

## Characterization of H,Na-Y Using Amine Desorption

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Received February 12, 1993; revised July 6, 1993

We have examined series of partially ion-exchanged H,Na-Y zeolites using temperature-programmed desorption (TPD) and thermogravimetric analysis (TGA) of isopropylamine and *n*-propylamine in order to examine the acid sites in H-Y zeolites as a function of Na poisoning. Both amines desorbed from Na-Y, unreacted, below 500 K; however, samples containing protonic sites exhibited two additional desorption features. First, unreacted amine molecules were observed leaving the samples between ~500 and 600 K. Second, reaction features appeared which were observed as the simultaneous desorption of propene and ammonia between 575 and 650 K for isopropylamine and between 625 and 700 K for *n*-propylamine. For a given sample, the number of both isopropylamine and *n*-propylamine molecules which desorbed in both features was identical. Furthermore, the number of molecules desorbing from the two high-temperature features was found to be equal to the number of protonic sites for the entire series, which indicates that both desorption features are associated with protonic sites. This finding was confirmed by infrared spectroscopy, which also demonstrated that the unreacting desorption feature was associated with the low-frequency, hydroxyl stretch at 3540  $\text{cm}^{-1}$  and that the reacting amine molecules were adsorbed at the high-frequency, hydroxyl stretch near 3640  $\text{cm}^{-1}$ . The implications of these results for understanding the use of TPD-TGA of amines for the characterization of acidity is discussed.

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### INTRODUCTION

A number of relatively recent studies have demonstrated the utility of temperature-programmed desorption (TPD) and thermogravimetric analysis (TGA) of simple amines for the characterization of Brønsted acidity in zeolites and other solid acids (1-7). These studies have shown that alkylamines are protonated by strong acid sites and that the protonated amines decompose to ammonia and olefin products at elevated temperatures (1-7). Therefore, the concentration of strong Brønsted-acid sites can be calculated from the number of alkylamine molecules which decompose during the temperature ramp. For example, in high-silica zeolites like H-ZSM-5 and H-ZSM-12, the concentration of sites which decompose either isopropylamine or *n*-propylamine to propene and ammonia is equal to the framework Al concentration of the zeolites (3, 4). It has also been pointed out that monitoring

amine decomposition during TPD has significant advantages over standard TPD measurements with ammonia for determination of acid-site concentrations. Ammonia can interact strongly with sites that are not normally thought to be acidic, such as those present on CaO (8). Also, there are ambiguities in the choice of the temperature used to discriminate weakly and strongly adsorbed species in ammonia adsorption, a problem which is severe due to the fact that this temperature is a strong function of the experimental parameters, including carrier-gas flow rate, particle size of the catalyst, sample weight, and site density of the sample (9, 10).

However, there are unanswered questions regarding the use of amine desorption for faujasites. In one study which showed a good correlation between the activity of fluid-catalytic-cracking (FCC) catalysts and the concentration of sites determined from TPD measurements of isopropylamine, the site concentrations appeared to be consider-

ably lower than the framework Al content of the faujasite phase (1). Later studies with pure faujasites made similar observations (2, 3, 9). For example, a standard US-Y with a framework, Si/Al ratio of 6.45 ( $Al_f = 25.8/\text{unit cell}$ , or  $2580 \mu\text{mol Al/g}$ ) was reported to have only 900 to  $950 \mu\text{mol/g}$  of Brønsted-acid sites, depending on the choice of amine used in the measurement (2). In similar studies, Juskelis *et al.* reported almost identical site concentrations using isopropylamine to characterize a fresh US-Y (8). There are a number of factors which could explain why the site concentrations measured using amine desorption are less than the framework Al concentrations in faujasites, including incomplete exchange of Na (11, 12), inaccessible protons in the sodalite cages (13–16), nonframework Al balancing the charge of framework species (17), and proximity of neighboring Al causing weaker acid strengths (18–20). However, the effect of these factors on amine desorption has not yet been examined systematically.

In this paper, we will study two of these factors by measuring TPD-TGA curves for isopropylamine and n-propylamine on a Y zeolite as a function of Na exchange. It will be shown that both amines desorb unreacted at low temperatures from Na sites and react to propene and ammonia at only a fraction of the protonic sites. IR measurements of the hydroxyl region suggest that the protonic sites associated with the low-frequency band centered at  $3540 \text{ cm}^{-1}$  do not cause the reaction of either amine in TPD and that the sites associated with this low-frequency hydroxyl band are only weakly acidic.

