

## Acidity Characterization of Ion-Exchanged Mordenite

### I. Temperature-Programmed Desorption of Pyridine

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Ammonium-sodium exchange levels and pretreatment temperatures of synthetic mordenite were varied to measure changes in the number and strength of acid sites by temperature-programmed desorption of pyridine. Both sodium ions and acid sites arising from deammoniation/dehydroxylation adsorbed pyridine. With respect to the latter, there was only one peak in all cases, and in addition a significant fraction of pyridine was found to adsorb irreversibly. At all calcination temperatures examined H-mordenite adsorbed the smallest number of pyridine molecules. Between calcination temperatures of 573 and 773 K, neither the number of acid sites adsorbing pyridine nor the peak temperature increased markedly with increasing  $\text{NH}_4^+$  level. At 873 K, the amounts of adsorbed pyridine decreased significantly, and the peak temperature shifted to higher values, with increasing  $\text{NH}_4^+$  level. The number of pyridine molecules adsorbed appeared to be limited by the volume of the main channel. © 1988 Academic Press, Inc.

#### INTRODUCTION

The present study investigates the effect of varying the degree of ammonium ion exchange and pretreatment temperature on the amount and strength of acid sites on sodium-ammonium-mordenite ( $\text{NaNH}_4\text{M}$ ) as measured by temperature-programmed desorption (TPD) of pyridine. Work has been reported in the literature characterizing the acidity of ion-exchanged mordenite using ammonia. Ratnasamy *et al.* (1) measured isosteric heats of adsorption of ammonia over  $\text{NH}_4\text{NaM}$  pretreated at 823 K and found that sites with heats of adsorption greater than 30 kcal/mole were formed only when approximately 50% of sodium ions were exchanged. Hidalgo *et al.* (2) studied TPD of ammonia from partially potassium-exchanged hydrogen-mordenite (HM) pretreated at 773 K. They observed two desorption peaks, both of which decreased in magnitude with increasing potassium content, and moreover the high-temperature peak dropped faster than the low-temperature peak.

In this study pyridine was used as a

probe because of the similarity in dimensions between pyridine and reactant or product molecules of many reactions, such as xylene isomerization and oligomerization of propene and butenes. In comparison to faujasites, steric factors play a far greater role in mordenite because of its smaller pore size. Therefore, while ammonia may fully characterize all the acid sites in mordenite, studies with pyridine might give better indications of catalytically relevant acid sites which would be accessed by molecules considerably larger than ammonia. Another advantage of using pyridine is unambiguous identification of the nature of acid sites by means of infrared analysis, and this is discussed in Part II of this series (3).

#### EXPERIMENTAL

*Materials.* Catalyst samples of hydrogen mordenite ( $\text{Si}/\text{Al} = 5.8$ , Z900H) and sodium mordenite ( $\text{Si}/\text{Al} = 6.0$ , Z900Na) were supplied by Norton Co. in the form of  $\frac{1}{16}$ -in. binderless extrudates.  $\text{NH}_4\text{NaM}$  samples were prepared by repeated exchange of NaM with  $\text{NH}_4\text{Cl}$ . Levels of exchange ex-

aminated were 11, 33, 55, 64, 85, and 97%. In what follows the number in parentheses next to  $\text{NH}_4$  denotes the percentage of  $\text{Na}^+$  replaced by  $\text{NH}_4^+$ , e.g.,  $\text{NH}_4(55)\text{NaM}$ . Thermogravimetry indicated that the total mass percentage losses of NaM, HM, and  $\text{NH}_4(97)\text{NaM}$  as the temperature was increased from ambient to 1050 K were 12.6, 13.6, and 13.5%, respectively.

