Acidity Characterization of Ion-Exchanged Mordenite

II. Infrared Spectroscopic Investigation

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The nature and number of acid sites formed at increasingly higher pretreatment temperatures and different levels of Na^+–NH_4^+ exchange in synthetic mordenite were investigated by infrared analysis using pyridine as a probe. The number of pyridine molecules interacting with acid sites represented a maximum of 50–70% pore filling and appeared to be limited by transport resistance arising from compacting of infrared waters. Lewis sites were found to introduce significance hindrance to pyridine uptake and required far greater thermal energy for adsorption than Brønsted sites. H-mordenite had markedly less pyridine adsorbing onto Brønsted sites than NH_4Na-mordenite at all calcination temperatures. At higher pretreatment temperatures pore diffusional limitations within the main channel played an important role. Of the pyridine which could gain access to acid sites given a contact time of the order of 1 h, the amount adsorbing onto Brønsted sites at 773 K, and onto Lewis sites at 823 K, was approximately linearly related to ammonium ion content. © 1988 Academic Press, Inc.

INTRODUCTION

In Part 1 (*1*) temperature-programmed desorption (TPD) of pyridine from ammonium-sodium-mordenite (NH₄NaM) exchanged to varying degrees was investigated and found to be markedly different from results of ammonia TPD. Because the number of pyridine molecules filling the main channel was smaller than the number of acid sites above an ammonium content of ca. 50%, pyridine was unable to gain access to all the acid sites and in particular distribution of the strength of sites as detected by pyridine was apparently independent of percentage exchange. Since there are many reactions which involve reactant or product molecules having dimensions comparable to or larger than those of pyridine, e.g., in cyclohexane hydroisomerization, xylene disproportionation, and butene oligomerization, it is of considerable interest to characterize the nature of acid sites on NH₄NaM using pyridine as a probe. In this paper changes in the amount and nature of acid sites formed at various levels of Na^+–NH_4^+ exchange in mordenite following in-creasingly higher pretreatment temperatures are examined by means of IR spectroscopy.

EXPERIMENTAL

Materials. Na-mordenite (NaM) (Si/Al = 6.0, Z900Na) and H-mordenite (HM) (Si/Al = 5.8, Z900H) in the form of $\frac{1}{16}$-in. binderless extrudates were obtained from Norton Co. The HM was prepared in a proprietary way by Norton and was not subjected to any further pretreatment. NaM was treated with NH₄Cl to yield an ammonium ion content of 11, 55, 64, 85, and 97%. After ion exchange the samples were dried overnight in static air at 357–373 K.

Infrared spectroscopy. Infrared spectra were recorded on a Perkin–Elmer 180 spectrophotometer. The IR cell has been described elsewhere (*2*). The mordenite samples were finely crushed and pressed under a pressure of 1550 kg/cm² into self-supporting wafers of 1 cm diameter with a mass density of 2 to 4 mg/cm². The sample was evacuated at a given temperature for 2 h and subsequently allowed to cool to the pyridine adsorption temperature. Pyridine

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(Merck spectroscopic grade) at 254 K (vapor pressure of 1 Torr) was adsorbed for 30 min, the cell was then evacuated for 30 min, and upon cooling the absorption spectrum was recorded at 313 K. The absorbance was determined by measuring the peak height relative to a straight line joining the trough on either side of the peak and the width at half-height. This process was repeated at successively increasing calcination temperatures for each degree of exchange. At calcination temperatures below 573 K pyridine was adsorbed and evacuated at 313 K, and above 573 K pyridine was adsorbed and evacuated as the cell was allowed to cool from 573 to 473 K. Immediately following calcination at 573 K the mordenite wafer was scanned twice, once after pyridine adsorption at 313 K and again after pyridine adsorption at 573 K.

RESULTS

Only bands of particular interest are reported in this paper. They include the band at 1545 cm^{-1} assigned to the pyridinium ion adsorbed onto a Brønsted acid site (BPy), the band at 1454 cm^{-1} assigned to coordinately bonded pyridine adsorbed onto a Lewis acid site (LPy), the bands at 1448–1441 cm^{-1} assigned to pyridine adsorbed on sodium cations (Cat-Py), and the ammonium NH bending vibration at 1445 cm^{-1} and the NH stretch vibration at 3255 cm^{-1}.