#### EXPERIMENTAL

The starting material for this work was Valfor CP300-63 Na-Y provided by the PQ Corporation. Measurements of the  $O_2$  sorption capacity, measured at  $P/P_0 = 0.4$  and 77 K, showed that it had a pore volume of  $0.321 \text{ cm}^3/\text{g}$ , and the X-ray diffraction patterns indicated that the material was

TABLE 1  
Preparation Conditions for the Samples Used in the TPD-TGA Studies

Sample	IE solution concentration <sup>a</sup>		Degree of exchange <sup>b</sup>
	$[NH_4^+]$	$[Na^+]$	
Na-Y	—	—	0.00
H,Na-Y (0.05)	0.0032	0.097	0.05
H,Na-Y (0.10)	0.0066	0.093	0.10 (0.18) <sup>c</sup>
H,Na-Y (0.20)	0.013	0.087	0.20 (0.27)
H,Na-Y (0.30)	0.020	0.080	0.30
H,Na-Y (0.40)	0.031	0.069	0.40 (0.44)
H,Na-Y (0.55)	0.050	0.050	0.55
H,Na-Y (0.62)	0.10	0.000	0.62

<sup>a</sup> In units of equivalents per liter. Total ionic strength was 0.10 N.

<sup>b</sup> Determined from literature exchange isotherms and reported as mol  $NH_4^+$  per mol ( $NH_4^+ + Na^+$ ).

<sup>c</sup> Values in parenthesis were obtained from  $Na^+$  contents measured using atomic absorption spectroscopy.

highly crystalline. After conversion of the sample to H,Na-Y (0.62) by  $NH_4$  exchange, followed by heating to 700 K in  $10^{-7}$  Torr, the unit cell size was  $24.730 \text{ \AA}$ , indicating a framework Al content of 52.6 Al/unit cell using the correlation of Sohn *et al.* (21) (The value in parenthesis indicates the percent of Na which had been exchanged. Using our experimental conditions, the maximum exchange was ~62%.) The bulk Si/ $Al_2$  ratio reported by PQ was 5.3, which corresponds to 53 Al/u.c., in close agreement with the framework Al content, indicating that calcination and pretreatment did not result in sample steaming.

To form materials with varying degrees of ion exchange, we prepared several solutions having the concentrations listed in Table 1. The concentrations were chosen by targeting the desired exchange level, using equilibrium data from the literature (11, 12). The total ionic strength of each solution was 0.10 N and less than 50 mg of hydrated Na-Y (~25 wt%  $H_2O$ ) were added to 300 ml of each solution so that concentrations of the solutions did not change significantly

upon addition of the zeolite. For all solutions, the counterion was  $\text{Cl}^-$ . As a check that the addition of zeolite did not significantly change the ionic concentrations, the amount of zeolites added to the ion-exchange solutions was decreased on selected samples and it was shown that the TPD-TGA measurements did not change with sample size. During the exchange, the samples were allowed to equilibrate for 1 h at room temperature while being stirred. Although the equilibrium constants for the  $\text{NH}_4$ -Na exchange have been reproduced by a number of groups without variation (11, 12), the sodium level for the most highly exchanged sample was measured by determining the  $\text{Na}^+$  content of the solution above the zeolite with sodium-specific conductivity measurements. For this experiment, a 42.431-mg sample of NaY was weighed in  $10^{-7}$  Torr after heating to 700 K using the Cahn microbalance described below. The sample was then added to 250.00 ml of 0.100 *n*  $\text{NH}_4\text{Cl}$  solution at room temperature for 1 h. After removal of the zeolite, the  $\text{Na}^+$  content of the solution was measured with a sodium-specific, conductivity electrode, and the results showed that 56% of the  $\text{Na}^+$  had been exchanged from sample, in excellent agreement with the equilibrium predictions. Multiple exchanges did not result in substantially higher exchange percentages. As a final check of the  $\text{Na}^+$  contents, atomic absorption spectroscopy was used to measure several samples and the exchange values calculated from these are listed in Table 1 in parenthesis. The  $\text{Na}^+$  contents from atomic absorption were in reasonable agreement with the isotherm measurements, although they tended to be consistently lower. Because the deviations in the measurements from atomic absorption were larger, we chose to work with  $\text{NH}_4^+$  contents from the isotherm.

