Effects of iron promoter on reactions of 1-butene adsorbed on sulfated zirconias

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Volatile hydrocarbons evolved by heating sulfated zirconia and iron promoted sulfated zirconias containing adsorbed 1-butene are detected and characterized by using temperature-programmed desorption coupled with mass spectrometry and with capillary gas chromatography–mass spectrometry. The presence of iron promoter has a dramatic effect on both the temperature at which volatile products evolve from catalysts and the composition of volatile hydrocarbon mixtures. These differences reflect differences in the reactivities of surface carbenium ions. Reactions on unpromoted and iron promoted catalysts are consistent with an apparent decrease in the Lewis acidity of surface carbenium ions when iron promoter is present.

Keywords: sulfated zirconia, promoted sulfated zirconia

1. Introduction

Sulfated zirconia has attracted considerable attention as a catalyst for the skeletal isomerization of alkanes at low temperatures [1]. When transition metals such as Fe, Mn, and Ni are incorporated into sulfated zirconia, a dramatic increase in the rate of isomerization of *n*-butane in the presence of these promoted catalysts can be detected [2–5]. Although several different theories have been proposed, no consensus has been reached regarding the role of the sulfated zirconia metal promoters in this increased catalytic activity. One explanation of the enhanced catalytic activity of promoted catalysts is that the metal promoters increase catalyst acidity [2,6,7]. Several attempts have been made to detect acidity differences between unpromoted and transition metal promoted sulfated zirconias. Adeeva et al. used infrared spectroscopy of adsorbed probe molecules to evaluate catalyst acidities and concluded that the unpromoted and promoted sulfated zirconia catalysts have about the same Lewis and Brønsted acid strengths [8]. Attempts to use temperature-programmed desorption (TPD) of bases to measure sulfated zirconia catalyst acidities have largely been unsuccessful because most adsorbed basic probes decompose rather than desorb [9–11]. Alternatively, it has been proposed that metal promoters facilitate dehydrogenation of butane to butene, which subsequently oligomerizes to form a C_8 intermediate that rearranges and cracks to produce isobutane [12–14]. Coelho et al. have further postulated that metal promoters facilitate accumulation of hydrogen-deficient species on catalyst surfaces [13]. Tabora and Davis [5] and Wan et al. [15] suggest that *n*-butane isomerization occurs by a bi-functional mechanism and that differences between unpromoted and promoted catalysts are not due to differences in catalyst acidities.

Oligomerization reactions such as those that have been proposed to form C_8 intermediates in the isomerization of *n*-butane involve reactions of carbenium ions. Olefins react with Brønsted acid sites to form carbenium ions and negative alkoxide surface ions. TPD studies of catalysts containing adsorbed olefins provide insight into the stabilities and reactions of surface carbenium ions. In fact, studies using small olefins have previously been employed to characterize zeolite reactivities [16–18]. Volatile species detected during TPD studies typically include oligomers and oligomer cracking products and reflect the reactivities of surface carbenium ions as well as interactions between carbenium ions and alkoxide surface ions [19–22]. A comparison of the volatile products evolved from 1-butene TPD studies of unpromoted and Fe promoted sulfated zirconia catalysts is presented here. Mass spectrometry was employed to detect and characterize volatile TPD hydrocarbons and GC/MS was used to separate and identify these substances.

2. Experimental

All catalysts were prepared by using a procedure published previously [23]. Zirconium hydroxide (BET 180 m^2/g) was precipitated from a 0.5 M solution of zirconium tetrachloride by dropwise addition of NH_4OH. Iron was added to the dried zirconium hydroxide by incipient wetness impregnation with an aqueous nitrate solution to yield the desired metal content. After drying in air at 473 K, sulfate was added by incipient wetness

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impregnation with a $(NH_4)_2SO_4$ solution resulting in a nominal sulfate loading of 8% by weight. Catalysts were then dried and calcined in air at 873 K for 4 h. After calcination, the sulfate content (as SO_4) was found to be 3–4% by weight. The surface areas of calcined samples were between 100 and 120 m^2/g. Catalyst designations, promoter loadings, amounts of butene that were adsorbed, and sulfate species concentrations for the catalysts used in this study are listed in table 1.