**TPD procedure.** A conventional TPD apparatus with a quartz cell connected to a vacuum line and a flame ionization detector located downstream of the cell was used. The line between the cell and the detector was lagged at 423 K. One hundred milligrams of mordenite having a size fraction 250–500  $\mu\text{m}$  was calcined under vacuum ( $<10^{-5}$  Torr) for 2 h. Unless otherwise stated, pyridine (Merck spectroscopic grade) at 255 K (1 Torr vapor pressure) was adsorbed onto mordenite at 573 K for 30 min; the sample was then cooled to 303 K, and subsequently the cell was evacuated for 17 h. Following evacuation the catalyst temperature was raised to 1023 K at a linear heating rate of 5  $\text{K min}^{-1}$  in a stream of high-purity nitrogen, further purified by an oxytrap, ethanol/dry ice trap, and 3A molecular sieves, flowing at 60  $\text{ml min}^{-1}$ . The cell temperature was maintained at 1023 K until the TPD spectrum returned to the baseline. Taking into account the slight nonlinearity of temperature programming and the time lag between the cell and the detector, temperatures shown in this paper are accurate to within 10 K. Estimates of inaccuracies arising from detector calibration indicate that the desorption rates presented here are accurate to within 8–12%. Evaluating the parameters proposed by Gorte (4) showed that lag times resulting from pore diffusion and the cell were negligibly small but concentration gradients and readsorption were present.

**Decomposition of pyridine.** In order to check for the presence of pyridine decomposition products in the desorption stream, helium was used as a carrier gas in one TPD run and the desorption stream was passed

through a GC column packed with OV-101 on Chromosorb W-HP to detectors (FID and TCD) via sampling valve at 80 K intervals. The column temperature was held at 323 K for 3 min after sampling, raised to 423 K in 2 min, and maintained at 423 K for a further 7 min.

## RESULTS

### *Reproducibility*

The reproducibility of TPD data was checked by performing two runs under identical conditions using the following four catalysts:  $\text{NH}_4(64)\text{NaM}$  calcined at 673 and 773 K,  $\text{NH}_4(97)\text{NaM}$  calcined at 673 K, and HM calcined at 773 K. The difference in the amount of pyridine desorbing varied between 1 and 8% from the mean, and that in the peak temperature between 7 and 15 K.

### *Pyridine Decomposition*

Calibration runs with a mixture of  $\text{C}_1$ – $\text{C}_4$  hydrocarbons showed that all of these hydrocarbons eluted through the column within 2 min and pyridine after 4 min of sample injection. During TPD experiments using  $\text{NH}_4(97)\text{NaM}$  calcined at 773 K, pyridine desorption was monitored at 308, 385, 465, 538, 668, 757, 827, 893, 959, and 1000 K. Only pyridine was detected in the effluent stream. Although this experiment does not show whether compounds with boiling points greater than 423 K (which will condense in the lines before reaching the detectors) have been formed, it does show that no decomposition products with boiling points lower than 423 K are formed. In terms of normal alkanes this means that compounds as long as *n*-octane are not present in detectable quantities.

### *Pyridine Adsorption and Evacuation Temperature*

The effects of adsorbing pyridine onto HM, previously calcined at 773 K, at four different temperatures, viz. 303, 483, 573 and 673 K, and evacuating the pyridine as the catalyst was cooled from the adsorption temperature to the ambient temperature are