Adsorption and evacuation at 313 K, or adsorption at 573 K and evacuation at 573–473 K, for 30 min each, respectively, removed absorption bands at 1437 and 1587 cm^{-1}, indicating removal of physisorbed pyridine. In addition when HM precalcined at 873 K, exposed to pyridine at 573 for 30 min, and evacuated at 313 K for 5 min, no physisorbed pyridine was detected. Although the wafers were subjected to repeated adsorption and desorption of pyridine at successively higher temperatures, no band at 1585 cm^{-1}, attributed by many workers (3–7) to highly dehydrogenated hydrocarbon, aromatic, or cyclic skeletal structures, was observed. However, at 923

K the wafers of low-sodium-containing mordenite turned gray and at 973 K they were nearly black.

Deammoniation was nearly complete by a calcination temperature of 573 K for mordenite with an ammonium ion content of 64% or lower, and by 623 K for ammonium ion exchange levels of 85 and 97%.

The effect of calcination temperature on the number of Brønsted sites is given in Fig. 1. The discontinuity at 573 K is a result of taking IR spectra twice after pyridine adsorption at 313 and 573 K. The number of Brønsted sites was at a maximum after calcination at 573 K. Between calcination temperatures of 313 and 473 K, NaM exhibited a small band at 1546 cm^{-1}. Above a calcination temperature of 673 K the absorbance of the BPy band decreased rapidly and by 873 K the intensity was only a small fraction of the values recorded at 573 K. The BPy band intensity of mordenite calcined above 573 K did not increase linearly with ammonium content from 0 to 97%, but reached a plateau at 55% as seen in Fig. 2.

The LPy band intensities for ammonium ion contents between 55 and 97% and for HM are plotted in Fig. 3. The curve corresponding to NH$_4$(33)NaM is the combined absorbance of the bands at 1448 and 1454 cm^{-1}. The intensities of the LPy band remained small below a calcination temperature of 700 K, even though the intensities of the BPy band had fallen markedly by 700 K. Above 700 K the LPy band intensities increased rapidly, peaking at 773 K for NH$_4$(55)NaM and NH$_4$(64)NaM and at 823 K for NH$_4$(85)NaM and NH$_4$(97)NaM. A plot of LPy band absorbances as a function of degree of exchange is given in Fig. 4. No LPy band was identified for NaM or NH$_4$(11)NaM. Only Cat-Py bands, which decreased in intensity with increasing calcination temperature, were observed. NH$_4$(11)NaM did not generate an LPy band at any calcination temperature. In contrast, NH$_4$(33)NaM yielded an LPy band at 1454 cm^{-1}. This band, however, was superimposed onto a Cat-Py band and they could not be re-
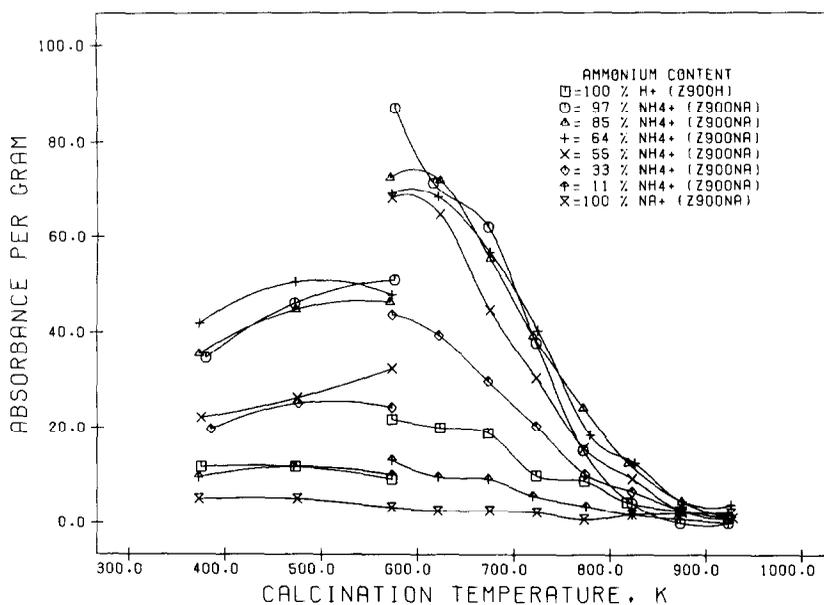
FIG. 1. Effect of calcination temperature on BPy band absorbances.

solved. None of the spectra showed a band at 1462 cm^{-1}, assigned to pyridine adsorbing onto strong Lewis sites (8–10).