Infrared measurements were made by using a Sirius 100 FT-IR (Mattson Instruments, Madison, WI) and a previously described modified Harrick Scientific variable temperature diffuse reflectance attachment [24,25]. Approximately 5 mg neat catalyst samples were loaded into the diffuse reflectance sample holder for analyses. Catalyst samples were heated to 873 K under vacuum (1×10^{-6} Torr) at a rate of 30 K/min to remove adsorbed water and organic impurities. Samples were then cooled to 323 K under vacuum and sufficient 1-butene was admitted into the sample chamber to achieve a 10 Torr pressure. After a 10 min equilibration period, the sample chamber was purged with He for 1 h to remove gas phase 1-butene. Infrared spectra were then acquired with a spectral resolution of 8 cm^{-1}.

TPD-MS and TPD-GC/MS measurements were made by connecting the gas outlet of a DuPont (Wilmington, DE) model 951 thermogravimetric (TG) analyzer to a Hewlett Packard (Palo Alto, CA) 5985 mass spectrometer. The combined TPD-MS and TPD-GC/MS interface was constructed in our laboratory and is described in detail elsewhere [26]. About 50 mg catalyst samples were placed in the TG sample pan for TPD-MS studies. For TPD-GC/MS studies, about 200 mg catalyst samples were placed in ceramic boats that were then placed inside the TG quartz furnace tube. Because the TG balance was not used for TPD-GC/MS studies, sample weight gain or loss information for samples studied by this method was not obtained. Samples were pretreated by heating them in air at 30 K/min from room temperature to 873 K. Samples were then evacuated and maintained at 873 K for another 30 min. After cooling samples to 323 K under vacuum, 1-butene was introduced to achieve a pressure of 10 Torr. After a 10 min equilibration period, the TG quartz tube was purged with He until 1-butene could no longer be detected by the mass spectrometer. Butene TPD studies were initiated by applying a 10 K/min heating ramp to catalyst samples. For TPD-GC/MS studies, 100 μl TG effluent samples were injected into a 10 m DB-5 capillary gas chromatography column maintained at 313 K. By making injections at 20 K catalyst sample temperature intervals, chromatograms were obtained at 2 min intervals. Mass spectra were acquired by using 70 eV electron bombardment ionization and scanning from m/z 10 to m/z 250.

Table 1
Characteristics of sulfated zirconia catalysts

Catalyst designation	Fe (%)	Butene (mmol/g)	Sulfate (mmol/g)
ZS	–	0.38	0.21
ZSF1	0.5	0.60	0.56
ZSF3	1.5	0.61	0.54
ZSF4	4.0	0.50	0.65

3. Results and discussion

Diffuse reflectance infrared spectroscopy was employed to characterize the interactions between catalyst surfaces and 1-butene. Infrared spectra for promoted and unpromoted catalyst samples obtained after catalyst samples were exposed to 10 Torr of 1-butene were similar. During He purge to remove gas phase 1-butene, absorbance bands at 3090 and 1644 cm^{-1}, which are representative of C=(CH–H) and –(C=C)– stretching vibrations respectively, disappeared leaving absorbance bands at 2877, 2935, and 2962 cm^{-1}, which are representative of protonated aliphatic hydrocarbons. Infrared spectra obtained for 1-butene adsorbed on unpromoted and Fe promoted sulfated zirconias were similar to those reported by Dakta [17] when 1-butene was adsorbed on sodium exchanged zeolites.

For both unpromoted and Fe promoted catalyst samples, TPD-MS mass spectrometric measurements made after 1-butene was adsorbed and during sample purging with He revealed the presence of volatile hydrocarbons larger than 1-butene in the purge effluent. This suggests that oligomerization occurred during 1-butene adsorption at 323 K. For three of the four catalysts used in this study, the sample weight gain attributed to 1-butene adsorption corresponded to more adsorbed butene than the number of sulfate surface sites (table 1), which also suggests that oligomerization occurred at 323 K. Butene oligomerization on sulfated zirconia catalysts at 323 K was not unexpected because low temperature propene oligomerization on zeolites has been previously reported [20].