The equipment and procedures used in the TPD-TGA experiments are described elsewhere (3). The apparatus consists of a Cahn microbalance which is mounted inside a high vacuum chamber equipped with a

quadrupole mass spectrometer. Approximately 5–10 mg of sample were spread in a thin layer over a flat sample pan in order to minimize bed effects in desorption (9, 10). Each sample was first cleaned by heating to 700 K in vacuum and then exposed at 300 K to  $\sim 5$  Torr of one of the amines until no further weight changes were observed. After dosing, the sample was evacuated for  $\sim 2$  h in order to remove some of the weakly adsorbed species, after which the desorption experiments were performed with a heating rate of 10 K/min (20 K/min for *n*-propylamine). The sample weight returned to its original value for each adsorbate on each sample, demonstrating that there were no undetected products remaining after the TPD-TGA measurement.

All of the TPD curves reported in this paper are arbitrarily scaled. In order to quantify the amounts of each product leaving a given sample, we used the TPD curve to determine the temperature range in which the product desorbed, while the amounts were determined from the mass changes in TGA. The peaks in the mass spectra that were used to identify products are given as follows: isopropylamine ( $m/e = 44, 41,$  and  $17$ ), *n*-propylamine ( $m/e = 30$ ), propene ( $m/e = 41$ ), and ammonia ( $m/e = 17$ ).

Infrared spectra were obtained in a vacuum cell which has also been described elsewhere (22). The cell could be evacuated to  $10^{-3}$  Torr with a liquid-nitrogen-trapped, mechanical pump and the sample could be heated to 750 K. The zeolite samples were pressed into an IR-transparent, stainless-steel mesh supplied by Buckbee-Mears Corp. and examined using a Mattson Instruments 2020 Galaxy Series FT-IR spectrometer.

## RESULTS

The effect of ion exchange on the TPD-TGA results for each of the probe molecules was dramatic. This is demonstrated for isopropylamine by the desorption curves shown in Fig. 1, which were taken from H,Na-Y samples with three different levels

