Neopentane cracking catalyzed by iron- and manganese-promoted sulfated zirconia

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Cracking of neopentane was catalyzed by a sulfated oxide of zirconium promoted with iron and manganese. Reaction at 300–450°C, atmospheric pressure, and neopentane partial pressures of 0.00025–0.005 bar gave methane as the principal product, along with C_2 and C_3 hydrocarbons, butenes, and coke. The order of reaction in neopentane was determined to be 1, consistent with a monomolecular reaction mechanism and with the formation of methane and *t*-butyl cations; the latter was presumably converted into several products, including only little isobutylene. At 450°C and a neopentane partial pressure of 0.005 bar, the rate of cracking at 5 min onstream was 5×10^{-8} mol/(g of catalyst s). Under the same conditions, the rates observed for unpromoted sulfated zirconia and USY zeolite were 3×10^{-8} and 6×10^{-9} mol/(g of catalyst s), respectively. The observation that the promoted sulfated zirconia is not much more active than the other catalysts is contrasted to published results showing that the former catalyst is more than two orders of magnitude more active than the others for *n*-butane isomerization at temperatures < 100°C. The results raise a question about whether the superacidity attributed to sulfated zirconia as a low-temperature butane isomerization catalyst pertains at the high temperatures of cracking.

Keywords: neopentane; cracking; zirconia; sulfated zirconia; superacid; zeolite Y

1. Introduction

Sulfated zirconia promoted with Fe and Mn is one of the most active known catalysts for *n*-butane isomerization [1]; its activity has been attributed to superacidity [2]. The product distributions in *n*-butane conversion at low temperatures (< 150°C) correspond to isomerization and disproportionation [3], and those at high temperatures [4] correspond to these reactions and cracking. Thus the available performance data for this catalyst are all consistent with the occurrence of acid–base catalysis.

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Neopentane cracking is a good probe reaction for solid-acid catalysts because it offers the following advantages: (1) neopentane has a simple symmetry and gives a small number of cracking products; (2) all the hydrogen atoms in the molecule are bonded to primary carbon atoms so that formation of carbenium ions by hydride abstraction is relatively slow; and (3) acid-catalyzed isomerization of neopentane is typically slow relative to cracking, so that simpler product distributions are observed for isopentane than for other pentanes. Gairbekov et al. [5] observed neopentane cracking catalyzed by HZSM-5 zeolite at 400°C; the products were methane and C_4 hydrocarbons with some C_2 and C_3. Engelhardt and Hall [6] made similar observations with other zeolites; the principal products were isobutylene and methane. The molar ratio of methane to isobutylene in some of these experiments was nearly 1, consistent with a simple cracking stoichiometry. Isomerization of neopentane to isopentane accounts for no more than a few percent of the products.

The promoted sulfated zirconia catalyst is much more active than sulfated zirconia and acidic zeolites for low-temperature butane isomerization. We sought to determine whether it also had an unusually high activity at high temperatures. Neopentane cracking was used as a probe reaction for a comparison of the performance of the promoted catalyst with those of sulfated zirconia and an acidic zeolite (USY) at 450°C.

2. Experimental

The catalyst, sulfated zirconia containing 1.0 wt% Fe, 0.5 wt% Mn, and 1.8 wt% sulfur, was prepared from sulfated zirconium hydroxide (Magnesium Elektron, Inc.), as described elsewhere [3]. Unpromoted sulfated zirconia was made by calcining zirconium hydroxide. USY zeolite (Si/Al atomic ratio 8.9) was obtained from W.R. Grace. The promoted and unpromoted sulfated zirconia catalysts were pretreated in N_2 flowing at 30 ml(NTP)/min at 450°C for 1.5 h. The zeolite was activated in air flowing at 30 ml(NTP)/min at 450°C for 1.5 h.

