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Abstract
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An Examination of Brønsted-Acid Sites in H-[Fe]ZSM-5 for Olefin Oligomerization and Adsorption

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ABSTRACT

The adsorption and reaction properties of an Al-free H-[Fe]ZSM-5 were examined and compared to an H-[Al]ZSM-5 sample with the same site density. H-[Fe]ZSM-5 was shown to have Brønsted-acid sites in a concentration equal to the framework Fe concentration. Differential heats of adsorption for ammonia and pyridine were shown to be identical to that obtained in H-[Al]ZSM-5, with differential heats of ~150 kJ/mol for ammonia and 200 kJ/mol for pyridine. For H-[Al]ZSM-5, adsorption of either propylene or 1-butene at room temperature results in rapid oligomerization. TPD-TGA measurements of the oligomers in H-[Al]ZSM-5 show evidence for hydride-transfer reactions, in addition to simple oligomer cracking. By contrast, it is necessary to heat H-[Fe]ZSM-5 to 370 K for rapid oligomerization of propylene and oligomerization of 1-butene occurs only slowly at 295 K. TPD-TGA measurements of the oligomers in H-[Fe]ZSM-5 show no evidence for hydride-transfer reactions and H-[Fe]ZSM-5 forms much less coke than H-[Al]ZSM-5 during steady-state reaction in 1-butene at 573 K. Adsorption measurements of 1-butene on D-[Fe]ZSM-5 suggest that the protonated complexes of 1-butene are formed but that these are relatively stable towards reaction, implying that the carbocation transition states are relatively unstable.

INTRODUCTION

Acid-catalyzed reactions are among the most important industrial reactions; and, even though there are significant advantages to heterogeneous processes, homogeneous acids are still used for all but a relatively small number of important industrial processes, especially in fine chemicals [1]. One barrier to applying solid acids more widely is that there is still considerable disagreement over how to characterize and control the “strength” of acid sites in solid acids [2]. Therefore, an important goal of the work in our group has been to develop a better understanding of the chemistry that occurs at the acid sites in well-characterized zeolites [3,4].

H-[Al]ZSM-5, the acidic form of the molecular sieve having the MFI structure, is ideal for studying fundamental aspects of acidity in solids due to the fact that the Brønsted-acid sites in this material appear to be catalytically equivalent, with a concentration equal to the framework Al concentration. Not only have researchers at Mobil shown that rates for a large number of reactions increase linearly with Al concentration [5,6], they also performed Cs-poisoning studies to show that all framework Al sites contribute a catalytic site [6]. They showed that reaction rates on partially exchanged materials decreased linearly with Cs content and that it was necessary to

have one Cs per Al to eliminate activity. Since one would expect Cs to poison the most active sites preferentially, this result, together with the linear increase in rates with Al content, implies that all Al sites in H-ZSM-5 must have essentially identical activities. In our own work, we have shown that stoichiometric adsorption complexes, one molecule per Brønsted site, can be formed for a wide range of compounds in H-ZSM-5, including alcohols [7-9], amines [10], nitriles [11], pyridines [12], thiols [13], ketones [14,15], CO [16], and diethyl ether [11]. In agreement with the concept of equivalent acid sites, the reactivities of molecules associated with the adsorption complexes are independent of site density [17]. Finally, calorimetry data also suggested equivalent sites in H-ZSM-5, since differential heats of adsorption were constant at coverages below one per site and independent of site density [18].

The substitution of Al^{+3} with Fe^{+3} in the MFI framework results in an interesting material in which the cavity surrounding the site is not affected but the proton-transfer properties are changed. Previous work has shown that H-[Fe]ZSM-5 has Brønsted-acid sites, although the ν(O-H) stretching frequency is higher than that found on H-[Al]ZSM-5 [19-21]. The acid sites in H-[Fe]ZSM-5 show activity for alcohol dehydration [22], but appear to be much less active for olefin oligomerization and n-hexane cracking reactions [19]. Indeed, it was suggested in the earlier work that all of the activity observed in H-[Fe]ZSM-5 for cracking of n-hexane may have been due to Al impurities [19]. Another interesting observation concerning H-[Fe]ZSM-5 is the report that the heats of adsorption for ammonia (145 kJ/mol) and pyridine (200 kJ/mol) are essentially the same for both Fe and Al sites. Furthermore, adsorption of CD_3CN on the acid sites leads to a ν(C≡N) stretch at 2298 cm^{-1} for both materials [21].