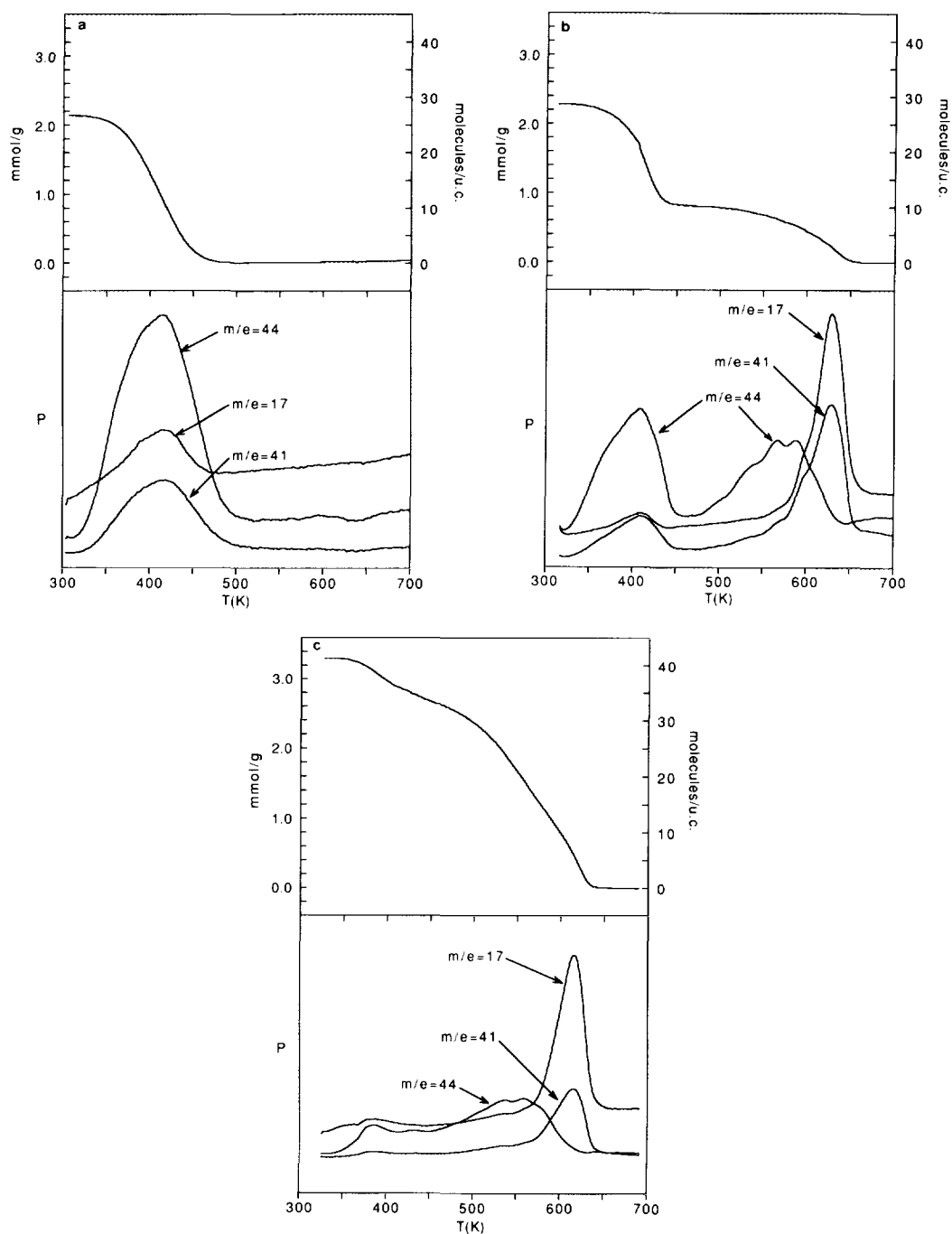


FIG. 1. TPD-TGA of isopropylamine on (a) Na-Y, (b) H,Na-Y (0.20), and (c) H,Na-Y (0.62).

of exchange. In this figure, the sample weights in TGA have been converted to moles of isopropylamine per gram of zeolite on the left and molecules per unit cell on the right and the weights are referenced to the weight of the zeolite prior to adsorption. Figure 1a was obtained on an unexchanged Na-Y and demonstrates that all of the isopropylamine is weakly held. The sample weight in this experiment had reverted to its original value by 500 K and the mass spectrum of the products leaving the sample below this temperature are indicative of only unreacted isopropylamine. In contrast to this, results from the samples shown in Figs. 1b and 1c, which had been partially exchanged with hydrogen, exhibited two additional desorption features: a second, unreacted-amine feature between 450 and 600 K and a reaction peak between 575 and 650 K for which only propene and ammonia are observed. The reaction feature between 575 and 650 K has been observed previously on other solid acids and has been assigned to the reaction of the amine at strong, Brønsted-acid sites (1-8). As mentioned earlier, the concentration of sites which cause the decomposition of the amine on high-silica zeolites is equal to the Al content (3-6).

The unreacted feature between 450 and 600 K had not been observed on high-silica zeolites. We assign it here to protonic sites which are weaker than those which cause the decomposition of the amine. The sites corresponding to this feature are either not able to protonate the amine or else they are too weak to hold the amine at the site up to the temperature at which reaction occurs. This assignment is based on several observations. First, since the unreacted feature is not present on the Na-Y sample, it must be associated with the protonic sites. Second, we ruled out the possibility that the unreacted feature between 450 and 600 K and the reacted feature above 575 K are due to the same species based on an additional experiment. Conceivably, isopropylamine could begin to desorb at 500 K with a second

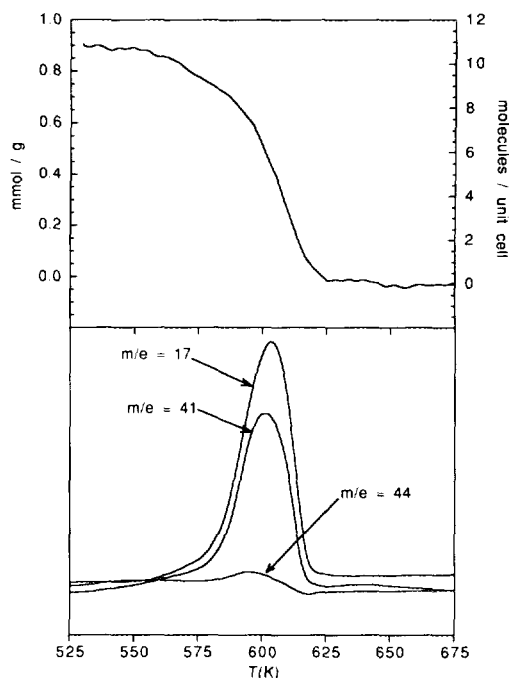


FIG. 2. TPD-TGA of isopropylamine on H,N<sub>a</sub>-Y (0.62) after heating the sample to 525 K for 2 h to remove molecules from sites which do not cause reaction.