Neopentane (Liquid Carbonic, $>99.9\%$, as shown by gas chromatography) mixed with N_2 was fed to a once-through flow reactor packed with catalyst powder. The products were analyzed by on-line gas chromatography. The equipment is described elsewhere [3]. The ranges of conditions used for testing the promoted sulfated zirconia catalyst were as follows: temperature, 300–450°C; pressure, 1 bar; mass of catalyst, 0.1–1.5 g; inverse space velocity, $(0.1\text{–}6.0)\times 10^7$ (g of catalyst s)/mol of neopentane fed; neopentane partial pressure, 0.00025–0.005 bar; and run length, <4 h. Results were obtained for the sulfated zirconia and the zeolite catalyst only under the following conditions: temperature, 450°C; mass of catalyst, 1.0 g; inverse space velocity, 3.7×10^6 (g of catalyst s)/mol of neopentane fed; neopentane partial pressure, 0.005 bar; other conditions were as stated above for the promoted sulfated zirconia.

3. Results

The following results were observed for the promoted sulfated zirconia catalyst. Conversions of neopentane ranged from 1 to 20%. The only gas-phase product of the reaction of neopentane at a partial pressure of 0.00025 bar was methane. At higher reactant partial pressures, other products were also observed, namely, ethane, propane, ethylene, propylene, butenes, and traces of isopentane (table 1). The methane selectivity (measured as the mole fraction of the gas-phase products) was >85%. The conversion of neopentane was always higher than the conversion to methane, which indicates that other reactions (such as coke formation) also occurred. At a neopentane partial pressure of 0.05 bar, a temperature of 450°C, and a space velocity of 1×10^{-6} (mol of neopentane/(g of catalyst s)) (the highest value used), the overall conversion after 5 min on stream was about 1%. Even at the lowest conversion (1%), no isobutylene was observed in the products.

The total number of turnovers observed for the promoted sulfated zirconia was small. If we assume, for a lower-limit estimate, that the number of active sites was equal to the number of sulfur-containing sites in the solid, then the number of turnovers per site in 1 h of operation was only about 0.03 for reaction at 400°C,

Table 1
Distribution of products in cracking of neopentane catalyzed by Fe- and Mn-promoted sulfated zirconia[a]

	Conversion[b] (%)					
	0.08 h time on stream		2 h time on stream		4 h time on stream	
	350°C	450°C	350°C	450°C	350°C	450°C
reactant						
neopentane[c]	9.87	21.5	1.69	4.77	2.01	3.36
products						
methane	1.4	2.7	0.07	0.26	0.03	0.04
ethane	0.05	0.04	0	0	0	0
propane	0.22	0.01	0	0	0	0
ethylene	0.13	0.09	0	0.04	0	0
propylene	0.02	0.04	0	0.06	0	0
trans-2-butene	0	0	0	0.02	0	0
isobutylene	0	0	0	0.05	0	0

[a] Mass of catalyst, 1.0 g; feed neopentane partial pressure, 0.005 bar; total feed flow rate, 80 ml(NTP)/min.

[b] Conversions to the individual products are normalized as follows: the conversion of neopentane to an n-carbon compound is ($n \times$ the number of moles of the product)/(5 × number of moles of neopentane fed).

[c] Neopentane conversion is higher than the sum of conversion to individual products because coke is not accounted for among the products.

a neopentane partial pressure 0.0005 bar, and a space velocity 1.1×10^{-7} mol/(s g of catalyst). The estimate is about 1.1 turnovers per site for 5 h of operation at 450°C, a neopentane partial pressure of 0.005 bar, and a space velocity of 2.7×10^{-7} mol(s g of catalyst). Because the estimate of the number of sites is a likely upper limit, the results suggest that the number of turnovers per site exceeded unity in many of the experiments and that the reactions were catalytic.

