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Characterization of H-FER and H-TON using temperature-programmed desorption of alkylamines

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Simultaneous temperature-programmed desorption (TPD) and thermogravimetric analysis (TGA) measurements were performed with n-propylamine and isopropylamine in H-FER and H-TON in order to test whether the Brønsted-acid sites associated with the 10-ring, straight channels in H-FER could be distinguished from the acid sites in the side cavities. In H-TON, the saturation uptakes were identical for both amines, as were the acid-site densities determined from the amounts of amine which reacted to olefin and ammonia products above 600 K. By contrast, the saturation uptake for isopropylamine in H-FER was much lower than the uptake of n-propylamine and the site density determined from the amounts which react were also significantly lower. It is argued that the n-propylamine results for H-FER provide a measure of the total Brønsted-acid-site density, while the isopropylamine results provide a measure of the site density in the 10-ring channels.

Keywords: characterization of Brønsted-acid sites, TPD of alkylamines

1. Introduction

Ferrierite (FER) is a zeolite structure which has received a great deal of attention recently due to the unusual selectivity it exhibits for some reactions, especially butene isomerization [1–6]. The interesting properties of FER almost certainly derive from its structure, which consists of one-dimensional, 10-membered-ring channels with side cavities accessible through 8-membered-ring openings [7]. Alkane adsorption studies have suggested that larger molecules only have access to sites in the straight channels, while smaller molecules can also enter the side cavities [8–10]. IR spectroscopic studies have shown that Brønsted sites exist in both the main channels and in the side cavities [11]. Since modification of FER can change the catalytic properties of the catalyst [5], it would obviously be useful to have a quick method for determination of the site densities in both parts of the crystal.

It has been demonstrated that temperature-programmed desorption (TPD) of alkylamines is a particularly useful technique for characterization of Brønsted-acid-site densities in solid acids [12–14]. The technique is based on the fact that many alkylammonium ions, formed by adsorption of the amines on the Brønsted sites, decompose via the Hoffman elimination reaction to the olefin and ammonia products in TPD. Since this reaction occurs over a narrow temperature range for a given amine and since molecules not associated with the Brønsted sites desorb unreacted, it is relatively easy to count the number of protonated molecules and, therefore, the number on Brønsted sites on a sample. So long as the alkylamines are small enough to access the available pore volume, the concentrations determined in TPD are independent of the amine that is chosen to measure the site concentration [13,15]. In the case of H-MFI and some other high-silica zeolites, the Brønsted-site concentration measured in this way has been shown to equal the concentration of framework Al sites [12]. For materials which have sites that are inaccessible to typical reactant molecules, such as H-FAU, the site density measured by TPD is much less than the framework Al content, but still independent of the alkyl group [16].

Based on earlier work with alkylamines of various sizes in medium- and large-pore zeolites [13], it is possible to choose amines which are too large to enter the smaller zeolites so that one can selectively count the number of sites which are present in large-pore zeolites. Applying this concept to a zeolite which has cavities with different dimensions, it should be possible to measure the site densities in each of the different regions of the zeolite. In the present study, we examined the adsorption of n-propylamine and isopropylamine to determine the efficacy of this approach for examining the location of Brønsted-site densities in H-FER. It was expected that isopropylamine would only be able to probe the Brønsted sites in the 10-ring channels, while n-propylamine would count sites in both the channels and the side cavities. For comparison, we also examined an H-TON (H-ZSM-22) sample to demonstrate that differences in the site densities measured by isopropylamine and n-propylamine in H-FER must be due to the side cavities.

2. Experimental

The equipment and procedures used to measure adsorption were the same as those used in previous studies [12]. TPD and TGA experiments were carried out simultaneously

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using a microbalance mounted within a high-vacuum chamber. The system could be evacuated to a base pressure below 1×10^{-6} Torr, and the composition of the desorbing gases could be monitored using a quadrupole mass spectrometer interfaced to a microcomputer. Between 10 and 12 mg of zeolite were spread over a flat sample pan to avoid bed effects in desorption [17]. Following a saturation exposure to the adsorbate of interest, at room temperature and 10 Torr, the samples were evacuated for 1 h before starting the TPD-TGA experiment. The heating rate for all the experiments was maintained at 15 K/min. The mass peaks used to identify the various desorption products in TPD are as follows: n-propylamine ($m/e = 30$), isopropylamine ($m/e = 44$, 41, and 17), propene ($m/e = 41$), and ammonia ($m/e = 17$).