TPD-MS studies indicated that the presence of the Fe promoter facilitated volatile product evolution at lower temperatures. Figure 1 shows TPD-MS total ion current temperature profiles for 1-butene TPD from unpromoted catalyst and catalyst samples containing 0.5, 1.5, and 4.0% Fe. The shapes of TG weight loss curve derivatives were similar to the total ion current temperature profiles in figure 1. Whereas the total ion current temperature profile for the unpromoted catalyst sample exhibits a single volatile species evolution peak, the promoted catalyst samples exhibit more asymmetric profiles with greater ion signals at lower temperatures. The Fe promoted catalyst sample total ion current temperature profiles appear to consist of at least two overlapping evolutions. One of these evolutions occurs near the total

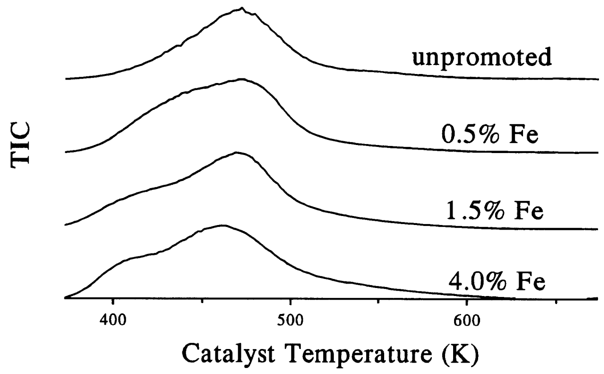


Figure 1. TPD-MS total ion current (TIC) temperature profiles representing volatile species evolved from 1-butene adsorbed on unpromoted and Fe promoted sulfated zirconia catalysts.

ion current maximum for the unpromoted catalyst sample and another evolution maximizes about 50 K lower. The relative integrated total ion current area for the low temperature evolution did not significantly increase with increased iron loading, suggesting that only some of the added iron promoter was responsible for this effect.

TPD-GC/MS studies revealed that the volatile species evolved during 1-butene TPD from unpromoted catalysts were very different from those evolved from Fe promoted catalysts. Figure 2 contains TPD-GC/MS chromatograms obtained during 1-butene TPD from an unpromoted catalyst sample and a catalyst containing 4.0% Fe. Results similar to those depicted in figure 2 for the 4.0% Fe promoted catalyst were also obtained for the 0.5 and 1.5% Fe promoted catalysts. The tic marks in figure 2 denote catalyst sample temperatures at which effluent was injected into the gas chromatograph. Successive chromatograms in figure 2 are separated by 2 min (20 K) intervals. Inspection of figure 2 reveals that the volatile product slate for both the unpromoted and promoted catalysts changed with temperature. TPD-GC/MS results indicated that more volatile products were detected at low temperatures for the Fe promoted catalysts than for the unpromoted catalyst, which is consistent with TPD-MS results (figure 1). At temperatures below 413 K, butene was a significant volatile product for both catalyst samples. At catalyst sample temperatures above 413 K, butene was still a significant volatile product for the Fe promoted catalysts but was not detected for the unpromoted catalyst. Above 413 K, most of the volatile species desorbed from the unpromoted catalyst were saturated hydrocarbons whereas most of the species desorbed from the Fe promoted catalysts were olefins. This is clearly illustrated in figure 3, which shows TPD-GC/MS chromatograms obtained