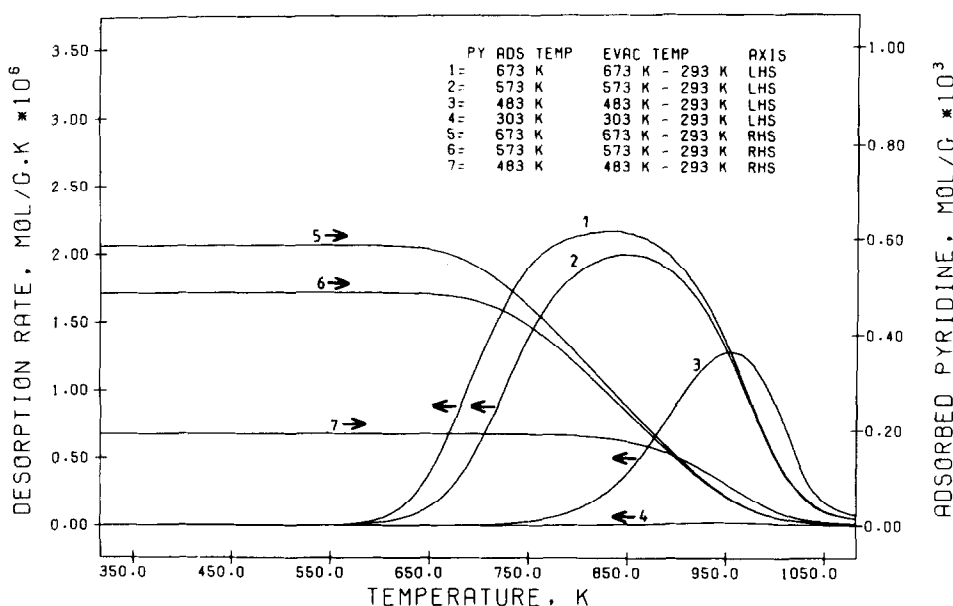


FIG. 1. Effect of varying pyridine adsorption/desorption temperature on H-mordenite calcined at 773 K.

shown in Fig. 1. No pyridine was detected during TPD after adsorption at 303 K. Two comparative runs were performed in which pyridine was adsorbed at 573 K onto HM previously calcined at 573 K. In the first run pyridine was evacuated as the sample was cooled from 573 K to room temperature, while in the second run the sample was allowed to cool to 303 K first before evacuation. In both cases pyridine began desorbing only above 750 K. In the second run the amount of pyridine desorbing increased by approximately 60% at temperatures below the peak temperature of the first run.

When  $\text{NH}_4(85)\text{NaM}$  was calcined at 773 K and the above two pyridine adsorption–evacuation procedures were followed, the TPD spectra obtained were essentially the same, while when NaM was calcined at 773 K, 2.5 times as much pyridine as in the first run desorbed after the second procedure, the bulk of the excess pyridine desorbing below 573 K.

#### Calcination Temperature

The effects of calcining mordenite under vacuum at 573, 673, 773, and 873 K for

varying degrees of exchange are shown in Figs. 2–5. Most mordenite samples darkened in color during TPD and some were even black when taken out of the cell. Carbon and nitrogen analyses of the samples (microanalysis using the Heraeus universal combustion analyzer, Model CHN-MICRO) confirmed the presence of nitrogen and undesorbed carbonaceous materials. From the amounts of carbon measured and on the basis of five carbon atoms for every pyridine molecule, the quantities of pyridine irreversibly adsorbed onto mordenite were computed. These results, together with millimoles of pyridine desorbing during TPD per gram of mordenite (mass of mordenite as weighed prior to TPD experiments, viz., includes physisorbed water) and the total amount of pyridine adsorbed, are shown in Tables 1–4.

As the calcination temperature was increased from 573 to 873 K, the amplitudes of the peaks in the TPD spectra of NaM and  $\text{NH}_4(11)\text{NaM}$  decreased uniformly over the entire temperature range scanned. For mordenite with an ammonium ion content of 55% or above, however, the amplitudes in

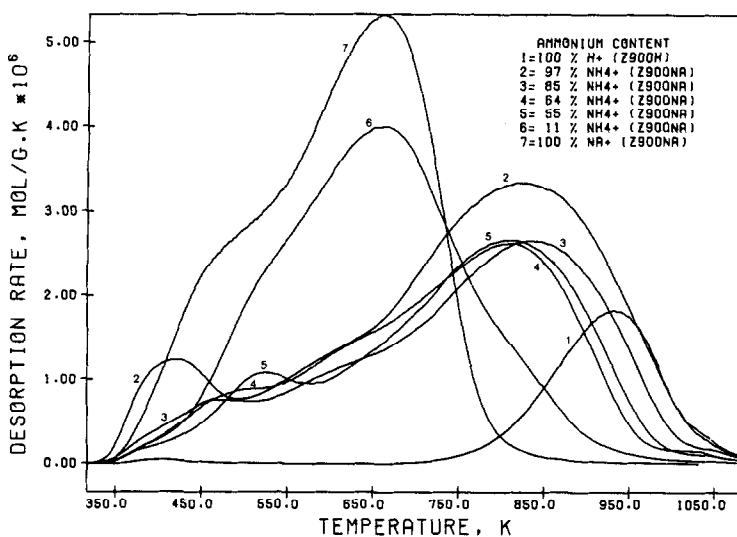


FIG. 2. Effect of ammonium ion content on TPD from mordenite calcined at 573 K.