The effect of pyridine adsorption proce-dure on band intensities was investigated in two sets of experiments. In one case using HM, at or below a calcination temperature of 773 K, pyridine was adsorbed and evacu-
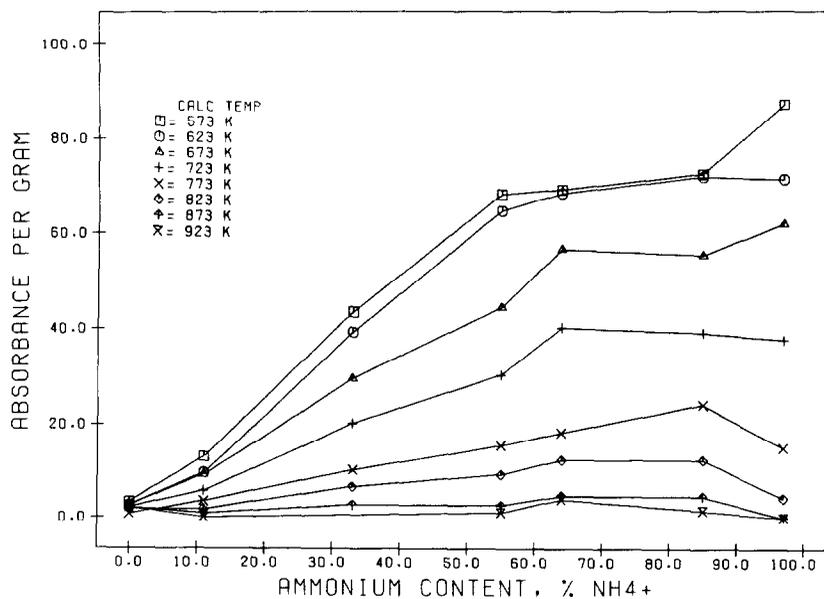

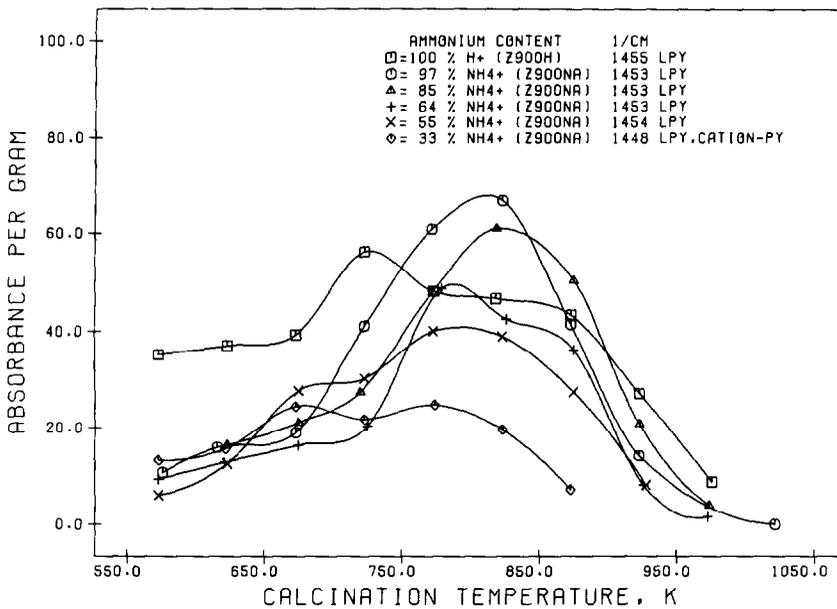FIG. 2. Effect of ammonium ion content on BPy band absorbances.

FIG. 3. Effect of calcination temperature on LPy and Cat-Py band absorbances.