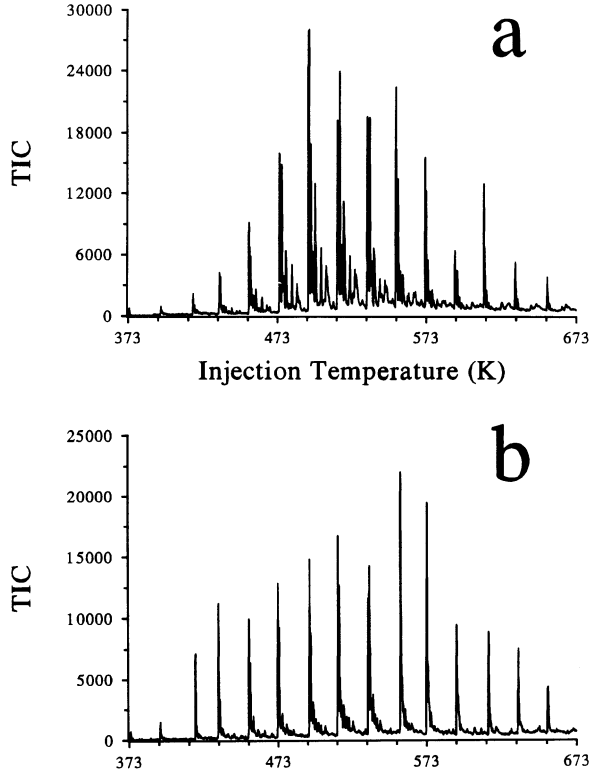


Figure 2. TPD-GC/MS total ion current chromatograms obtained for (a) unpromoted and (b) 4.0% Fe promoted sulfated zirconia catalysts containing adsorbed 1-butene.

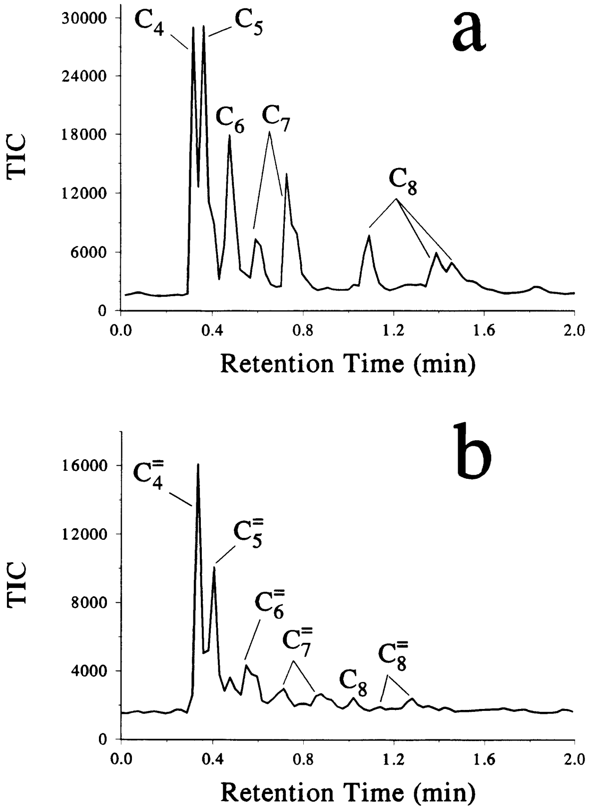


Figure 3. TPD-GC/MS total ion current chromatograms obtained at 493 K for (a) unpromoted and (b) 4.0% Fe promoted sulfated zirconia catalysts containing adsorbed 1-butene.

from each catalyst sample when the catalyst temperature had reached 493 K. Chromatographic peaks in figure 3 labeled C_n denote saturated hydrocarbons with n carbon atoms and peaks labeled by $C_n^=$ denote corresponding unsaturated hydrocarbons. Table 2 lists the relative yields of volatile products detected in the TPD-GC/MS chromatograms shown in figure 3. Relative yields were calculated by integrating the total ion current under chromatographic peaks representing isomeric species, adding peak areas for isomers with the same number of carbon atoms, and dividing this integrated total ion current by the integrated total ion current determined for the entire chromatogram. Curve fitting was employed to obtain chromatographic peak area estimates for severely overlapping elutions. Nearly 86% of the volatile products detected at 493 K for the unpromoted catalyst sample were saturated hydrocarbons. In contrast, less than 20% of the volatile products detected at 493 K for the 4.0% Fe promoted catalyst were saturated hydrocarbons. Butene evolution was responsible for about 31% of the products evolved from the 4.0% Fe promoted catalyst sample at 493 K but was not detected in the TPD-GC/MS chromatogram obtained for the unpromoted catalyst sample at this temperature.