competing process, the decomposition of the amine, taking over above 575 K before desorption could completely remove isopropylamine. However, we performed an additional TPD measurement, shown in Fig. 2, in which the temperature ramp was stopped at 525 K for 2 h before continuing. During the second half of the TPD-TGA experiment, only propene and ammonia were observed leaving the sample and the amount of these products was the same as that observed in a normal TPD-TGA experiment. Therefore, we conclude that the reacted and unreacted desorption features are due to molecules at two different types of sites.

It is informative to examine the concentrations of molecules corresponding to each type of site as a function of exchange level. These concentrations, given in Table 2, are approximate since they were obtained from the gravimetric results at specified temperatures and not from integration of the desorp-

TABLE 2

Summary of TPD-TGA Results for Isopropylamine

Sample	[Total Site] (mmol/g)	[Strong Sites] <sup>a</sup> (mmol/g)
Na-Y	0.000	0.00
H,Na-Y (0.05)	0.240	0.24
H,Na-Y (0.10)	0.474	0.37
H,Na-Y (0.20)	0.812	0.49
H,Na-Y (0.30)	1.03	0.74
H,Na-Y (0.40)	1.56	0.98
H,Na-Y (0.55)	2.15	1.1
H,Na-Y (0.62)	2.88	1.4

<sup>a</sup> Measured from 575 to 650 K.

tion features. They have been plotted as a function of protons/unit cell in Fig. 3, from which several important conclusions become apparent. First, the total amount of isopropylamine which desorbs above 500 K, corresponding to the sum of both types of sites, increases linearly, in a one-to-one manner, with the concentration of protonic sites per unit cell. This is further indication that all of the isopropylamine desorbing from the sample above 500 K in our measurements is interacting with protonic sites. Second, the concentration of sites which cause the reaction of isopropylamine

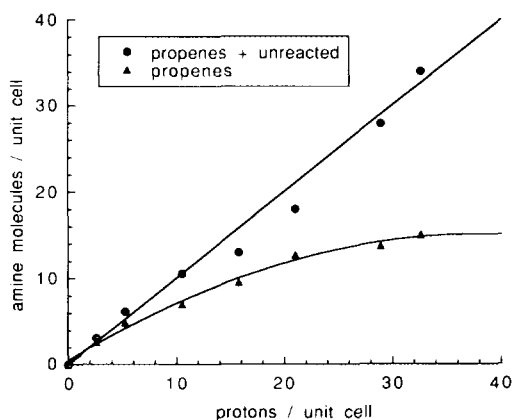


Fig. 3. Summary of the amounts of isopropylamine which desorbed in each of the two high-temperature states in TPD-TGA as a function of the proton exchange level.

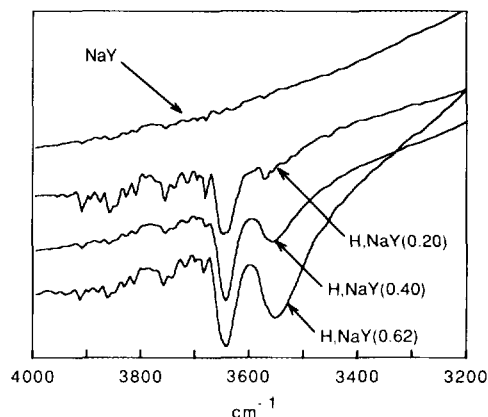


Fig. 4. IR spectra of the hydroxyl region on selected samples H,Na-Y samples.

reaches a plateau near a concentration of 20 protons/unit cell. Further increases in the exchange level do not cause substantial increases in the number of sites which lead to reaction.