Initial selectivity and conversion data (determined from analyses of products at 5 min on stream) for all three catalysts are summarized in table 2. The product distribution characterizing the promoted sulfated zirconia is about the same as that characterizing the sulfated zirconia at a given conversion. The conversion observed for the promoted catalyst was about twice that for the unpromoted catalyst at a given space velocity. In contrast, the product distribution characterizing the zeolite catalyst is much different from those of the other two. The molar ratio of methane to butenes was 1.5 at 5 min on stream, and approached 1.1 after 1 h for the zeolite. The conversion observed for the zeolite catalyst was an order of magnitude less than that for the promoted sulfated zirconia at a given space velocity.

Data indicating the activity of the promoted sulfated zirconia catalyst (represented by the conversion of the neopentane determined by the difference in neopen-

Table 2
Comparison of initial[a] activity and selectivity for neopentane cracking[b] at 450°C catalyzed by Fe- and Mn-promoted sulfated zirconia, unpromoted sulfated zirconia, and USY zeolite

	Catalyst				
	Fe- and Mn-promoted sulfated zirconia			sulfated zirconia	USY zeolite
10^7 × space velocity[c]	2.7	4.1	21.6	2.7	2.7
neopentane conversion (%)	17	10	1.5	10	2
product selectivities[d] (mol%)					
methane	97.4	97.3	96.0	97.2	57
ethane	0.70	0.60	0	0.62	0
ethylene	1.5	1.6	1.9	1.8	0
propane	0	0	0	0	0
propylene	0.31	0.40	1.3	0.51	3.1
trans-2-butene	0	0	0	0	8.5
1-butene	0	0	0	0	4.7
isobutylene	0	0	0	0	18.1
cis-2-butene	0	0	0	0	6.2
isopentane	0.10	0.13	0.82	0	2.3

[a] The data were taken at 5 min on stream.

[b] Feed: neopentane at a partial pressure of 0.005 bar. Total feed flow rate: 80 ml(NTP)/min.

[c] Space velocity is expressed in mol/(s g of catalyst).

[d] Selectivity for product i is defined as the molar ratio of the gas-phase product i to the sum of the gas-phase products.

tane partial pressure in the inlet and outlet streams) are shown for various temperatures and times on stream in fig. 1. The activity declined rapidly, indicating catalyst deactivation. For example, at 400°C with a neopentane partial pressure of 0.005 bar (fig. 1), the catalyst lost more than 70% of its activity in the first hour on stream. The rate of deactivation of the catalyst, measured by the rate of loss of fractional conversion of neopentane, increased with increasing temperature and with increasing neopentane partial pressure.

The fresh catalyst was rust colored; it became dark gray after operation at 300°C and black after operation at 450°C, consistent with the formation of coke. The mass balances on carbon, determined from the gas-phase analyses, did not close, consistent with the formation of high yields of coke. These closures were typically only 30%. If we assume equimolar yields of methane and isobutylene and that all the coke was formed from isobutylene, then the carbon balances close within 95% at low neopentane partial pressures.

The data obtained at lower partial pressures of neopentane allow accurate extrapolation of conversion to zero time onstream (fig. 2). The extrapolated data are taken as measures of the activity of the undeactivated catalyst. The conversion data obtained at 400°C and 0.0005 bar neopentane partial pressure and extrapolated to zero on-stream time are plotted vs. inverse space velocity in fig. 3. The data fall on a straight line through the origin, demonstrating that the conversions were differential when they were less than about 15%. The slope of the line represents the intrinsic reaction rate for the fresh catalyst. We have assumed that the other measured conversions were also differential and estimated rates from these conversions. Rates estimated in this way are plotted in fig. 4 as a function of time on