Reactions of C_4 carbenium ions formed by Brønsted acid protonation of butene with gas phase butene can produce C_8 carbenium ions. These C_8 carbenium ions may react further with butene to form larger carbenium ions, crack to form species smaller than C_8, abstract hydrides from neighboring surface species to form saturated C_8 species, or deprotonate to form C_8H_{16}. Volatile C_8H_{16} species were detected during TPD-GC/MS analyses for both unpromoted and Fe promoted catalysts and are represented in figure 4 by m/z 112 (C_8H_{16} molecular ion) mass-selected ion chromatograms for the unpromoted and 4.0% Fe promoted catalyst samples. Like the total ion current TPD-GC/MS chromatograms, the m/z 112 mass-selected ion chromatograms indicate that more species yielding m/z 112 were evolved from Fe promoted catalysts than from the unpromoted catalyst at low catalyst sample temperatures. Several chromatographic elutions having mass spectra containing m/z 112 were detected for both catalyst samples. However, differences in retention times for species yielding m/z 112 in figure 4 indicate that the species that yielded m/z 112 for the unpromoted catalyst were not the same as those that yielded m/z 112 for the 4.0% Fe promoted catalyst sample. This is consistent with the great disparity in the volatile product slates for these two catalysts (table 2). Inspection of mass spectra for the chromatographic elutions containing m/z 112 revealed that some of the m/z 112 mass-selected chromatographic peaks represented C_8H_{16} molecular ions but that others resulted from fragmentation of volatile species that had molecular weights larger than 112. In fact, only two of the elutions in the m/z 112 mass-selected chromatogram for the unpromoted catalyst and three of the elutions in the m/z 112 mass-selected chromatogram for the 4.0% Fe promoted catalyst sample represented C_8H_{16} molecular ions. Table 2 shows that the relative yields of total C_8H_{16} volatile products at 493 K were similar for the unpromoted and 4.0% Fe promoted catalysts. Mass spectra obtained for the two C_8H_{16} species evolved from the unpromoted catalyst were consistent with dimethylcyclohexane structures. In contrast, mass spectra for the

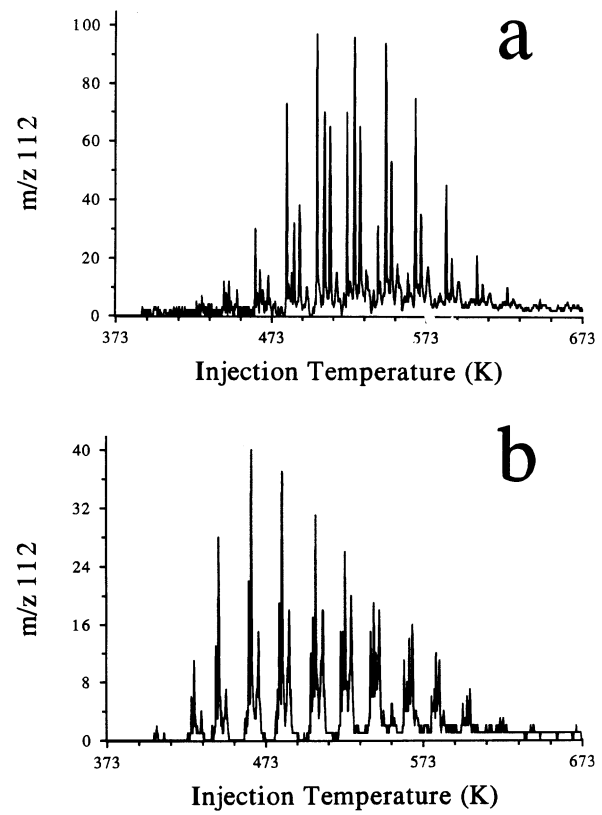


Figure 4. TPD-GC/MS m/z 112 mass-selected chromatograms for (a) unpromoted and (b) 4.0% Fe promoted sulfated zirconia catalysts containing adsorbed 1-butene.