Figure 3 is reminiscent of similar plots of the IR intensities of the two hydroxyls observed in H-Y as a function of exchange levels (14, 23). The IR spectra of these hydroxyls have been reproduced on our samples in Fig. 4. Excluding silanols which terminate the zeolite crystals (24) and other bands which occur on steamed samples (25), there are two hydroxyls corresponding to the protonic sites and these occur at  $\sim 3640$  and  $3540 \text{ cm}^{-1}$ . Starting from Na-Y with increasing proton exchange, the  $3640\text{-cm}^{-1}$  peak grows in first, followed by the  $3540\text{-cm}^{-1}$  peak. The correspondence between the desorption and IR results suggest that the reaction feature in TPD is due to molecules associated with the high-frequency hydroxyl, while the unreacted species is due to the low-frequency hydroxyl. This is confirmed by IR measurements of the hydroxyl region following adsorption of isopropylamine on the most highly exchanged sample, shown in Fig. 5. At low temperatures, both hydroxyls disappear upon adsorption of the amine, but the low-frequency band reappears first during desorption.

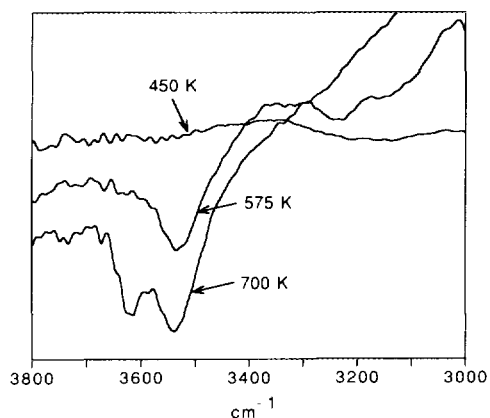


FIG. 5. IR spectra of the hydroxyl region on H,Na-Y (0.62) following isopropylamine adsorption and heating in vacuum to the indicated temperature.

The origin of the two types of hydroxyls has been discussed extensively in the literature (26). The high-frequency peak is generally assigned to hydroxyls in the supercages, while the low frequency band is due to hydroxyls in the sodalite cages. This second type of hydroxyls presumably has enough mobility to interact with strong bases, although earlier studies have also demonstrated that the sites corresponding to these hydroxyls are much weaker acid sites. There is even some question whether the low-frequency hydroxyls are able to protonate pyridine to form a pyridinium ion or whether pyridine interacts with these sites via hydrogen bonding. Our results are completely consistent with this previous work and suggest that the reaction of isopropylamine occurs only at the  $3640\text{-cm}^{-1}$  sites, which clearly are Brønsted-acid sites.

In order to further test our assignment of the two isopropylamine desorption features, we also examined the adsorption of *n*-propylamine on selected samples. In previous studies of *n*-propylamine adsorption, it was demonstrated that this molecule also undergoes decomposition to propene and ammonia at Brønsted-acid sites, but that the decomposition of *n*-propylamine occurs at slightly higher temperatures, between 625 and 700 K (7). If the two-site model for iso-

propylamine desorption is incorrect, the relative amounts of *n*-propylamine which do or do not react might be very different. Figure 6 shows the TPD-TGA results for *n*-propylamine on Na-Y and H,Na-Y (0.62). On Na-Y, all of the amine molecules again desorb unreacted below 500 K. In contrast, one again observes an unreacted feature at higher temperatures on the H,Na-Y sample and a second reaction feature between 625 and 675 K. Since the mass-spectrometer intensities are arbitrary, one must use the TGA results in the appropriate temperature region to determine the concentration of sites which are responsible for each type of desorption event. Within experimental error, the concentrations of both types of sites are identical to that corresponding to the results for isopropylamine desorption from the same sample,  $1380\ \mu\text{mol/g}$  of weak sites and  $920\ \mu\text{mol/g}$  of strong, Brønsted-acid sites.

#### DISCUSSION

The TPD-TGA results for isopropylamine and *n*-propylamine on the samples studied in this paper further demonstrate the utility of using temperature-programmed desorption of reactive probe molecules for characterizing the acidity of zeolites. The amounts of both isopropylamine and *n*-propylamine which decompose in TPD give a very reasonable value for the concentration of strong, Brønsted-acid sites in these materials. Sodium-poisoned samples, which do not contain Brønsted-acid sites, do not cause the decomposition of amines. This eliminates problems associated with unreactive probe molecules for which overlap between the catalytic sites and other adsorbed states complicate the analysis.

