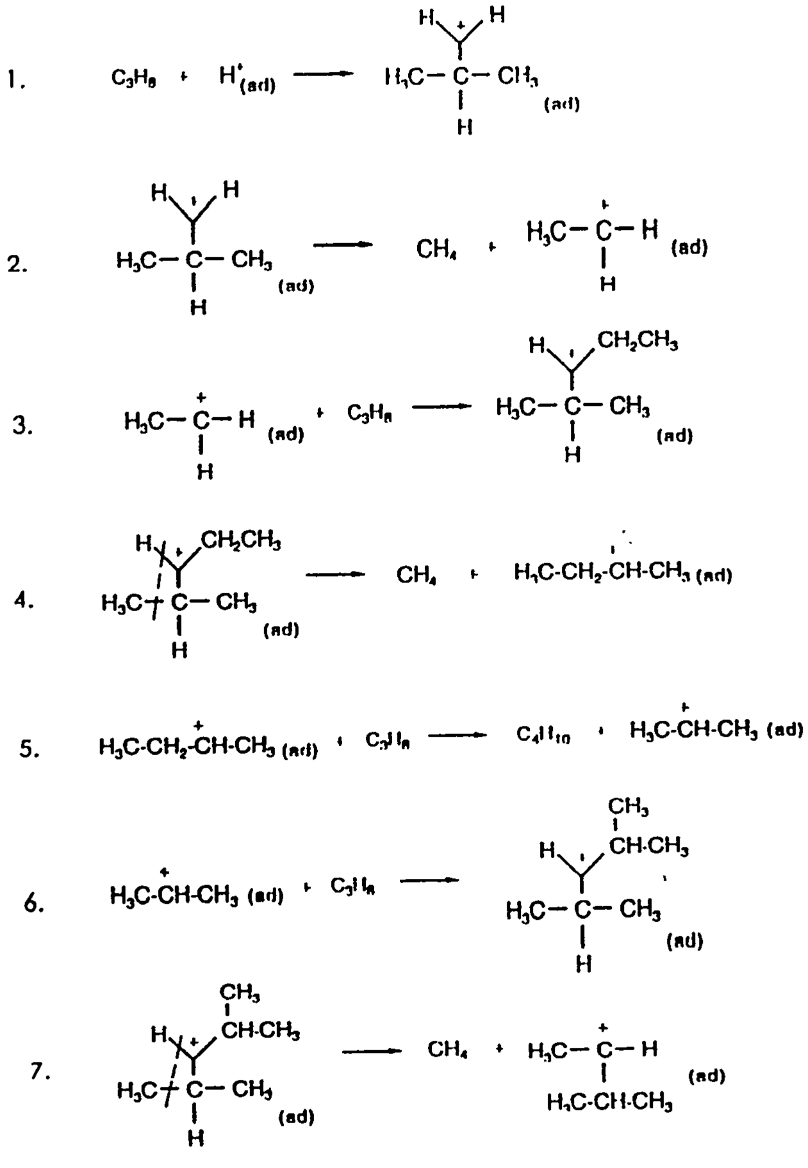

Fig. 8. Reaction network postulated for propane conversion in the presence of iron- and manganese-promoted sulfated zirconia. The dashed lines represent bond cleavages.