Table 2
Relative volatile species yields at 493 K[a]

Volatile species	Unpromoted catalyst (%)	Fe promoted catalyst (%)
C_4H_8	–	30.9
C_4H_{10}	9.6	–
C_5H_{10}	7.2	24.4
C_5H_{12}	19.8	2.2
C_6H_{12}	–	15.2
C_6H_{14}	16.4	4.5
C_7H_{14}	1.9	8.1
C_7H_{16}	15.4	7.4
C_8H_{16}	1.3	1.4
C_8H_{18}	16.1	5.4
C_9H_{20}	8.4	–

[a] Computed as the percentage of the GC/MS chromatogram integrated total ion current.

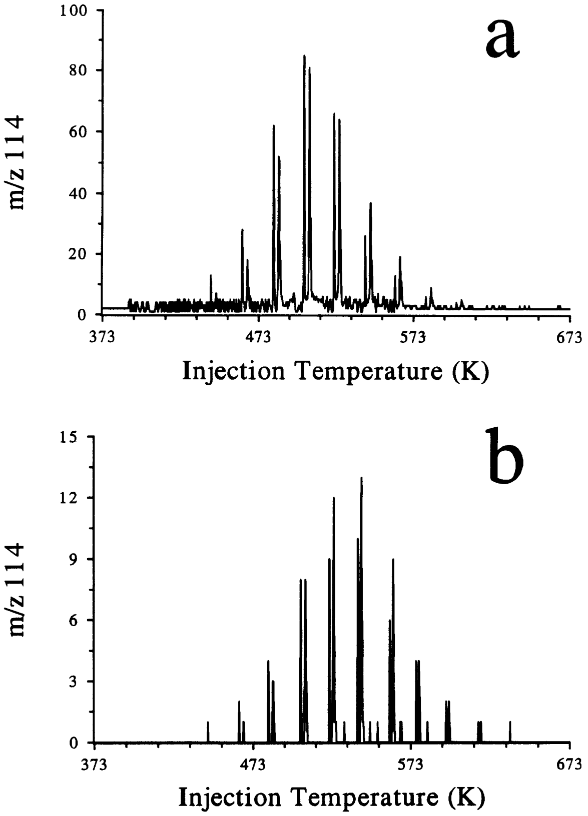
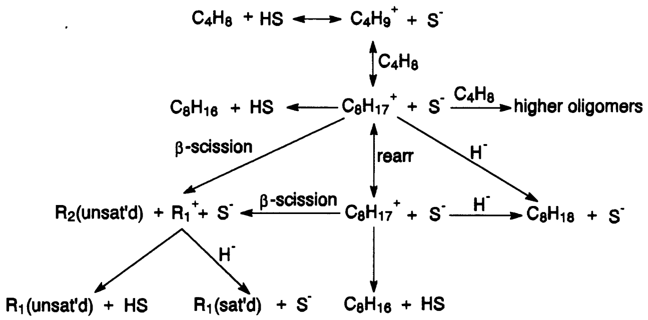


Figure 5. TPD-GC/MS m/z 114 mass-selected chromatograms for (a) unpromoted and (b) 4.0% Fe promoted sulfated zirconia catalysts containing adsorbed 1-butene.

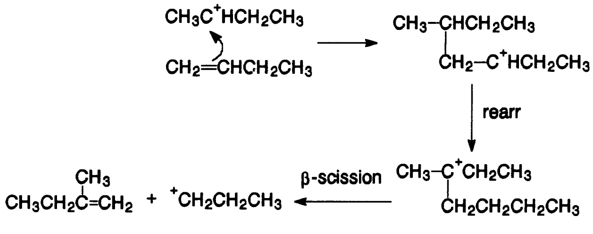
three C_8H_{16} species evolved from the 4.0% Fe promoted catalyst were consistent with C_8 olefin isomers.