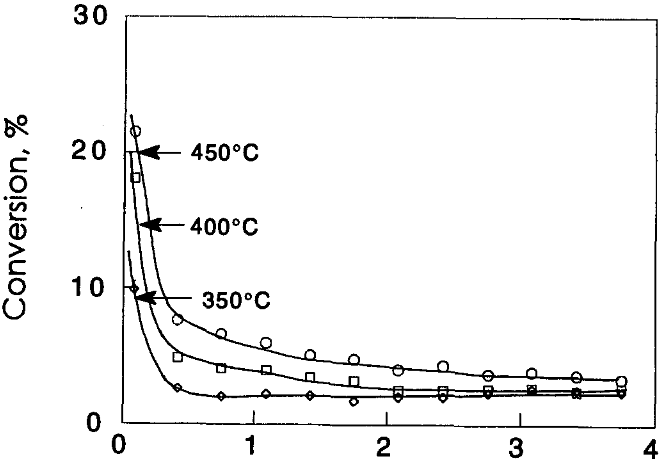

Fig. 1. Effect of reaction temperature on neopentane conversion to gas-phase products and coke catalyzed by Fe- and Mn-promoted sulfated zirconia. Feed neopentane partial pressure = 0.005 bar. Total feed flow rate = 80 ml(NTP)/min. Catalyst mass = 1.0 g.

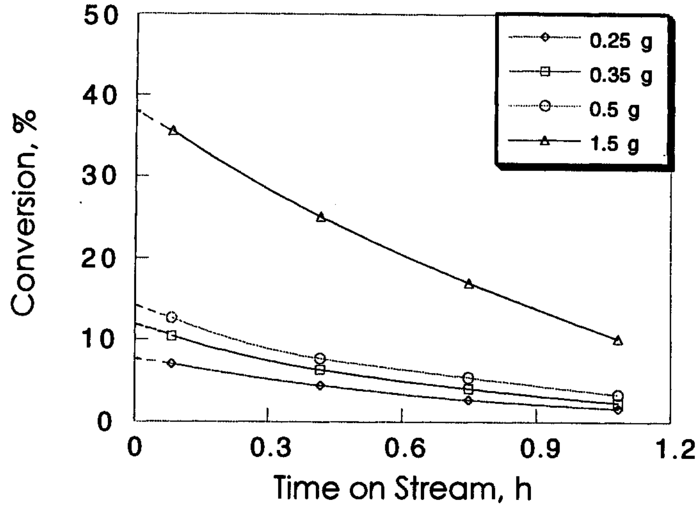

Fig. 2. Effect of catalyst weight on neopentane conversion to gas-phase products and coke catalyzed by Fe- and Mn-promoted sulfated zirconia. Feed neopentane partial pressure = 0.0005 bar. Total feed flow rate = 80 ml(NTP)/min. Reaction temperature = 400°C.

stream for various neopentane partial pressures. The rates estimated from the data at the highest temperature and the highest reactant partial pressures are the least accurate; the error in rate is estimated to be as much as ±50%. Under the other conditions, the typical errors in rate are estimated to be ±20% or less.

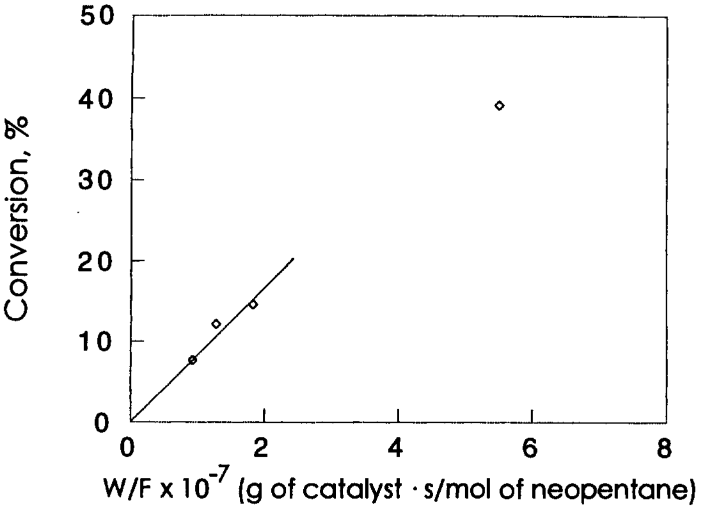

Fig. 3. Differential conversion of neopentane catalyzed by Fe- and Mn-promoted sulfated zirconia at 400°C in a flow reactor. Values reported are from extrapolation to zero time on stream. Feed neopentane partial pressure = 0.0005 bar. Total feed flow rate = 80 ml(NTP)/min.