In the present paper, we have investigated the properties of an H-[Fe]ZSM-5 sample more thoroughly. To avoid questions concerning Al impurities, we have synthesized a sample with a much higher Fe content, using a high-purity silica source to minimize Al content. The Brønsted-acid sites were then characterized using simultaneous temperature-programmed-desorption (TPD) and thermogravimetric analysis (TGA), FTIR, and microcalorimetry. Finally, the catalytic properties of the Bronsted sites were monitored for reactions of 1-butene. The results suggest that Brønsted sites associated with framework Fe are catalytically active for olefin oligomerization, but are much less active for the hydride-transfer reactions that lead to coke formation. We suggest that these materials may be very interesting for reactions requiring high selectivity.

EXPERIMENTAL PROCEDURES

In order to prepare an Al-free ferrosilicate, [Fe]ZSM-5 was synthesized using fumed silica (Cab-O-Sil from Cabot) as the silica source. To prepare the silica, 29.6 g of Cab-O-Sil (97% SiO_2 with the remainder water) was slurried in a solution of 11.6 g of NaOH (98.9% NaOH) in 58.5 g of deionized water, using a polypropylene container. The resulting paste was transferred to a freshly cleaned, Teflon-lined autoclave and heated to 400 K for 2 days to get a clear, viscous solution.

The ferrosilicate was then prepared as follows: 5.0 g $Fe(NO_3)_3*9H_2O$ was dissolved in 33.33 g of deionized water. After adding 5.33 g of concentrated H_2SO_4 to this solution, 8 g of tetrapropyl-ammonium bromide in 13.33 g of deionized water was added. This turned the mixture brown. Next, 66.66 g of the sodium silicate prepared in the first step was diluted with 66.6 g of deionized water, while stirring, and added to the brown mixture, changing the solution to a light yellow color. Finally, the mixture was sealed and heated in a stirred autoclave to 450 K for 3 days. The final product was a white powder in a clear liquid. Microscopic examination showed small particles of indefinite shape but uniform size. XRD measurements of the product agreed with published data for the MFI structure, and the lattice parameter gave an estimate for the framework Si/Fe_2 ratio that agreed with the value targeted in the synthesis [23]. The target Si/Fe_2 of 60 was chosen to match the Si/Al_2 ratio of the [Al]ZSM-5 sample used in this study.

To place the sample in its acidic form, the [Fe]ZSM-5 was calcined in flowing air at 750 K for 4 hr and ion exchanged three times with 0.1 M NH_4Cl at 345 K. Between each ion exchange, the sample was washed with distilled water until no Cl^- was detected by $Ag(NO_3)$ solutions on the filtrate. Evidence that most of the Fe remained in the framework of the [Fe]ZSM-5 sample was shown by the fact that the sample remained off-white in color after calcination and ion exchange. Furthermore, TPD-TGA results with iso-propylamine, shown in Fig. 1, demonstrated that the sample had a Brønsted-acid site density of 0.50 mmol/g, close to the target Fe concentration, 0.55 mmol/g. In iso-propyl amine TPD-TGA measurements, the Brønsted-acid site density is determined from the amount of iso-propylamine that decomposes to propylene (m/e=41) and ammonia (m/e=17) between 575 and 650 K [17,24]. Because the decomposition reaction is similar to the Hofmann elimination, molecules associated with this reaction must be protonated.