the low desorption temperature ranges decreased as the calcination temperature increased, while those in high temperature ranges remained the same or increased. At calcination temperatures of 573 and 673 K, TPD spectra of  $\text{NH}_4(55, 64, 85)\text{NaM}$  were similar. There was little overlap in the TPD spectra of  $\text{NaM}$  and  $\text{NH}_4(11)\text{NaM}$  on the one hand and  $\text{NH}_4(55-96)\text{NaM}$  on the

other.  $\text{NH}_4(11)\text{NaM}$  and  $\text{NaM}$  had substantially lower peak temperatures than the other samples, and the total amount of pyridine adsorbed decreased as the calcination temperature was raised from 573 to 873 K.

In view of the findings of Hidalgo *et al.* (2) that the amount of desorbed ammonia increased almost linearly with increasing proton content, it is worth noting the ab-

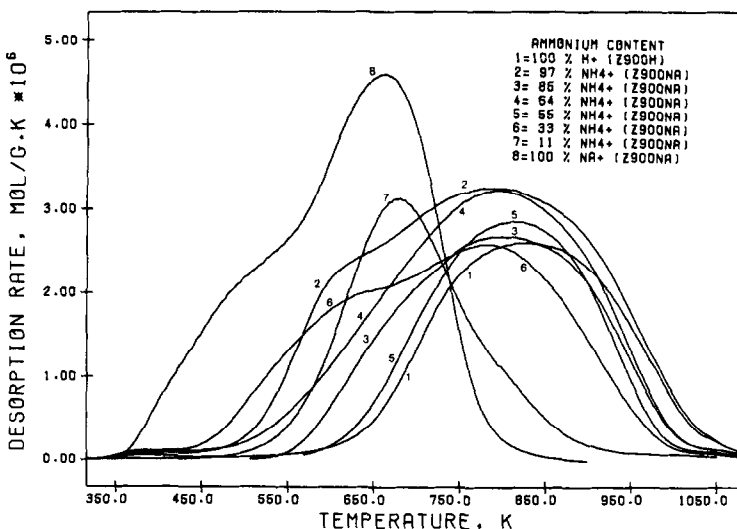


FIG. 3. Effect of ammonium ion content on TPD from mordenite calcined at 673 K.

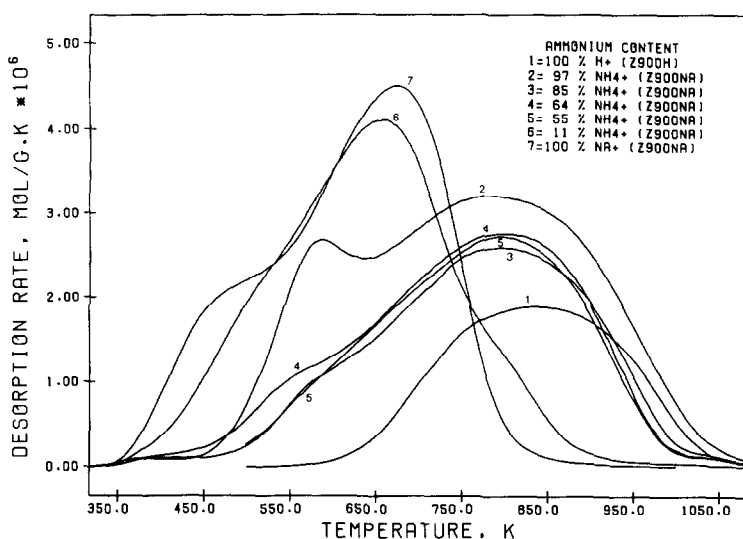


FIG. 4. Effect of ammonium ion content on TPD from mordenite calcined at 773 K.

sence in this work of a linear relationship between the number of adsorbed pyridine molecules and the initial ammonium ion content of the mordenite.

Calcination at 873 K was unique in that for exchange levels greater than 50% the amount of pyridine adsorbed was substantially reduced, and moreover decreased with increasing degree of exchange. The behavior of HM was also unusual in that it

adsorbed many fewer pyridine molecules than any other samples after calcination at 573 K, and the total amount of adsorbed pyridine doubled as the calcination temperature was raised from 573 to 773 K.