ated at 373 K for 30 min each, whereas at 773 K or above, the pyridine adsorption temperature was raised to 573 K. The data were compared to those obtained following the previously described standard adsorption procedure. When the pyridine adsorption temperature was raised to 573 K, the BPy band absorbance immediately in-
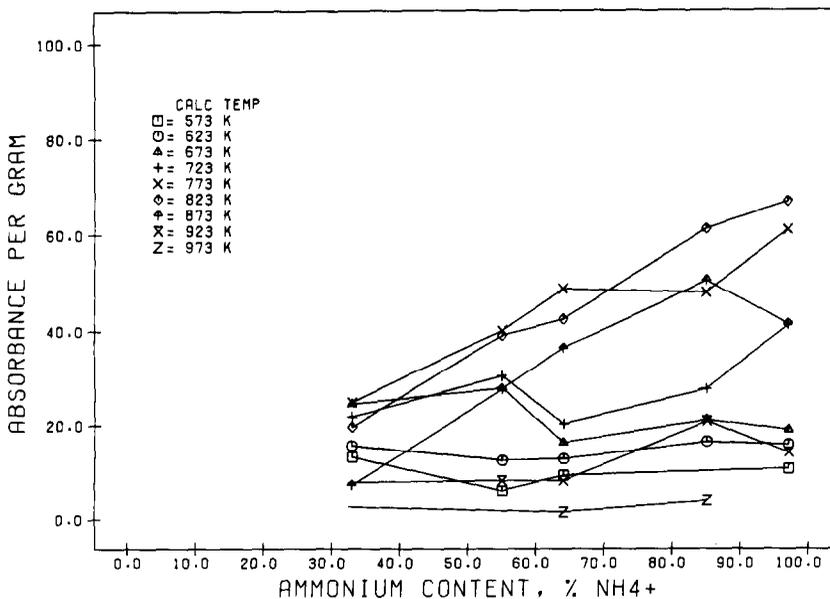

FIG. 4. Effect of ammonium ion content on LPy band absorbances.

creased to that in the standard procedure while the LPy band absorbance did not increase at all in all the subsequent calcination between 773 and 923 K. In another experiment NH$_4$(64)NaM was evacuated at 773 K for 4 h in a single calcination and pyridine was adsorbed as usual at 573 K. The BPy band absorbance was similar to, but the LPy band absorbance was much smaller than, those obtained after calcination at successively higher temperatures.

HM behaved differently from the samples containing ammonium ions in several ways. Subsequent to calcination at 573, 623, and 673 K, the LPy band intensity was considerably larger than those of NH$_4$NaM samples, and comparable in magnitude to those of NH$_4$NaM calcined at 773 K. The maximum intensity of the LPy band of HM was similar to that of NH$_4$(85)NaM, but as has already been shown, its BPy band absorbance was lower than that of NH$_4$(33) NaM.

HM calcined below 523 K showed a band absorbing at 1445 cm^{-1}. The frequency of this band at first seemed to suggest the presence of NH bending vibration. However, when NH$_4$(64)NaM was calcined at 773 K for 4 h followed by pyridine adsorption at 573 K, and then water (21 Torr) was adsorbed for 2.5 h at 313 K followed by pyridine adsorption and evacuation at 313 K for 30 min each, a band at 1448 cm^{-1}, similar in shape and intensity to the 1445 cm^{-1} band of HM, was also observed. Calcining the above-treated catalyst sample at 573 K for 2 h removed this band. Therefore it appears that the band observed did not arise from NH$_4^+$ which should be completely absent on NH$_4$(64)NaM after calcination at 773 K but was due to the combined presence of water and protons.

A set of rehydration experiments was also performed. In one experiment, HM was calcined at 873 K for 2 h followed by pyridine (1 Torr) adsorption at 573 K for 30 min. When this sample was exposed to water (16 Torr) at 313 K for 5 min, the absorbance at 1545 cm^{-1} was 56% of that of HM calcined at 573 K. In another experiment NH$_4$(64)NaM was rehydrated as described in the preceding paragraph. The 1545 cm^{-1} absorbance was one-third of that subsequent to calcination at 573 K. When this sample was contacted with water (21 Torr) at 573 K for 15 min and pyridine (1 Torr) adsorbed at 573 K for 30 min, the 1545 cm^{-1} absorbance increased to 46% of that measured following calcination at 573 K. When HM was calcined at 982 K and exposed to water (18 Torr) at 313 K for 5 min followed by pyridine adsorption at 313 K for 30 min the absorbance at 1545 cm^{-1} was negligibly small. Similarly when NH$_4$(55)NaM calcined at 923 K was contacted with water (16 Torr) at 313 K for 5 min, the absorbance at 1545 cm^{-1} was small.

DISCUSSION

The numbers of Brønsted and Lewis sites were estimated for degrees of exchange above 50% between calcination temperatures of 573 and 923 K using the integrated extinction coefficients of Hughes and White (11) (Table 1). These results must be seen in light of the fact that other workers (12) have obtained different values of extinction coefficients and moreover that these coefficients may, to some extent, depend on the nature of the particular adsorbent. Figure 5 shows the total number of acid sites, together with the number of pyridine molecules remaining on mordenite above 550 K during TPD, the maximum theoretical amount of acid sites computed from the aluminium content, and the number of pyridine molecules needed to occupy the entire main channel (taking the density of pyridine to be that of the liquid at 293 K). The unit mass of mordenite includes physisorbed water. In plotting TPD data, only the pyridine molecules desorbing above 550 K and irreversibly adsorbed pyridine were included in order to exclude pyridine–cation (sodium or ammonium) interactions. IR studies showed that the number of pyridine molecules interacting with acid sites was only about one-half of that needed to fill the