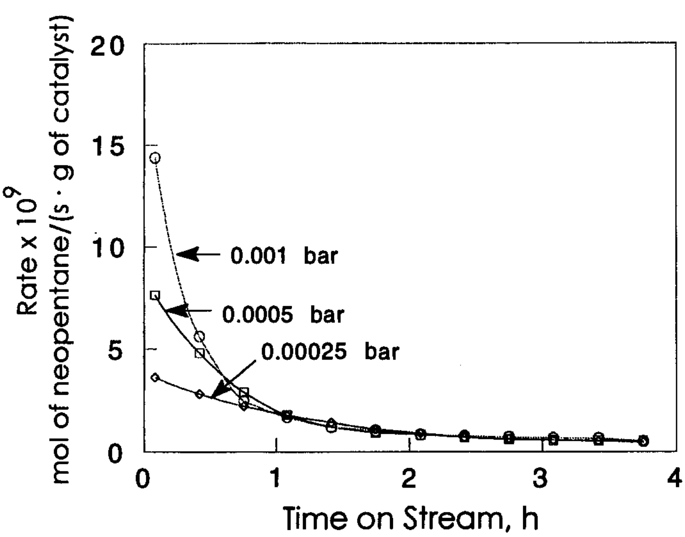

Fig. 4. Effect of neopentane partial pressure on rate of overall conversion catalyzed by Fe- and Mn-promoted sulfated zirconia. Reaction temperature = 400°C, total feed flow rate = 80 ml(NTP)/min, catalyst weight = 0.25 g.

The secondary reactions at 450°C and a fixed neopentane partial pressure of 0.005 bar were investigated by varying the space velocity. The initial selectivity for methane formation, determined at 5 min on stream, was around 97%, independent of inverse space velocity in the range from 1.8×10^6 to 3.6×10^6 (g of catalyst s)/(mol of neopentane fed). As the time on stream increased, the methane selectivity decreased; the rate of decrease in this selectivity was greatest at the highest space velocity.

Plots of rate versus neopentane partial pressure on logarithmic coordinates at various temperatures (fig. 5) indicate a reaction order of 1.0 ± 0.05. The temperature dependence of the first-order rate constant for neopentane cracking, determined by extrapolating data for the rate of neopentane conversion to zero on-stream time for estimation of the rate constants, is shown in the Arrhenius plot of fig. 6. The apparent activation energy is about 12 kcal/mol. The apparent activation energy for methane formation is about 17 kcal/mol. Gairbekov et al. [5] reported a value of 16 kcal/mol for methane formation from neopentane catalyzed by a high-silica zeolite.

4. Discussion

In agreement with the consensus in the literature [5,6], the data demonstrate that for all three catalysts the principal reaction of neopentane was cracking. The results obtained for the promoted and unpromoted sulfated zirconia catalysts indicate that methane was always formed as a product, but isobutylene was formed