The [Al]ZSM-5 sample used for the adsorption studies was one of the standard samples available from NIST and was reported to have a Si/Al_2 ratio of 60. It was obtained in the ammonium-ion form and simply calcined in flowing air at 773 K to obtain the acidic form, H-[Al]ZSM-5. The TPD-TGA results for iso-propylamine from this sample were indistinguishable from that shown in Fig. 1 and indicated that the Brønsted-acid site density of this H-[Al]ZSM-5 was also 0.50 mmol/g, in reasonable agreement with the Al concentration.

Reaction measurements for 1-butene isomerization and oligomerization were carried out on the H-[Fe]ZSM-5 and a second zeolite, designated H-[Al]ZSM-5(30). H-[Al]ZSM-5(30) was obtained from Zeolyst in the ammonium-ion form and was reported to have a Si/Al_2 ratio of 30. Rate measurements were performed in a pilot-plant reactor at 573 K, using 500 mg of catalyst and 0.15 atm of 1-butene in dry N_2. The weight-hourly-space velocity (WSHV) was maintained at 0.63 g 1-butene/g catalyst*hr. Following the rate measurements, temperature-programmed oxidation (TPO) experiments were performed to determine the final carbon content of the samples.

FTIR spectra were collected on a Mattson Galaxy FTIR with a diffuse-reflectance attachment (Collector II™) purchased from Spectra-Tech Inc. This system allowed measurements to be performed at temperatures ranging from room temperature to 800 K in flowing, dry N_2. The calorimetric measurements were performed at 500 K using a home-built microcalorimeter described elsewhere [25].

RESULTS

Pyridine and Ammonia Adsorption

While the TPD-TGA results for isopropyl amine suggest that the framework Fe results in Brønsted-acid sites, we also performed FTIR measurements to establish the nature of the acid sites unambiguously. FTIR data for both H-[Fe]ZSM-5 and H-[Al]ZSM-5 are shown in Fig. 2. It is well known that two, well-defined hydroxyl groups are observed on H-[Al]ZSM-5, with stretching frequencies at 3740 and 3605 cm^{-1}, and that only the 3605-cm^{-1} peak is associated with Brønsted acidity [26]. This is demonstrated in spectra shown in 2a) and b), which were taken before and after adsorption of pyridine, followed by flushing the sample with dry N_2 at 470 K. Upon adsorption of pyridine, the 3605-cm^{-1} peak is lost and peaks at 1540 and 1485 cm^{-1}, which can be associated with pyridinium ions [27], are observed. Evidence for Lewis-acid sites, normally associated with nonframework Al, would be given by a peak at 1440 cm^{-1}; however,

the sites in this H-[Al]ZSM-5 sample are primarily Brønsted in nature. With H-[Fe]ZSM-5, the Brønsted-acid sites are associated with a peak at ~3630 cm^{-1} [20,21], as shown in Fig. 2c). Again, adsorption of pyridine removes the 3630-cm^{-1} peak from the spectrum in Fig. 2d) and causes the formation of peaks associated with pyridinium ions. Clearly, the exchange sites associated with framework Fe provide Brønsted-acid sites strong enough to protonate pyridine. Since most of the Fe is in the framework of the H-[Fe]ZSM-5, the Lewis-acid site concentration is again very low.

It should be noted that, other than using dry air for sample calcination, no special care was taken for the H-[Fe]ZSM-5 samples used in the results shown in Figs. 1 and 2. While we found the ferrosilicate to be somewhat more sensitive towards steaming than its aluminosilicate analog, Fe remained in the framework after heating to high temperatures and after exposure to amines, olefins, and pyridine. Qualitatively, H-[Fe]ZSM-5 appears to have a stability similar to that of SAPO-5 [28]. This is important in establishing that the ferrosilicate could be applied in commercial processes.

In a previous calorimetric study of ammonia and pyridine in H-[Fe]ZSM-5, it was reported that differential heats of adsorption were similar to values found on H-[Al]ZSM-5 [19]. Because the sample used in that study had a low Fe content and traces of Al, we repeated the measurements on the present sample, with the results shown in Fig. 3. These microcalorimetric measurements were performed on both the H-[Fe]ZSM-5 and H-[Al]ZSM-5 samples at 500 K by pulsing small gas doses onto the evacuated sample. The high adsorption temperature was chosen to ensure that equilibration was rapid and that the calorimetric results were representative of adsorption at the Brønsted-acid sites [25]. The runs were terminated when some of the gaseous pulse did not adsorb on the sample, as demonstrated by an increase in the pressure above the sample to above 0.01 torr.