#### DISCUSSION

In interpreting the results obtained, it must be noted first that, during TPD, samples were always heated to temperatures

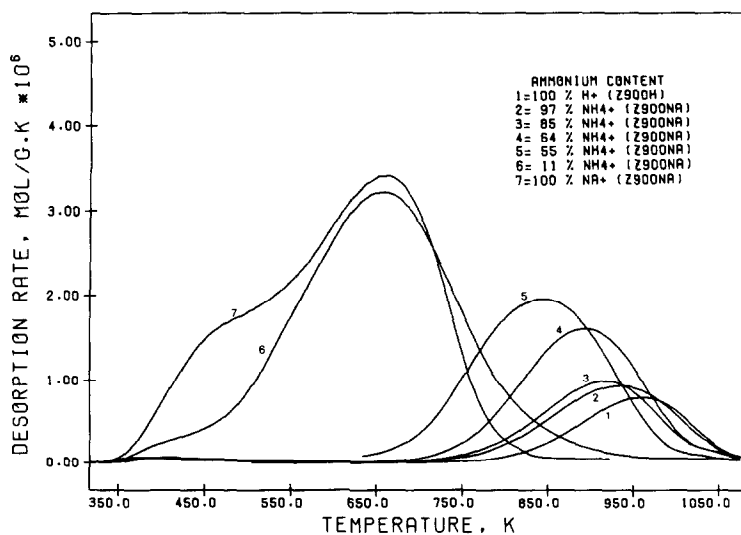


FIG. 5. Effect of ammonium ion content on TPD from mordenite calcined at 873 K.

TABLE 1

Amount of Pyridine (Py) Adsorbed on Mordenite  
Calcined at 573 K

Catalyst	Total Py adsorbed (mmol/g)	Py desorbed during TPD (mmol/g)	Irreversibly adsorbed by	
			(mmol/g)	(% of total)
NaM	1.31	1.29	0.023	2
NH <sub>4</sub> (11)NaM	1.15	1.11	0.038	3
NH <sub>4</sub> (55)NaM	1.05	0.86	0.19	18
NH <sub>4</sub> (64)NaM	1.06	0.86	0.20	19
NH <sub>4</sub> (85)NaM	1.12	0.90	0.22	20
NH <sub>4</sub> (97)NaM	1.42	1.22	0.20	14
HM	0.43	0.30	0.13	30

TABLE 3

Amount of Pyridine Adsorbed on Mordenite  
Calcined at 773 K

Catalyst	Total Py adsorbed (mmol/g)	Py desorbed during TPD (mmol/g)	Irreversibly adsorbed by	
			(mmol/g)	(% of total)
NaM	1.07	1.05	0.02	2
NH <sub>4</sub> (33)NaM	0.99	0.88	0.11	11
NH <sub>4</sub> (55)NaM	0.89	0.69	0.19	21
NH <sub>4</sub> (64)NaM	1.21	0.99	0.22	18
NH <sub>4</sub> (85)NaM	1.02	0.79	0.23	23
NH <sub>4</sub> (97)NaM	1.39	1.20	0.19	14
HM	0.90	0.72	0.18	20

considerably above the respective calcination temperatures, and in particular peak temperatures were generally higher than the calcination temperatures. Hence during TPD new acid sites may form onto which pyridine could readsorb before desorbing into the carrier stream. Second, although Mirodatos *et al.* (5) detected unidentified pyridine decomposition products desorbing from NH<sub>4</sub>NaM containing nickel (pre-treated in wet air) heated above 573 K, in this study only pyridine was detected in the desorption stream.

The evacuation procedure was found to be an important factor in this study. When pyridine was adsorbed at 573 K onto NaM calcined at 773 K, evacuation at 573 K rather than at 303 K essentially removed pyridine which would otherwise desorb in the temperature range 303–573 K. In the

case of HM calcined at 573 K, however, evacuation at 573 K removed 60% of pyridine which, when HM was evacuated at 303 K, desorbed in a temperature range far above 573 K. As discussed below, HM calcined at 573 K for only 2 h may present substantial diffusional resistance to pyridine, and cooling HM from 573 to 303 K in the absence of evacuation may provide additional equilibration time for adsorption of pyridine.