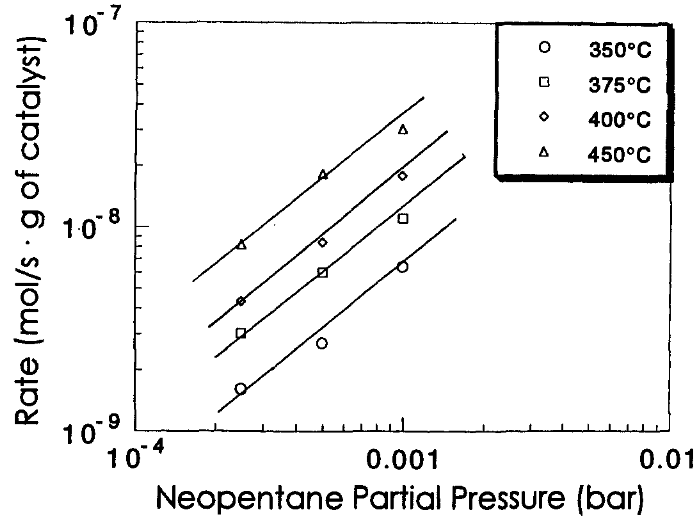

Fig. 5. Rate of neopentane conversion catalyzed by Fe- and Mn-promoted sulfated zirconia versus partial pressure of neopentane on a logarithmic coordinate. Catalyst mass = 0.25 g; total feed flow rate = 80 ml(NTP)/min.

only under some conditions. The stoichiometry was not that of simple cracking (i.e., that giving a 1/1 molar methane/isobutylene product ratio), which indicates that side reactions were significant. Even at the highest space velocity, no isobutylene was observed at 1% initial neopentane conversion. We suggest that cracking of neopentane occurred to give *t*-butyl cations, which remained adsorbed on the acidic sites or reacted on the surface before forming isobutylene.

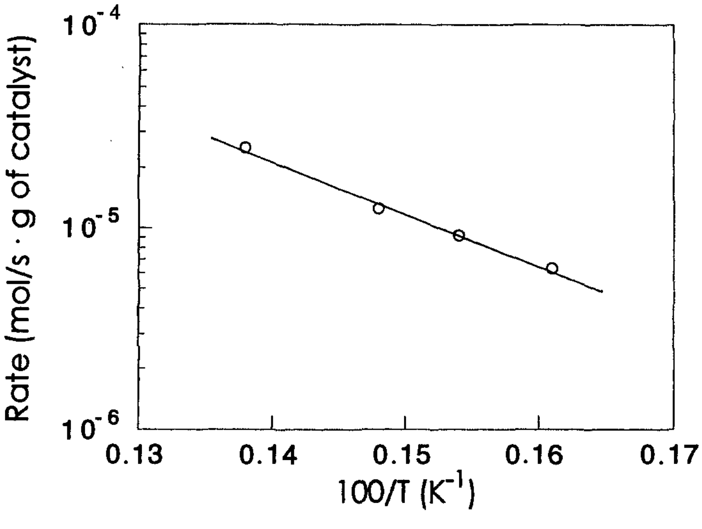

Fig. 6. Arrhenius plot for neopentane conversion catalyzed by Fe- and Mn-promoted sulfated zirconia. Catalyst mass = 0.25 g; total feed flow rate = 80 ml(NTP)/min.

In contrast, isobutylene (along with other butenes) was observed as a product of reaction catalyzed by the USY zeolite (table 2). The molar ratio of methane to butenes shown in table 2 (determined at 5 min on stream and at a low conversion, 2%) is about 1.5. This value is greater than the stoichiometric ratio of 1 for simple cracking of neopentane. These results imply that secondary reaction of butenes also occurred, at least at earlier times on stream when the catalyst was USY zeolite.

After 1 h on stream, however, the ratio approached 1.1, and the neopentane conversion remained about 2%. Engelhardt and Hall [6], using a variety of aluminosilicate catalysts, also observed ratios near the stoichiometric value of unity at low conversions ($<1\%$); Gairbekov et al. [5] also observed almost simple stoichiometric cracking with high-silica zeolites. Our data are consistent with the cracking to give methane and isobutylene accompanied by secondary reaction of isobutylene.

A mechanism for neopentane cracking at low conversions is the Haag–Dessau mechanism [5,6], whereby the catalyst protonates neopentane to give a pentacoordinated carbonium ion, which undergoes fission to give methane and a *t*-butyl cation; in the simplest situation, the *t*-butyl cation gives back a proton to the catalyst and forms isobutylene, which desorbs. The formation of methane and isobutylene is explained by this mechanism, but, because we did not observe isobutylene as a product under most of the conditions, we postulate the occurrence of the Haag–Dessau mechanism without substantial conversion of the *t*-butyl cation into isobutylene.