Fig. 3a) plots the differential heats for pyridine on the H-[Fe]ZSM-5 and H-[Al]ZSM-5 samples as a function of coverage; and, in agreement with previous work [19], demonstrates that the results for the two samples are essentially indistinguishable. The differential heats at coverages below 350 μmol/g are 200±10 kJ/mol. For higher coverages, the heats fall significantly and we simultaneously begin to observe gas-phase pyridine above the sample. Because pyridine adsorption at Brønsted-acid sites is irreversible at 500 K, differential heats of pyridine cannot be used to measure the distribution of differential heats, as discussed in detail

elsewhere [25]. Nonetheless, it is significant that the differential heats are the same for both samples. Fig. 3b) shows the analogous results for ammonia on H-[Fe]ZSM-5 and H-[Al]ZSM-5. Again, the conclusion is that the heat of formation of the ammonium-ion complexes are the same in these two materials, since the differential heats on both samples are 150±5 kJ/mol at coverages below one per site. As with pyridine, the gas-phase pressure of ammonia in equilibrium with the sample at coverages below one per site was too small to be measured; however, in the case of ammonia, the adsorbate molecules have some mobility at 500 K. Therefore, the coverage independence of the differential heats at coverages below one per site suggest that the heats of formation for all ammonium-ion complexes in both H-[Fe]ZSM-5 and H-[Al]ZSM-5 are identical.

Olefin Adsorption

Previous work with H-[Fe]ZSM-5 has suggested that its activity for hydrocarbon cracking and olefin oligomerization is much lower than that of H-[Al]ZSM-5 [19]. However, because traces of Al were present in the H-[Fe]ZSM-5 samples that were used, it was difficult to establish the true, intrinsic activity of Brønsted sites associated with framework Fe and separate it from the reactions associated with residual Al sites. In the present study, the H-[Fe]ZSM-5 was Al free. Because the H-[Al]ZSM-5 and H[Fe]ZSM-5 samples in this study had the same Brønsted-acid site densities, the comparison of activities is also more appropriate.

Adsorption on H-[Al]ZSM-5

Because olefin oligomerization proceeds through a well understood, carbenium-ion mechanism, most of our attention was focused on these reactions rather than catalytic cracking. Indeed, based on previous work with H-[Al]ZSM-5 zeolites, the relative activity of olefins depends strongly on the stability of the initial carbenium ion [9,28]. In the case of ethylene, reaction to form adsorbed oligomers is very slow at room temperature and it is necessary to heat the sample to ~370 K before reaction rates are significant [29]. The relatively low reactivity of ethylene is due to the fact that oligomerization proceeds through an unstable, primary carbocation. By comparison, the reaction of propylene to form adsorbed oligomers occurs rapidly on H-[Al]ZSM-5 at room temperature in the presence of just a few torr of propylene and stops only after a coverage corresponding to approximately 4 molecules/site is obtained [29].

The adsorption characteristics of 1-butene on H-[Al]ZSM-5 are essentially identical to what has been reported for propylene, and oligomerization occurs rapidly at room temperature.

Fig. 4 shows TPD-TGA results for the H-[Al]ZSM-5 sample following exposure to 15 torr of 1-butene at 295 K for 60 sec. The coverages in this figure were determined from the sample mass and the mass is referenced to the mass of the sample prior to adsorption. Following evacuation to 10^{-7} torr, the coverage remains at 1900 μmol/g, or approximately 4 molecules/site, corresponding to a tetramer. If one assumes that the oligomers of 1-butene have a density of 0.8 g/cm^3, a typical density of hydrocarbon liquids, 2000 μmol/g of 1-butene corresponds to a volume of 0.14 cm^3/g, which is a substantial fraction of the theoretical pore volume, 0.19 cm^3/g, available in the MFI structure. Two desorption events are observed in the TPD-TGA curves, one centered at ~450 K and the other at 550 K. While the fragmentation patterns of the products in both desorption features are complex, both exhibit peaks with m/e ratios greater than 56, the molecular weight of 1-butene. Therefore, both peaks must be associated with cracking (or depolymerization) of oligomer products. Since the sample weight returns to its initial value upon heating to 700 K, there is no carbonaceous residue remaining in the sample.