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Estimated Numbers of Brønsted and Lewis Sites Expressed in Millimoles per Gram as a Function of
Ammonium Ion Exchange Level and Pretreatment Temperature

	NH₄(55)NaM		NH₄(64)NaM		NH₄(85)NaM		NH₄(97)NaM		HM	
	BPy	LPy	BPy	LPy	BPy	LPy	BPy	LPy	BPy	LPy
573 K	0.56	0.03	0.58	0.05	0.56	a	0.66	0.04	0.15	0.25
623 K	0.53	0.06	0.56	0.09	0.56	0.09	0.56	0.14	0.14	0.25
673 K	0.33	0.22	0.45	0.12	0.42	0.16	0.51	0.17	0.13	0.26
723 K	0.22	0.25	0.31	0.16	0.28	0.24	0.32	0.34	0.07	0.37
773 K	0.11	0.37	0.14	0.41	0.17	0.40	0.15	0.42	0.06	0.29
823 K	0.06	0.31	0.10	0.33	0.09	0.47	0.03	0.45	0.03	0.26
873 K	0.01	0.22	0.02	0.26	0.03	0.34	0	0.24	0.02	0.24
923 K	0.004	0.05	0.02	0.05	0.004	0.10	0	0.09	0.003	0.15

a Not measurable.

main channel. TPD studies, however, indicated that, with the exception of HM, even after discounting pyridine desorbing below 550 K, pyridine filled nearly 100% of the pore volume for degrees of exchange above 50% between calcination temperatures of 573 and 773 K.

Karge (9) showed that increasing the pyridine adsorption temperature from 473 to 573 K increased the amount of pyridine adsorbed onto HM, particularly onto Lewis sites, and increasing the adsorption time from 2 to 17 h also enhanced the number of pyridine molecules interacting with acid sites on mordenite. The latter finding is consistent with the incomplete pore filling observed in the present work after 30 min of pyridine adsorption. For example, Karge observed that 0.62 mmol/g (dry basis) of pyridine adsorbed onto HM (Si/Al = 5.5) calcined at 623 K after adsorbing pyridine at 573 K for 15 h. This is approximately
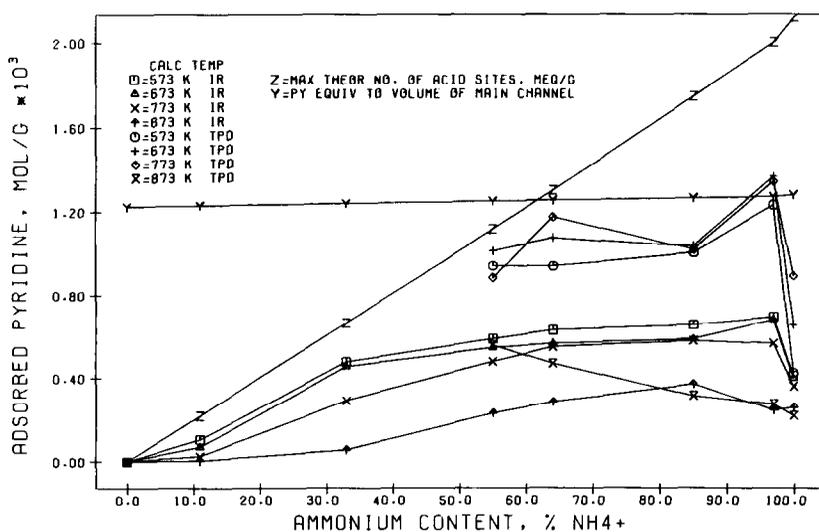

FIG. 5. Total amount of pyridine adsorbed as a function of ammonium ion content, calculated from infrared and TPD data.

0.53 mmol pyridine/g including hydration (assuming 15 wt% water content) (13), as opposed to 0.39 mmol/g obtained in this work. At a calcination temperature of 673 K TPD indicated that 0.65 mmol pyridine/g adsorbed onto acid sites of HM while the IR measurements in this work gave 0.39 mmol/g. Clearly in the IR procedure pyridine encountered significant resistance to uptake which was not present in TPD experiments.