Furthermore, the results from this study help explain why the strong Brønsted-acid-site concentrations measured from amine decomposition in TPD are frequently lower than the framework Al content of at least some faujasites. In agreement with conclusions of previous studies on the hydroxyls in H-Y, our measurements suggest that not

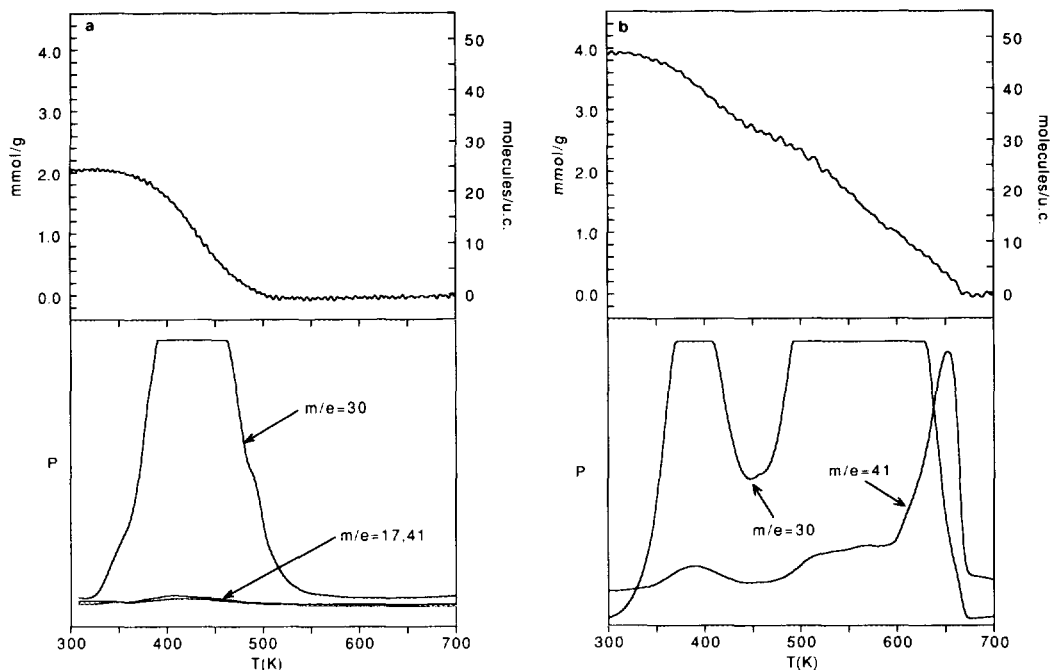


FIG. 6. TPD-TGA results for *n*-propylamine adsorbed on (a) Na-Y and (b) H,Na-Y (0.62).

all protonic sites in H-Y lead to strong, Brønsted-acid sites. Amine decomposition is apparently not sensitive to the weak sites associated with the hydroxyl feature at  $3540\text{ cm}^{-1}$  in infrared spectroscopy.

In our measurements, we were able to associate the desorption of unreacted amine molecules above 500 K with the weaker protonic sites by comparison to results obtained on the unexchanged Na-Y. However, due to the fact that desorption temperatures are strongly altered by the experimental apparatus and the conditions used for the measurements (9, 10), it may not be possible to separate weakly adsorbed species which desorbed below 500 K in our measurements from the unreacted species which desorbed between 500 and 600 K. It is likely that, if the measurements were carried out using a carrier gas or with a larger sample size, these features would have been convoluted.

In our study, we intentionally examined a zeolite which had not been steamed in

order to avoid issues associated with non-framework Al species. It is well known that steaming results in sites with much higher catalytic activities, and some have speculated that only those framework sites which are associated with nonframework species are actually active in hydrocarbon cracking (17, 25, 27). Based on previous studies of isopropylamine decomposition in Fe- and Ga-substituted, ZSM-5, the decomposition temperature for isopropylamine does not appear to be sensitive to the strength of the acid sites, so that our measurements cannot say anything about the relative strengths of sites which cause the decomposition of the amines (5, 6). However, it should be noted that a recent study of H-D exchange with *n*-hexane on a faujasite catalyst has shown that isotopic exchange occurs at much lower temperatures than that necessary for cracking. This may imply that steps other than the protonation of the alkane may limit the reaction (28). For example, the presence



of nonframework species may create sites which facilitate the transfer of a hydride species to allow bond scission in the hydrocarbon (15, 27, 29, 30). Given that the mechanism for the formation of carbenium ions and the subsequent cracking reactions are not clearly understood, questions concerning the strength of the sites are difficult to address. Clearly, there is much to learn about the detailed nature of the catalytic sites in H-Y.