It is interesting to investigate the reason for two desorption events in the TPD-TGA curves and several experiments shed light on the nature of the species involved. First, there is a significant increase in the size of the second feature, with a simultaneous decrease in the size of the first, when adsorption of 1-butene is carried out at 370 K. This implies that species present in the low-temperature feature can be converted to the species in the high-temperature feature. Second, while similar peaks are observed in the mass spectra of the products in Fig. 4, a close examination of the peak ratios in the fragmentation pattern reveal that the products are different. In particular, the ratio of the peaks at m/e = 58 and 41 amu are higher for the low-temperature desorption event. Finally, the peak at m/e = 78 amu, which can be due to benzene among other products, is significantly larger in the second desorption feature. Notice that no attempt was made to calibrate the partial pressures from the intensities of the features in the mass spectra.

The identification of complex hydrocarbons in a residual-gas analyzer is uncertain; therefore, we examined the products formed in desorption by trapping them with a liquid-nitrogen trap and analyzing the products formed between 300 to 500 K and between 500 to 700 K using gas chromatography. The product distribution, shown in Fig. 5, is quite different in the two temperature ranges. At the lower temperatures, the products are primarily small olefins. All of the C-6 products were linear and branched olefins, with no aromatics observed. At the higher temperatures, essentially all of the C-6 product was benzene and most of the desorbing products

were either benzene or propylene. The fact that benzene can be evacuated from an acidic zeolite at room temperature [30] indicates that the formation of benzene in the TPD-TGA measurements is reaction limited. However, formation of aromatics in the high-temperature range is clear evidence for hydride transfer.

Based on the above products, we suggest that the first desorption event in Fig. 4 is olefinic in nature and that the second feature is a combination of paraffinic and aromatic species. According to this picture, hydride-transfer reactions could either saturate or aromatize adsorbed molecules, leaving a less reactive product that could not diffuse out of the zeolite channels without first cracking. The higher desorption temperature would then be due to the lower reactivity of paraffins and aromatics compared to olefins at Brønsted sites. If this were true, exposure of the olefinic oligomers to D_2O should give rise to rapid H-D exchange at room temperature according to the following reactions:

$$ZOH + D_2O = ZOD + HDO$$

$$C_nH_{2n} + ZOD = ZOH + C_nDH_{2n-1}$$

Previous work has suggested that this exchange occurs rapidly for olefins due to reversible adsorption of olefins to form alkoxide or carbenium-ion intermediates [9]. By contrast, paraffins should be much less reactive for H-D exchange. Results for this experiment are shown in Fig. 6. Here, H-[Al]ZSM-5 was exposed to 15 torr 1-butene at 400 K for 60 sec, evacuated, and then exposed to 10 torr D_2O for 60 sec and evacuated. As discussed earlier, the adsorbate coverage following this procedure, ~2000 μmol/g, is essentially the same as that following room-temperature exposure but the amount of product desorbing at high temperatures has increased dramatically. Most simple olefins other than ethylene have a major peak at m/e = 41 amu in their mass spectrum, but do not show peaks in the range from 43 to 45 amu unless they have been partially deuterated. Therefore, this region of the spectrum is useful for examining H-D exchange. The data in Fig. 6 demonstrate that there is significant H-D exchange in both desorption features, but that more exchange has occurred in the low-temperature feature, in agreement with the concept that the olefinic products formed at high temperature likely result from cracking of large paraffins. Although the data for aromatics is not shown, H-D exchange did occur freely into the aromatic products formed at high temperatures, similar to what has been observed for toluene in H-[Al]ZSM-5 [30].