Infrared spectra of pyridine adsorbed onto H-mordenite (6) showed that physisorbed pyridine was removed from high ammonium ion content mordenite by evacuation at 313 K. Indeed, for mordenite with degrees of exchange equal to or above 55% and calcined at or above 673 K, there was virtually no pyridine desorbing below 450 K subsequent to evacuation at 313 K. After

TABLE 2

Amount of Pyridine Adsorbed on Mordenite  
Calcined at 673 K

Catalyst	Total Py adsorbed (mmol/g)	Py desorbed during TPD (mmol/g)	Irreversibly adsorbed by	
			(mmol/g)	(% of total)
NaM	1.15	1.13	0.023	2
NH <sub>4</sub> (11)NaM	1.10	1.06	0.035	3
NH <sub>4</sub> (55)NaM	1.04	0.83	0.21	20
NH <sub>4</sub> (64)NaM	1.15	0.92	0.23	20
NH <sub>4</sub> (85)NaM	1.08	0.84	0.24	22
NH <sub>4</sub> (97)NaM	1.47	1.28	0.19	14
HM	0.65	0.52	0.13	20

TABLE 4

Amount of Pyridine Adsorbed on Mordenite  
Calcined at 873 K

Catalyst	Total Py adsorbed (mmol/g)	Py desorbed during TPD (mmol/g)	Irreversibly adsorbed by	
			(mmol/g)	(% of total)
NaM	0.88	0.84	0.034	4
NH <sub>4</sub> (11)NaM	0.83	0.77	0.061	7
NH <sub>4</sub> (55)NaM	0.57	0.38	0.17	30
NH <sub>4</sub> (64)NaM	0.47	0.30	0.17	36
NH <sub>4</sub> (85)NaM	0.31	0.18	0.13	42
NH <sub>4</sub> (97)NaM	0.27	0.18	0.095	35
HM	0.22	0.13	0.09	41

calcination at 573 K, low-temperature desorption peaks starting in the region of 350 K were observed on mordenite with an ammonium ion content of 55 to 97%. These most probably arise from pyridine interacting with cations such as ammonium or sodium, or with polarized water which was not removed at this calcination temperature. The peak at 420 K in the case of  $\text{NH}_4(97)\text{NaM}$  calcined at 573 K is likely to be due to  $\text{Py-H}_2\text{O-NH}_4^+$  interactions, since no such prominent peak was present on any other  $\text{NH}_4\text{NaM}$ .

Figure 1 shows that the amount of pyridine desorbing from HM previously calcined at 773 K increased with increasing adsorption/evacuation temperature. It is widely accepted in the literature that Lewis sites exist as nonframework hydroxyaluminum species (7, 8), and as such they will reduce the diffusion rate of pyridine in the main channels of mordenite. The increase in population of sites detected by pyridine molecules as the adsorption temperature is increased is probably due to a better accessibility of Lewis sites at higher temperatures. When Karge and Klose (9) and Ghosh and Curthoys (10) carried out thermodesorption of pyridine from HM calcined at 673 K, and dealuminated HM calcined at 773 K, respectively, IR spectra showed that as pyridine desorbed from Brønsted sites it readsorbed onto Lewis sites, as a result of which the amount of pyridine adsorbed onto Lewis sites rose markedly from 473 to 673 K. Further evidence of an increase in temperature enhancing adsorption onto Lewis sites is given by Karge (11, 12) who upon increasing the pyridine adsorption temperature found a greater increase in the amount of pyridine adsorbed onto Lewis than onto Brønsted sites. The effect shown in Fig. 1 can thus be ascribed to the predominance of Lewis sites at a calcination temperature of 773 K (12).