#### CONCLUSIONS

In this work, we have demonstrated the utility of TPD-TGA of simple amines for the characterization of high-Al faujasites. Strong Brønsted-acid sites associated with protons balancing the charge on framework Al sites cause isopropylamine and *n*-propylamine to decompose in well defined temperature regions. Furthermore, only the strong Brønsted-acid sites associated with the high-frequency, hydroxyl stretch at 3640  $\text{cm}^{-1}$  are observed to cause amine decomposition, suggesting that the protons associated with the low-frequency, hydroxyl stretch at 3540  $\text{cm}^{-1}$  are not capable of protonating the amines.

#### ACKNOWLEDGMENTS

This work was supported by the NSF, Grant CBT-8720266. We thank the PQ and Buckbee-Mears Corporations for supplying materials.

#### REFERENCES

1. Biaglow, A. I., Gittleman, C., Gorte, R. J., and Madon, R. J., *J. Catal.* **129**, 88 (1991).
2. Pereira, C., and Gorte, R. J., *Appl. Catal. A* **90**, 145 (1992).
3. Gricus Kofke, T. J., Gorte, R. J., and Farneth, W. E., *J. Catal.* **114**, 34 (1988).
4. Gricus Kofke, T. J., Gorte, R. J., Kokotailo, G. T., and Farneth, W. E., *J. Catal.* **115**, 265 (1989).
5. Gricus Kofke, T. J., Gorte, R. J., and Kokotailo, G. T., *J. Catal.* **116**, 252 (1989).
6. Gricus Kofke, T. J., Gorte, R. J., and Kokotailo, G. T., *Appl. Catal.* **54**, 177 (1989).
7. Parrillo, D. J., Adamo, A. T., Kokotailo, G. T., and Gorte, R. J., *Appl. Catal.* **67**, 107 (1990).
8. Juskelis, M. V., Slanga, J. P., Roberi, T. G., and Peters, A. W. *J. Catal.* **138**, 391 (1992).
9. Gorte, R. J., *J. Catal.* **75**, 164 (1982).
10. Demmin, R. A., and Gorte, R. J., *J. Catal.* **90**, 32 (1984).
11. Sherry, H. S., *J. Phys. Chem.* **70**, 1158 (1966).
12. Theng, B. K. G., Vansant, E., and Uytterhoeven, J. B., *Trans. Faraday Soc.* **64**, 3370 (1968).
13. Olson, D. H., and Dempsey, E., *J. Catal.* **13**, 221 (1969).
14. Ward, J. W., and Hansford, R. C., *J. Catal.* **13**, 364 (1969).
15. Dempsey, E., and Olson, D. H., *J. Catal.* **15**, 309 (1969).
16. Ward, J. W., and Hansford, R. C., *J. Catal.* **15**, 311 (1969).
17. Lunsford, J. H., *ACS Symp. Ser.* **452**, 1 (1991).
18. Dempsey, E., *J. Catal.* **33**, 497 (1974).
19. Dempsey, E., *J. Catal.* **39**, 155 (1975).
20. Mikovksy, R. J., and Marshall, J. F., *J. Catal.* **44**, 170 (1976).
21. Sohn, J. R., DeCanio, S. J., Fritz, Lunsford, J. H., and O'Donnell, *Zeolites* **6**, 225 (1986).
22. Ison, A., and Gorte, R. J., *J. Catal.* **89**, 150 (1984).
23. Angell, C. L., and Schaffer, P. C., *J. Phys. Chem.* **69**, 3463 (1965).
24. Uytterhoeven, J. B., Christner, L. G., and Hall, W. K., *J. Phys. Chem.* **69**, 2117 (1965).
25. Lonyi, F., and Lunsford, J. H., *J. Catal.* **136**, 566 (1992).
26. Breck, D. W., "Zeolite Molecular Sieves." Wiley, New York, 1975.
27. Beyerlein, R. A., McVicker, G. B., Yacullo, L. N., and Ziemiak, J. J., *J. Phys. Chem.* **92**, 1967 (1988).
28. Mota, C. J. A., Nogueira, L., and Kover, W. B., *J. Am. Chem. Soc.* **114**, 1121 (1992).
29. Barthomeuf, D., *J. Phys. Chem.* **88**, 42 (1984).
30. Hughes, T. R., and White, H. M., *J. Phys. Chem.* **71**, 2192 (1967).