The FER sample was received from PQ Corp. and was reported to have a Si/Al_2 ratio of 21. To obtain the hydrogen form for FER, the zeolite was first ammonium-ion exchanged and then heated in vacuum to 750 K in the TPD-TGA apparatus. The TON sample was prepared in our laboratory with a Si/Al_2 of 52. It was heated to 750 K in flowing N_2 for 1 h, after which it was exposed to flowing air at 750 K for 2 h. The calcined TON was then ammonium-ion exchanged twice, with calcination to 750 K after each exchange.

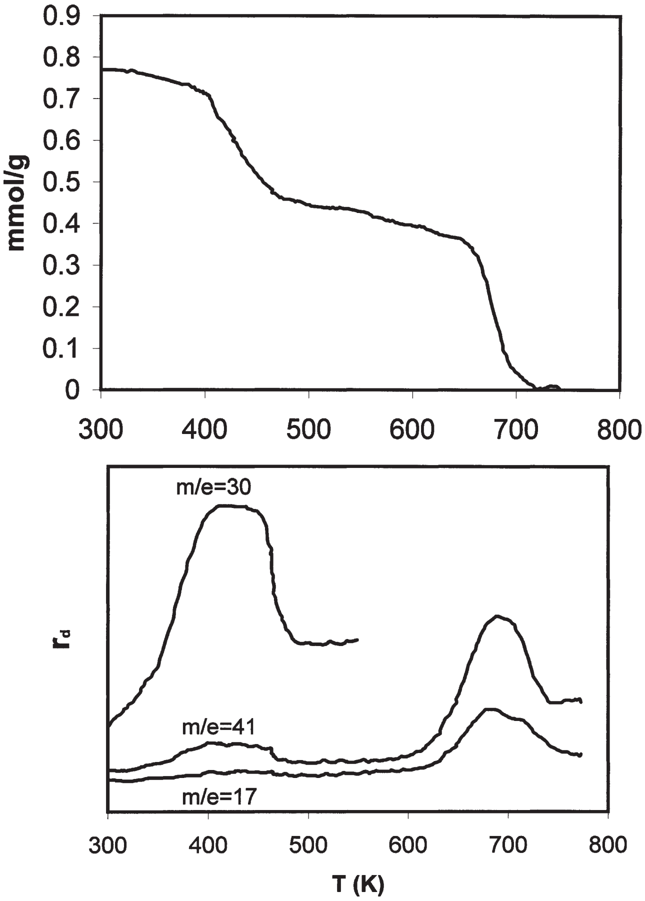

Figure 1. TPD-TGA curves for n-propylamine in H-TON. Only n-propylamine ($m/e = 30$), ammonia ($m/e = 17$), and propene ($m/e = 41$) were observed in desorption.

3. Results

The saturation uptakes for n-propylamine and isopropylamine at 10 Torr and 295 K are shown in table 1 for both samples. Results are also shown for n-pentane, because simple alkanes are frequently used to measure the total pore volume in the zeolites. The uptakes in table 1 were measured gravimetrically, and the volumes reported in the table were calculated assuming each adsorbate packs with its liquid density. For H-TON, the pore volume calculated from all three adsorbates is similar, ranging from 0.075 cm^3/g with n-pentane and isopropylamine to 0.078 cm^3/g with n-propylamine. Clearly, the zeolite cavities in H-TON are available to all three adsorbates in a similar manner.

For H-FER, however, the pore volume accessible to isopropylamine is significantly less than the pore volume available to n-propylamine and n-pentane. For isopropylamine, the uptake, 0.05 cm^3/g, is comparable to that measured in H-TON, suggesting that this molecule is only able to enter the 10-ring, straight channels. As expected, isopropylamine cannot fill the side cavities which must be entered through an 8-ring window. In contrast to this, the volume accessible to n-propylamine, 0.15 cm^3/g, is essentially the same as that for n-pentane, 0.14 cm^3/g. Because the packing of straight-chain alkanes, like n-pentane, may be partially hindered in FER [8–10], the true pore volume may be somewhat larger than 0.14 cm^3/g. However, the similarity in the numbers for n-pentane and n-propylamine suggests that both molecules are able to access both the straight, 10-ring channels as well as the side cavities.

The TPD-TGA results for n-propylamine and isopropylamine on H-TON and H-FER are shown in figures 1–4. In all cases, we observed the desorption of only unreacted amines below 500 K. Above 600 K, only the Hoffman elimination products, propene and ammonia, were observed. As discussed in previous papers [12–14], the Hoffman elimina-

Table 1
Saturation gravimetric uptakes for each adsorbate on each of the zeolite samples at 295 K and 10 Torr.