Adsorption on H-[Fe]ZSM-5

The reactivity of the H-[Fe]ZSM-5 sample for olefin oligomerization is dramatically different from that of H-[Al]ZSM-5. At room temperature, propylene is physically adsorbed only and desorbs rapidly and completely upon evacuation. In previous studies [19], a small amount of irreversible adsorption did occur at room temperature but this adsorption can be assigned as due to residual Al impurities. Similar to the situation for ethylene in H-[Al]ZSM-5, oligomerization of propylene does occur on H-[Fe]-ZSM-5 at elevated temperatures. Upon ramping the sample in 1 torr of propene at 2 K/sec, we observed a rapid uptake beginning at approximately 370 K. TPD-TGA results for the oligomers formed by propylene in H-[Fe]ZSM-5 are shown in Fig. 7. In this experiment, the sample was ramped at 2 K/sec in 1 torr propylene up to 400 K, then evacuated and cooled to room temperature. The final coverage of oligomers was slightly less than 4 molecules/site, similar to the final coverage on H-[Al]ZSM-5. The propylene oligomers in H-[Fe]ZSM-5 crack in a narrow temperature window between 450 and 500 K, slightly higher than the low-temperature peak for oligomer cracking on H-[Al]ZSM-5. Again, peaks at m/e = 55 and 69 demonstrate that products larger than propylene are leaving the sample. GC analysis of the products show formation of a complex mixture of olefins, similar to the product distribution observed for 1-butene in H-[Al]ZSM-5 below 500 K. It is noteworthy that, unlike the H-[Al]ZSM-5 case, there is no high-temperature feature in the TPD-TGA of the oligomers on H-[Fe]ZSM-5 and no evidence for hydride-transfer reactions.

The results for 1-butene adsorption in H-[Fe]ZSM-5 are more interesting and will be discussed in more detail. 1-Butene oligomerizes at the acid sites in H-[Fe]ZSM-5 at room temperature, but slowly. Fig. 8 shows TPD-TGA curves obtained after exposure of the H-[Fe]ZSM-5 to 15 torr of 1-butene for 60 sec at 295 K. The initial coverage, 800 μmol/g, is greater than one per site. Indeed, a feature centered at 380 K can be identified as unreacted 1-butene based on the absence of a peak at m/e = 69 amu in the mass spectrum and GC analysis. The TGA suggests that approximately 200 μmol/g of 1-butene desorbs from this feature. If one assumes that this number of acid sites are occupied by a single molecule and all of the remaining acid sites in the sample are occupied by dimers which desorb in the feature centered at ~460 K, all of the acid sites in the sample are accounted for. Again, there is no high-temperature feature, which should occur if hydride transfer were important, in the TPD-TGA curves.

The interpretation of the results in Fig. 8 assumes that 1-butene forms relatively stable, unreactive complexes with the Brønsted sites in H-[Fe]ZSM-5. To establish whether or not such

complexes are formed, the H-[Fe]ZSM-5 sample was converted to its deuterium analog, D-[Fe]ZSM-5, by repeated exposure to D_2O and evacuation at 700 K, then exposed to a controlled dose of 1-butene at room temperature. Basically, 1-butene was admitted to the sample until the weight change indicated a coverage of approximately one per site. TPD-TGA results obtained following this procedure are shown in Fig. 9. Unreacted 1-butene is the main desorption product in the feature at 380 K; however, the mass spectrum shows that most of the 1-butene leaves the sample as C_4H_7D, as evidenced by the peak at m/e = 57 amu. This implies that the butene molecules interact with and are protonated by the Brønsted sites in H-[Fe]ZSM-5, even though reaction to oligomers is slow.