We also postulate that the subsequent reactions of the *t*-butyl cation are more important in the reactions catalyzed by the sulfated zirconia than in those catalyzed by the zeolite because the acidic sites on the former are stronger than those on the latter, binding the cation more tightly and favoring reactions other than deprotonation/desorption. This interpretation implies the presence of Brønsted acid sites on the promoted and unpromoted sulfated zirconia; there is spectroscopic evidence of Brønsted acid sites on the latter [7]. The observed reaction order of 1 for the neopentane conversion is consistent with the hypothesis that monomolecular cracking dominated the reaction network.

Because of the difficulty of forming neopentyl cations, which are primary and highly unstable, it is inferred that the predominant reactions leading to other cracking products involve bimolecular reactions of *t*-butyl cations formed with methane by decomposition of protonated neopentane. This is the suggestion of Lombardo et al. [8], who investigated neopentane conversion catalyzed by HZSM-5, H-mordenite, and other zeolites. The adsorbed *t*-butyl cations could combine with butenes to form C_8 intermediates, which would crack to give hydrocarbons such as a C_3 and C_5. Pentenes thus produced can undergo further cracking to give ethylene and propylene. Thus we suggest that the observed C_2 and C_3 products are secondary products.

The various butene isomers observed in the product might have arisen from skeletal rearrangement of *t*-butyl cations, but they might also have arisen from intermediates such as C_8.

Because the selectivity for methane formation decreased as the catalyst deactivated, we infer that methane formed not only as a primary product of neopentane cracking, but also as a secondary product at the higher temperatures and neopentane partial pressures. Consistent with this interference, the methane selectivity declined faster with time on stream at the lower inverse space velocities than at the higher inverse space velocities.

The most active of the three catalysts investigated here was the promoted sulfated zirconia, but its activity is only roughly twice that of the unpromoted sulfated zirconia (at 5 min time on stream) and an order of magnitude greater than that of the zeolite. Thus the activity advantage of the promoted catalyst is much less than that shown by its performance in butane isomerization at temperatures $<100°C$ [1]. Similarly, the cracking of *n*-butane catalyzed by the promoted sulfated zirconia at 450°C was only an order of magnitude faster than that catalyzed by HZSM-5 [4]. Perhaps the sites of the promoted sulfated zirconia are so strongly acidic such that the olefinic product does not desorb and deactivation occurs rapidly once neopentane is in contact with the catalyst. Alternatively, these results raise a question about the nature of the promoted catalyst, which has been postulated to be a superacid [1,2]. There is no evidence in the high-temperature cracking data for any extraordinary acid strength of the promoted catalyst, nor for that of the unpromoted sulfated zirconia. Perhaps there is more to the catalytic nature of the promoted sulfated zirconia than superacidity.

5. Conclusions

Iron- and manganese-promoted sulfated zirconia catalyzes neopentane cracking, with an activity only slightly greater than that of sulfated zirconia and that of USY zeolite. The major product was methane; isobutylene was observed under some conditions. Secondary reactions were significant under almost all conditions, giving ethylene, propylene, butenes, and traces of ethane, propane, and isopentane. The catalyst underwent rapid deactivation, losing about 70% of its activity in 1 h on stream at 400°C and a neopentane partial pressure of 0.05 bar. The neopentane conversion data indicate first-order kinetics. The data are consistent with the Haag–Dessau mechanism of cracking, whereby the neopentane is protonated by the catalyst to give a carbonium ion, which undergoes fission to give methane and the *t*-butyl cation. The observation that the neopentane cracking activity of the promoted sulfated zirconia is not much higher than that of unpromoted sulfated zirconia and USY zeolite at 450°C raises questions about the nature of the catalytic sites in these materials and whether there is more to their catalytic character than superacidity.

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