Sample	n-propylamine		Isopropylamine		n-pentane	
	(g/100 g)	(cm^3/g)[a]	(g/100 g)	(cm^3/g)[a]	(g/100 g)	(cm^3/g)[a]
H-TON	5.6	0.078	5.1	0.075	4.7	0.075
H-FER	11.1	0.15	3.6	0.05	8.8	0.14

[a] Assumes that each adsorbate packed at its liquid density into the zeolite.

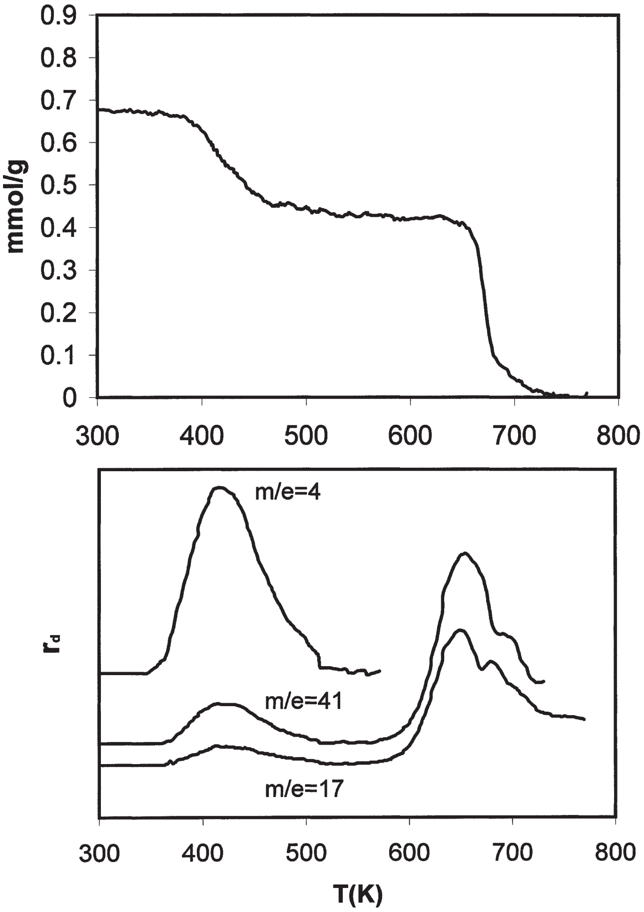

Figure 2. TPD-TGA curves for isopropylamine in H-TON. Only isopropylamine ($m/e = 44$, 41, and 17), ammonia ($m/e = 17$), and propene ($m/e = 41$) were observed in desorption.

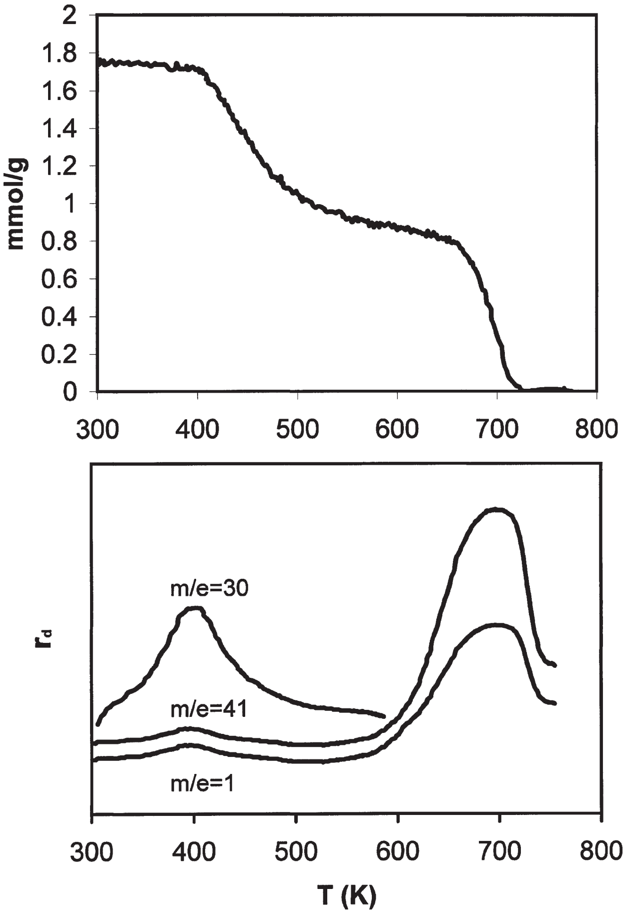

Figure 3. TPD-TGA curves for n-propylamine in H-FER. Only n-propylamine ($m/e = 30$), ammonia ($m/e = 17$), and propene ($m/e = 41$) were observed in desorption.

tion reaction requires adsorption of the amines on Brønsted sites because reaction occurs through decomposition of the alkylammonium ions. For adsorption on Lewis acids, like alumina, no reaction is observed in TPD, even though alkylamines remain on the surface to temperatures above 600 K [18].