FTIR experiments for 1-butene adsorption in D-[Fe]ZSM-5 at 295 K, shown in Fig. 10, confirm the conclusions from TPD-TGA. The spectrum of the clean, D-[Fe]ZSM-5 is shown in Fig 10a), where the peaks at 2750 and 2670 cm^{-1} are the ν(O-D) stretches corresponding to terminal silanols and bridging hydroxyls associated with framework Fe, respectively. After exposure to a controlled dose of 1-butene, Fig. 10b), ν(C-H) stretches between 2800 and 3000 cm^{-1} were observed, which are typical of saturated hydrocarbons. The spectrum in 10b) also shows a ν(C-D) stretch at 2170 cm^{-1} due to the formation of a C-D bond. Formation of a C-D bond suggests a complete and rapid deuterium transfer to the olefin. Unlike such protonated molecules in H-[Al]ZSM-5, the complexes are relatively stable towards formation of oligomers. Heating to 600 K drives off all of the adsorbate and leaves a partially, D-exchanged sample, Fig. 10c). As discussed in previous papers for H-[Al]ZSM-5 [30], exchange occurs between the terminal silanols and the Brønsted sites at elevated temperatures.

1-Butene Isomerization

Steady-state, 1-butene isomerization was also performed on the H-[Fe]ZSM-5 and the H-[Al]ZSM-5(30) samples using the conditions described in the Experimental section. Under these experimental conditions, the conversion of 1-butene was above 90% on both samples for a period of at least 200 min. The iso-butene yield on H-[Fe]ZSM-5 remained steady during the 200-min period and was significantly higher than the yield on H-[Al]ZSM-5(30), ~10% compared to less than 5%; however, the low value on both samples did not suggest that these catalysts are worth pursuing for this reaction.

More interesting and more relevant to the present discussion is the fact that the amount and type of coke formed in these two molecular sieves was dramatically different. Temperature-

programmed-oxidation (TPO) curves for these samples following 200 min of exposure to the reaction environment are shown in Fig. 11. Results for H-[Al]ZSM-5(30) show the formation of almost 7 wt% carbon, coming off in two oxidation peaks. The two peaks probably imply that two forms of carbonaceous residue are present on the sample; approximately half of this residue can only be removed by oxidation at high temperatures. By comparison, significantly less coke was present on the H-[Fe]ZSM-5 sample and most of this reacted off at low temperatures. Again, this result is consistent with the fact that hydride-transfer reactions are largely absent on the H-[Fe]ZSM-5.

DISCUSSION

A number of important conclusions can be taken from the results reported in this paper concerning the nature of Brønsted acid sites in solids and the methods used to characterize those sites. First, the data show that the Brønsted sites formed by framework Fe in a siliceous MFI structure are much different from acid sites formed by framework Al. Oligomerization of olefins and hydride transfer reactions are significantly slower in H-[Fe]ZSM-5. Both of these reactions occur through a carbenium-ion mechanism, suggesting that the carbenium ion is less stable in the ferrosilicate. The relative reactivities of propylene and 1-butene in H-[Fe]ZSM-5 suggest that carbenium-ion intermediates are also important in this material.

The adsorption measurements with 1-butene, particularly on the deuterated sample D-[Fe]ZSM-5, are particularly revealing. These experiments show that relatively stable, protonated complexes are formed with 1-butene, but that these complexes decompose reversibly upon heating without undergoing oligomerization. The protonated complex should therefore be viewed as a relatively unreactive alkoxide, C_4H_9-OZ, with covalent bonding between the butyl carbon and the framework oxygen, rather than as a reactive carbocation, $C_4H_9^+$-O^-Z. Indeed, NMR spectra of small olefins indicate alkoxide formation even in aluminosilicates [31], even though the relative reactivities of olefins imply that carbocation mechanisms are present. One should therefore view the reactive, carbocation-like species as unstable transition states for small olefins in both H-[Fe]ZSM-5 and H-[Al]ZSM-5. We suggest that the difference between Brønsted sites associated with framework Al and framework Fe is simply the equilibrium constant, or energy, separating these two species:

$$C_4H_9\text{-}OZ = C_4H_9^+\text{-}O^-Z$$

Framework Fe sites obviously stabilize the formation of the alkoxide in a manner similar to that of framework Al, but Fe sites are not as effective in stabilizing the formation of the carbocation transition state required for reactions.