Oligomer carbenium ions can abstract hydrides from neighboring adsorbates to form volatile hydrocarbons. Volatile C_8H_{18} hydrocarbons formed after $C_8H_{17}^+$ hydride abstraction were detected during TPD-GC/MS analyses of both unpromoted and Fe promoted catalysts. However, as table 2 shows, the relative yield of volatile C_8H_{18} species evolved from the unpromoted catalyst was about three times that for the 4.0% Fe promoted catalyst. As shown in figure 5, mass-selected chromatograms for m/z 114 were similar for both catalysts and contained two chromatographic peaks. Inspection of TPD-GC/MS mass spectra indicated that m/z 114 was the molecular ion in the mass spectra obtained for each of these elutions. Retention times and mass spectra for each of the C_8H_{18} species evolved from unpromoted and Fe promoted catalysts were similar, suggesting that the same two species were evolved from both catalysts. In contrast to the C_8H_{16} evolution temperature profiles, the catalyst temperature at which C_8H_{18} evolution maximized was higher for the 4.0% Fe promoted catalyst (533 K) than for the unpromoted catalyst (493 K).

The volatile products detected during TPD-GC/MS analysis of Fe promoted catalysts can be explained by the following reaction scheme:



In this reaction scheme, C_4H_8 represents 1-butene and HS denotes a Brønsted acid site on the catalyst surface. One source of butenes detected by TPD-GC/MS analysis of Fe promoted catalysts may have been deprotonation of $C_4H_9^+$ species when thermal energy due to sample heating exceeded the interaction energy between the carbenium ion and the catalyst surface. In addition, reactions of 1-butene with $C_4H_9^+$ carbenium ions to form $C_8H_{17}^+$ must have occurred to produce the detected volatile products that were larger than C_4. Initially formed $C_8H_{17}^+$ carbenium ions may rearrange, react with additional 1-butene to form larger carbenium ions, or may be converted to volatile products by: deprotonation to regenerate HS Brønsted acid sites and form C_8H_{16} species, hydride abstraction from neighboring adsorbates to form C_8H_{18} species, or by β-scission to produce unsaturated products and smaller carbenium ions. These smaller carbenium ions may desorb as olefins or abstract hydrides and desorb as saturated hydrocarbons. The selectivity for unsaturated volatile products and the relatively low yields of C_8H_{16} and C_8H_{18} detected by TPD-GC/MS analysis of Fe promoted catalysts (table 2) suggest that $C_8H_{17}^+$ β-scission was a dominant process and that carbenium ions formed by β-scission desorbed primarily as olefins when iron was present in sulfated zirconia catalysts. The large yield of butenes evolved from Fe promoted catalysts may have resulted from a combination of $C_4H_9^+$ deprotonation and oligomer carbenium ion β-scission. The TPD-GC/MS chromatogram in figure 3b and volatile species yields contained in table 2 show that C_5H_{10} species were also evolved from the 4.0% Fe promoted catalyst in relatively large yields. C_5H_{10} can readily be formed from $C_8H_{17}^+$ carbenium ions after they rearrange to form tertiary cations:



This should be a significant reaction path due to the increased stability of the tertiary cation intermediate compared to the secondary cation initially formed.