The TPD-TGA curves for n-propylamine in H-TON, shown in figure 1, are typical of results observed in acidic zeolites. Based on the bulk Si/Al_2 for this material, one would expect a Brønsted site density of 0.64 mmol/g. Following evacuation for 1 h, the coverage of n-propylamine remains close to 0.8 mmol/g, significantly higher than the concentration of Al. As discussed elsewhere [19], the excess amine molecules could be associated with defect sites in the zeolite structure or be hydrogen bonded to amine molecules which are themselves protonated by the Brønsted sites. However, those molecules in excess of the Brønsted sites desorb unreacted below 500 K ($m/e = 17$, 41, and 30), leaving approximately 0.40 mmol/g to desorb above 600 K as propene ($m/e = 41$) and ammonia ($m/e = 17$). Even though 0.40 mmol/g is significantly less than the Al concentration, it is a very reasonable site density for H-TON. Because some of the Al may not be in the framework and some of the one-dimensional pores may be inaccessible due to pore blockage, one would expect the true site density to be somewhat less than the framework Al content. Alternatively, if some of the sites are too closely spaced, it may not be possible to achieve a stoichiometry of one n-propylamine molecule for each Brønsted site due to steric constraints.

Figure 2 shows the analogous TPD-TGA results for isopropylamine in H-TON. Again, unreacted amine molecules ($m/e = 17$, 41, and 44) desorb below 500 K, leaving only the reaction products to desorb from the sample above 600 K. Using the amount of reaction products as a measure of the Brønsted-site density, one obtains a value of 0.42 mmol/g with isopropylamine, slightly higher than the value obtained for n-propylamine. The difference in site densities measured by n-propylamine and isopropylamine appears to be larger than the uncertainty in the measurements, but the numbers are still very close. One complication observed in the TPD-TGA results for isopropylamine is that the propene and ammonia peaks are broader than normally observed for medium- and large-pore zeolites [12]. This may suggest that there is some diffusion limitation to the desorption process.

The TPD-TGA result for n-propylamine in H-FER is shown in figure 3. Very little of the n-propylamine could

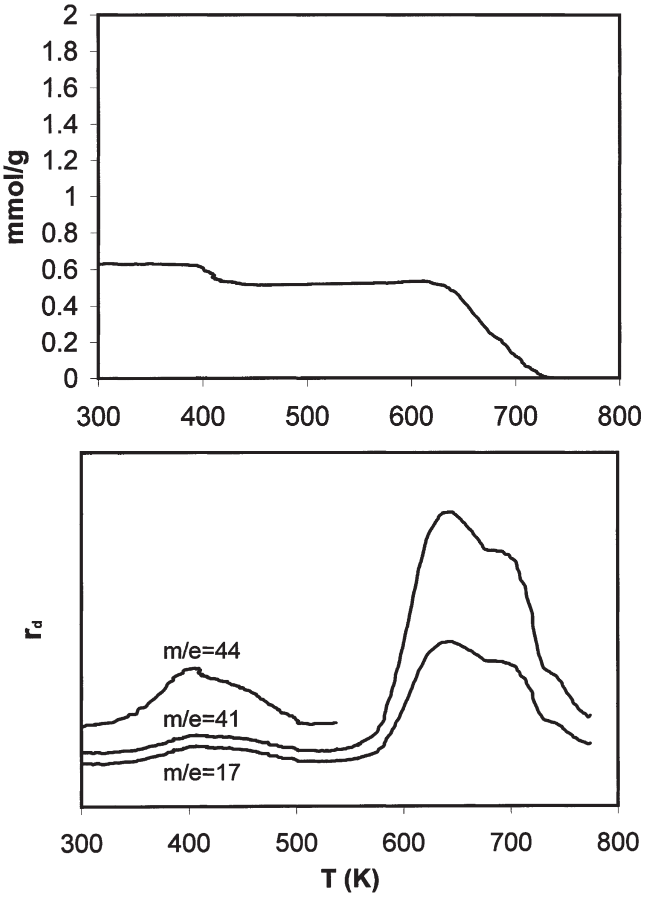

Figure 4. TPD-TGA curves for isopropylamine in H-FER. Only isopropylamine (m/e = 44, 41, and 17), ammonia (m/e = 17) and propene (m/e = 41) were observed in desorption.

be evacuated, so that the initial coverage, 1.8 mmol/g, was close to the saturation uptake. As in the case for H-TON, this initial coverage is higher than the bulk Al content (1.6 mmol/g), so that some of the amine molecules must be associated with sites other than Brønsted sites or hydrogen bonded to other amine molecules. In TPD-TGA, about half of the n-propylamine desorbs unreacted below 500 K, leaving approximately 0.85 mmol/g to react above 600 K. As discussed above for H-TON, we cannot determine why the Brønsted-site density determined from the TPD-TGA results is less than the Al content, but this is commonly observed in materials with high Al contents [16].