The calorimetry results imply that some common assumptions about the measurement of acidity are incorrect. It is almost universally assumed that one can rank the acidities of various solid acids by measuring the adsorption energetics for common bases like ammonia and pyridine. However, in the case of H-[Fe]ZSM-5 and H-[Al]ZSM-5, the heats of adsorption for these strong bases are identical, even though the site activities are dramatically different. Obviously, the stability of protonated complexes does not appear to provide a useful measure of the relative stability of transition states required for reaction. While it has been suggested that weaker bases, like acetonitrile, may be more useful as probes of acidity, our earlier measurements indicate that this base is also incapable of distinguishing differences in the nature of the Brønsted sites in H-[Fe]ZSM-5 and H-[Al]ZSM-5 [21]. Clearly, we still need better methods for measuring and describing acid sites in solid acids.

The results we have presented suggest that ferrosilicates may provide an opportunity for catalyzing selective chemistries. A major reason why zeolites are not commonly applied to production of fine chemicals is that they are not selective. As shown in this paper, one produces a significant amount of aromatics, even for adsorption of 1-butene at room temperature. With hydride-transfer reactions being so rapid, selective chemistry become very difficult. The sites in ferrosilicates are obviously much less able to carry out the hydride-transfer reactions. Because of this, ferrosilicates will not be effective catalysts for cracking of paraffins, as previous work from our laboratory has already shown [19], but they may be very useful for reactions which require milder reaction conditions.

CONCLUSIONS

The Brønsted-acid sites in Al-free, H-[Fe]ZSM-5 are capable of performing olefin oligomerization; however, the sites are much less active than those in H-[Al]ZSM-5 and do not readily catalyze hydride-transfer reactions. Due to this difference, H-[Fe]ZSM-5 appears to exhibit a much lower tendency to form coke during reactions of olefins. Differential heats of adsorption for ammonia and pyridine are not capable of distinguishing Brønsted sites in H-[Fe]ZSM-5 from those in H-[Al]ZSM-5.

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1) TPD-TGA curves for isopropyl amine in H-[Fe]ZSM-5. The formation of propylene (m/e = 41 amu) and ammonia (m/e = 17) between 575 and 650 K are is indicative of Brønsted-acid sites.

2) Diffuse Reflectance, FTIR spectra of the following samples: a) clean H-[Al]ZSM-5; b) H-[Al]ZSM-5 after exposure to pyridine, followed by flushing in dry N_2 at 470 K; c) clean H-[Fe]ZSM-5; and d) H-[Fe]ZSM-5 after exposure to pyridine, followed by flushing in dry N_2 at 470 K.

3) Microcalorimetric results for H-[Al]ZSM-5 (open symbols) and H-[Fe]ZSM-5 (filled symbols) for a) pyridine and b) ammonia.

4) TPD-TGA results following exposure of H-[Al]ZSM-5 to 1-butene at room temperature.

5) GC Analysis of the products formed in the two temperature ranges for the results in Fig. 4.

6) TPD-TGA results on H-[Al]ZSM-5 following exposure to 1-butene at 400 K for 60 sec, then D_2O for 60 sec.
7) TPD-TGA results following exposure to propylene onto H-[Fe]ZSM-5. Because adsorption at room temperature was completely reversible, the H-[Fe]ZSM-5 sample was exposed to 1 torr propylene while ramping the temperature to 400 K at 2 K/sec.
8) TPD-TGA following exposure of H-[Fe]ZSM-5 to 15 torr of 1-butene at 295 K.
9) TPD-TGA following a controlled exposure of D-[Fe]ZSM-5 to 1-butene at 295 K.
10) Diffuse Reflectance FTIR spectra of the following samples: c) clean D-[Fe]ZSM-5, b) sample c) after exposure to 1-butene, and a) the sample in b) after heating to 600 K in flowing N_2.
11) TPO results for samples after running 1-butene isomerization at 573 K for 200 min: a) H-[Al]ZSM-5(30) and b) H-[Fe]ZSM-5.