In contrast to the adsorbed 1-butene TPD-GC/MS results obtained for Fe promoted catalysts, unsaturated species were not the primary volatile products for the unpromoted catalyst and butenes were only detected at relatively low catalyst temperatures. The lack of a substantial yield of butenes suggests that $C_4H_9^+$ was not present in significant amounts on the unpromoted catalyst. Instead, oligomeric carbenium ions were more likely the dominant species on the surface of the unpromoted catalyst. The fact that 8.4% of the chromatogram total ion current measured by TPD-GC/MS for the unpromoted catalyst at 493 K corresponded to saturated C_9 hydrocarbons (table 2) suggests that surface concentrations of oligomeric carbenium ions that were larger than C_8 were significant on the unpromoted catalyst. Furthermore, the facts that the amount of butene that was adsorbed by the unpromoted catalyst was almost twice the number of sulfate groups on the catalyst whereas the amounts of butene adsorbed on Fe promoted catalysts were about the same as the number of sulfate groups (table 1) also suggest that larger oligomers were formed on the unpromoted catalyst than on the Fe promoted catalysts. Many of the saturated hydrocarbons that constituted most of the volatile products detected by TPD-GC/MS for the unpromoted catalyst likely resulted from β-scission of these large oligomeric carbenium ions. Apparently, the neutral unsaturated β-scission products from oligomer carbenium ions were too large to be volatile at the catalyst temperatures at which scission occurred. The carbenium ions also formed by these scissions subsequently reacted by hydride abstraction to form the detected saturated hydrocarbon products.

4. Conclusions

The results described here illustrate the utility of TPD-GC/MS for characterizing catalyst surfaces. By removing gas phase reactants prior to analysis, TPD-GC/MS provides a means of probing catalytic reactions without the complexities due to successive reactions that are unavoidable in catalytic reactor studies. By using GC/MS instead of only MS for detection, volatile species can be more accurately identified and semi-quantitative analyses for multiple species are possible.

Many of the volatile hydrocarbons evolved by heating iron promoted sulfated zirconias containing adsorbed 1-butene can be derived by β-scission of a $C_8H_{17}^+$ surface carbenium ion. A $C_8H_{17}^+$ carbenium ion has also been proposed as a reaction intermediate by Adeeva et al. to explain the isomerization of *n*-butane to isobutane on Fe, Mn promoted sulfated zirconias [4]. In their mechanism, $C_8H_{17}^+$ carbenium ion intermediates are formed that crack by β-scission to form butene and *t*-$C_4H_9^+$ carbenium ions, which subsequently abstract hydrides to form isobutane. Results described here suggest that this process can readily occur with Fe promoted catalysts but is not favored on unpromoted catalysts due to competition from reactions leading to larger oligomeric carbenium ions. This may explain why the *n*-butane isomerization catalytic activities for unpromoted catalysts are so much lower than for metal promoted catalysts.

In the absence of iron promoter, oligomeric carbenium ions formed on sulfated zirconia surfaces undergo β-scission followed by hydride abstraction to produce volatile saturated hydrocarbons that are released from the surface when the catalyst is heated. This must necessarily lead to a decrease in the H/C ratio of species remaining on the catalyst surface. As a result, this carbenium ion behavior on unpromoted sulfated zirconia should quickly lead to char formation. Catalyst deactivation caused by rapid coking as a result of these surface reactions may also be a factor in the weaker catalytic activity for *n*-butane isomerization for unpromoted catalysts compared to metal promoted catalysts. Unfortunately, we were unable to measure char contents remaining after TG-MS studies because the amount of char was below the detection limit of our apparatus.

The dramatic differences in the reactivities of unpromoted and Fe promoted catalysts containing adsorbed 1-butene may be explained by differences in the electrophilic properties of surface carbenium ions. Comparing the reactions that occurred on unpromoted and Fe promoted catalysts, carbenium ions formed on unpromoted catalysts reacted as if they were stronger Lewis acids (better electrophiles) than those formed on Fe promoted catalysts. The observed increase in the tendency to form oligomers, cyclization of oligomeric carbenium ions to form dimethyl cyclohexanes, and the increased abundance of volatile products formed by hydride abstraction (i.e. saturated hydrocarbons) suggests that carbenium ion positive charge centers were better electrophiles when they were in contact with the unpromoted catalyst surface compared to the Fe promoted catalyst surface. This apparent change in carbenium ion Lewis acidity undoubtedly resulted from perturbations of the catalyst surface by the iron promoter. Thus, one role of iron promoter in sulfated zirconia catalysts is to perturb the catalyst surface in a way that strengthens interactions between the catalyst and carbenium ions and consequently decreases the Lewis acidity of surface carbenium ions.

Acknowledgement

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