The amount of pyridine adsorbed onto NaM decreased with increasing calcination temperature. Some possible explanations

are (i) loss of residual water enhancing pyridine-sodium interaction at low temperatures; (ii) sodium ions migrating to inaccessible sites (13, 14), and (iii) a structural rearrangement occurring upon heating. However, a thermogravimetric analysis of NaM showed that loss of water between 573 and 973 K amounted to only 0.6 wt% or the equivalent of 1.1 water molecules per unit cell. Therefore it is unlikely that such a small loss of water accounts for the reduction in the amount of adsorbed pyridine. All the TPD spectra of NaM showed pronounced shoulders at 475 K. Since such shoulders were not present on  $\text{NH}_4(11)\text{NaM}$ , these must be due to sodium cations which exchange easily with ammonium ions. The fact that pyridine desorbed at much lower temperatures from sodium than from acid sites confirms that sodium cations are weaker adsorbing sites in agreement with the results of Karge and Klose (15).

The amount of pyridine adsorbed onto HM doubled as the calcination temperature was increased from 573 to 773 K. The low quantity of pyridine adsorbed after calcination at 573 K may be due to a short calcination time of 2 h. There exists evidence in the literature (16, 17) that low-temperature calcination of HM for a short time leads to significant diffusional limitations for benzene-type molecules which can be eliminated by longer calcination.

At a calcination temperature of 873 K, the amount of pyridine adsorbed onto low-sodium-content mordenite was greatly reduced. The most probable explanation is the presence of oxoaluminium species in the mordenite pores as Lewis sites which present significant steric hindrance. That the amount of adsorbed pyridine decreased with increasing degree of exchange may indicate that either an increasing number of Lewis sites presents increasing diffusional restrictions or larger oxoaluminium species are formed (as proposed, for example, by Shannon *et al.* (18)) which do not necessarily act as multiple adsorbing sites, as sug-

gested by Karge (12). Although the number of sites interacting with pyridine increases with decreasing ammonium ion content, these additional sites are weaker, as seen from the decrease in peak temperature and the percentage that irreversibly adsorbed pyridine constitutes of the total.

The TPD results obtained using pyridine as a base contrast markedly with those obtained with ammonia. Hidalgo *et al.* (2) adsorbed and evacuated ammonia at 373 K on HM (Norton Z100H, Si/Al = 6.8), calcined at 773 K for 1 h and found that the total amount of desorbing ammonia, excluding that desorbing below 373 K, was 1.28 mmol/g while the value obtained in this work was 0.90 mmol/g despite a slightly lower Si/Al ratio. They found that the desorption was complete by 800 K and the TPD spectrum contained two distinct desorption peaks at 426 and 681 K, with the latter accounting for 0.87 mmol/g of ammonia. Mirodatos *et al.* (5) also recorded multiple ammonia desorption peaks using  $\text{NH}_4\text{M}$  calcined at 773 K. When Hidalgo *et al.* (2) performed TPD using HM ion-exchanged with potassium, the amount of desorbing ammonia decreased with increasing potassium content and was only 0.04 mmol/g for KM; moreover, both peak temperatures shifted to lower values.

Geometric considerations in part explain the data obtained in this work. First, the work of Eberly (19) and of Barrer and Peterson (20) indicates that benzene cannot gain access to the side pockets of NaM or HM. Since pyridine is comparable in size to benzene, it can be assumed that the side pockets of mordenite are also inaccessible to pyridine. Therefore, although pyridine interacts with sodium ions, at every calcination temperature the total amount of pyridine adsorbed onto NaM was less than that of sodium ions present. Indeed, Meier (21) and Schlenker *et al.* (22) found that one-half of the sodium ions in natural mordenite were located inside side pockets, and Gray and Cobb (23) reported that, above an exchange level of 84%, less acces-

sible sites seemed to be selectively filled by ammonium ions.

Second, it is likely that the number of pyridine molecules required to fill the main channels of mordenite is smaller than the number of acid sites present. In order to check this hypothesis, the crystal structure and pore size of natural NaM (21, 24–26) were used to compute the volume of the main channel and this value ( $0.554 \text{ nm}^3/\text{unit cell}$ ) was in turn used to calculate the number of pyridine molecules needed to fill the main channel, assuming the density of pyridine to be that of the liquid at 293 K. Table 5 gives the theoretical maximum number of (Brønsted) acid sites and the amount of pyridine needed to fill the main channel for each degree of exchange. A comparison with Tables 1–4 shows that the total amount of pyridine measured during TPD approached, and in some cases exceeded, the amount necessary to fill the main channels of mordenite. The TPD results of  $\text{NH}_4\text{NaM}$  calcined at 573 and 673 K showed a volumetric main channel filling of approximately 70 to 95% for all degrees of exchange except for  $\text{NH}_4(97)\text{NaM}$  which showed a pore filling of 110–115%. Since taking the density of pyridine at 293 K