Finally, results for isopropylamine in H-FER are shown in figure 4. A much lower fraction of the isopropylamine desorbs intact and approximately 0.5 mmol/g reacts to propene and ammonia. There appear to be two, unresolved desorption features above 600 K, the origin of which is unclear. Since the decomposition of the alkylammonium ion does not appear to be a function of the site strength [20], the second peak may result from molecules that are not initially adsorbed on Brønsted sites. If some molecules are held in the zeolite beyond the temperature at which the protonated molecules react, they could then adsorb on the vacant sites and undergo reaction at a higher temperature. Whatever the explanation for the two peaks, it is clear that the amount of n-propylamine which reacts in TPD-TGA is considerably higher than the amount of isopropylamine which reacts, by more than 0.3 mmol/g. These extra sites must clearly be associated with the side cavities in the H-FER structure.

4. Discussion

The Brønsted-site densities calculated from TPD-TGA measurements of n-propylamine and isopropylamine have been summarized in table 2. For H-TON, which has only 10-ring, straight channels, the site densities calculated for both amines are the same. For H-FER, which has Brønsted sites in both the 10-ring, straight channels and in side cavities accessible through 8-ring windows, the site density calculated from n-propylamine is approximately 0.35 mmol/g higher than the site density calculated from isopropylamine. Clearly, these additional sites in H-FER must be associated with the side cavities.

One important question concerns how well isopropylamine is able to discriminate between the various locations in H-FER. At saturation, the volume of isopropylamine which adsorbs is only one third as much as that of n-propylamine. If one assumes that the site densities of the two regions in H-FER are proportional to the volume of amine which can adsorb in that region, one would have expected there to be a bigger difference between the results for the two amines in H-FER. While movement of the protons from the side cavities into the 10-ring channels might explain the higher site density in the 10-ring channels, we suggest it is more likely that the amine group from isopropylamine is able to enter the 8-ring window. Some sites in the side cavities would then be sampled by the amine, even though the molecule itself was unable to enter the side cavity. One might expect that pyridine, for which the nitrogen atom would not be expected to enter the 8-rings, might be more discriminating. However, depending on the reaction, the amine results may well be more representative of the site concentration that would be accessible to reactants. For example, in the butene isomerization reaction, methylpropene would be expected to have a size and shape similar to isopropylamine. Reactions involving aromatics, on the other hand, may well be excluded from sites inside the 8-ring windows.

It must be acknowledged that adsorption of an amine molecule on one site may well prevent adsorption of a second molecule on an adjacent site. The site densities reported here would then be lower limits of the true site density. Obviously, pyridine adsorption would have simi-

Table 2
Site densities obtained for each adsorbate on each of the zeolite samples.

Sample	n-propylamine (mmol/g)	Isopropylamine (mmol/g)
H-TON	0.40	0.42
H-FER	0.85	0.50

lar limitations; only very small probe molecules, such as ammonia, could be used to avoid these issues. However, it has been demonstrated that there are severe problems with interpretation of results from ammonia adsorption [14,21]. First, adsorption is not selective for Brønsted sites. More important, it has been shown that ammonia adsorbs very strongly on solids that are not normally considered to be acidic, such as CaO [14]. Furthermore, if a probe molecule is excluded from adsorbing on a site adjacent to a filled acid site, adsorption would also be excluded for typical reactant molecules. Therefore, one would expect the site densities measured by TPD-TGA of amines to be representative of the situation for reaction conditions.

In summary, we believe the approach described in this paper may well be useful for the characterization of site densities in materials which contain channels of different sizes. This approach may well prove useful for understanding how materials change with pretreatment and which sites are poisoned by coking [4].

5. Summary

The results suggest that TPD-TGA measurements with selected amines can be used to determine the Brønsted-acid-site densities associated with different cavities in a multi-dimensional zeolite. In the case of H-FER, n-propylamine and isopropylamine appear to be excellent probes of the total acid-site density and the acid-site density in the larger channels.

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