TABLE 5

The Theoretical Number of Acid Sites (Based on the Effective Aluminium Content, i.e., Excluding Aluminium Associated with Sodium) and the Amount of Pyridine Required to Fill the Volume of the Main Channels of Mordenite

Catalyst	Theoretical number of acid sites (meq/g)	Amount of Py equivalent to main channel volume (mmol/g)
NaM	0(1.99 <sup>a</sup> )	1.23
$\text{NH}_4(11)\text{NaM}$	0.220	1.23
$\text{NH}_4(33)\text{NaM}$	0.665	1.24
$\text{NH}_4(55)\text{NaM}$	1.12	1.25
$\text{NH}_4(64)\text{NaM}$	1.30	1.26
$\text{NH}_4(85)\text{NaM}$	1.75	1.27
$\text{NH}_4(97)\text{NaM}$	2.00	1.27
HM	2.14	1.28

<sup>a</sup> Equivalent number of sodium sites.



would give a conservative estimate of degree of pore filling, it follows that there was no diffusional resistance to pyridine uptake in  $\text{NH}_4\text{NaM}$  calcined in the range 573–773 K but that the uptake was limited only by the main channel pore volume.

At a calcination temperature of 773 K, there was virtually no overlap between the TPD spectrum of NaM and that of  $\text{NH}_4(55)\text{NaM}$ . This absence of overlap of TPD spectra suggests that even if some of the pyridine molecules were initially adsorbed onto sodium ions, they readsorbed onto acid sites before desorbing downstream to the FID and thus the TPD spectrum represents primarily pyridine–acid site interaction. It follows then that the TPD spectra of  $\text{NH}_4(64,85,97)\text{NaM}$ , which show greater quantities of adsorbed pyridine than that of  $\text{NH}_4(55)\text{NaM}$ , also correspond to pyridine desorbing from mordenite acid sites. What is unexpected, however, is that most of the additional pyridine molecules are found to desorb in lower, rather than higher, temperature regions, i.e., 450–650 K. In other words, the number of stronger acid sites, as detected by pyridine, does not increase with increasing percentage exchange. Further evidence in accordance with this trend is that the amount of irreversibly adsorbed pyridine also does not increase at higher exchange levels. The above observation is in contrast to the findings of Hidalgo *et al.* (2) and Ratnasamy *et al.* (1). At high  $\text{NH}_4^+$  content, Hidalgo *et al.* found that the size of the high-temperature peak relative to that of the low-temperature peak increased, and Ratnasamy *et al.* found a greater proportion of acid sites with high heats of ammonia adsorption. One possible explanation for this discrepancy is that stronger acid sites generated at high exchange levels are inaccessible to pyridine which are much larger than ammonia.

Ratnasamy *et al.* (1) examined isomerization and disproportionation of *o*-xylene over  $\text{NH}_4\text{NaM}$  (starting material NaM, Si/Al = 5.8, calcination at 823 K in static air)

with exchange levels between 0 and 100% and found the conversion of *o*-xylene to increase faster with increasing  $\text{NH}_4^+$  ion content above 61% than below this level. They attributed this observation to the formation of strong acid sites, e.g., nonframework hydroxoaluminium species, at high degrees of exchange. However, since disproportionation of *o*-xylene involves a reaction between two bulky molecules larger than pyridine, and pyridine did not seem able to gain access to strong sites in this work, our data indicate that the increase in strength of sites with increasing exchange level as determined by ammonia adsorption does not adequately explain their findings.

#### CONCLUSIONS

Pyridine TPD from  $\text{NH}_4\text{NaM}$  was significantly different from ammonia TPD. Steric factors played a dominant role and eclipsed variations in the number or strength of acid sites with degrees of cation exchange. For reactions involving aromatics or highly branched hydrocarbons, similar steric considerations should be taken into account in explaining the activity of mordenite.

#### ACKNOWLEDGMENTS

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