One possible explanation for the discrepancy in the values obtained by TPD and IR studies is the fact that in order to make IR wafers mordenite was crushed, ground, and compacted under a pressure of 1550 kg/cm^2 for 1 to 2 min, while the conditions for TPD sample preparation were much milder, i.e., crushing and sieving to a 250- to 500-μm size fraction. Satterfield and Frabetti (14) reported that mechanical treatments such as grinding had marked effects on the diffusivity of propane in NaM obtained from Norton. The propane diffusivity in mordenite, ground to a 7.5-μm-diameter fraction, calculated from transient sorption rate measurements, was $\frac{1}{35}$ of that in 21 × 21 × 22-μm samples. They offered as an explanation for this reduction in measured diffusivity partial blockage and closing of mordenite pores as a result of local temperature rises and surface stressing during crushing. Moreover, the large pressure exerted to make wafers could decrease intercrystalline diffusivity by markedly reducing macropore volume.

Karge (9, 13) concluded from his data that adsorption onto Lewis sites typically requires more thermal energy than that onto Brønsted sites. In this work two sets of experiments were carried out to examine the effect of varying pyridine adsorption temperature, and adsorption onto Lewis sites was found to be markedly less when the standard procedure was not followed. This is probably due to the fact that when mordenite is calcined successively, pyridine which adsorbs onto Brønsted sites at 573 K can desorb and readsorb onto newly formed Lewis sites during subsequent calcination. This readsorption takes place at temperatures higher than 573 K. If pyridine is adsorbed at 373 K onto samples calcined sequentially at 50 K intervals to a temperature of 773 K, or if pyridine is adsorbed at 573 K onto a mordenite sample freshly calcined at 773 K, the above source of pyridine bonded to Brønsted sites is not available for readsorption and the thermal energy provided at 573 K for 30 min is evidently not sufficient to enable much pyridine adsorption onto Lewis sites. Similar increases in LPy absorbances, without additional pyridine dosage, with increasing temperature, were recorded by Ghosh and Curthoys (10) and Karge and Klose (15) between 473 and 673 K during thermodesorption of pyridine. In addition, when the adsorption temperature of pyridine was increased from 473 to 573 K in Karge's work (9), the BPy absorbance did not change as long as there was little or no Lewis acidity. However, at a calcination temperature of 773 K which gave the maximum LPy absorbance, the BPy absorbance doubled upon increasing the adsorption temperature. This seems to indicate that the presence of Lewis sites also prohibits rapid interaction of pyridine with Brønsted acidity.

There is one critical difference between the procedure followed here and that in the work of Karge (9, 13). Karge used a fresh sample of mordenite for each experiment, and hence in his work the adsorption temperature used was the actual temperature at which pyridine adsorbed onto the mordenite acid sites. In this work, above a calcination temperature of 573 K, readsorption onto Lewis sites was probably taking place at each calcination temperature as long as BPy band absorbances were falling. For this reason, in order to achieve the same degree of pyridine adsorption less time would be needed if the same sample was calcined successively than if a fresh catalyst sample was used for each calcination temperature.

The above-observed resistance to pyridine uptake onto, and in the presence of, Lewis acidity begs the question why in TPD studies pyridine uptake was complete following single calcination (2 h) at 773 K (1). One difference is the pyridine evacuation procedure; in TPD studies the sample was evacuated at 303 K while here the sample was evacuated as the cell cooled from 573 to 473 K. However, while TPD data showed that the latter procedure removed more pyridine than the former from HM calcined at 573 K, the effect of varying the evacuation procedure in the above manner was negligibly small on NH$_4$(85)NaM calcined at 773 K.

The extent of dehydroxylation appears to depend on, in addition to temperature (13, 16), the sample environment (vacuum or gas), duration, and bed depth where applicable (possibly even wafer thickness); for example, Karge (9) was able to deammoniate NH$_4$NaM with no dehydroxylation taking place at 650 K whereas in this work there was considerable Lewis acidity by 623–673 K. It is thus possible that particularly at 773 K, which corresponds to the onset of significant dehydroxylation, the amounts of Lewis sites were different in the IR and TPD experiments. Having been evacuated at 50 K intervals for 2 h each, HM calcined at 773 K in the IR setup might have been much more dehydroxylated than in TPD. Similarly doubling the calcination time from 2 to 4 h in the case of NA$_4$(64) NaM might have generated more Lewis sites. Moreover, different configurations (a thin bed of small particles versus compacted powder) and particle sizes might have contributed further to achieving different levels of dehydroxylation.

At a calcination temperature of 873 K, the amounts of pyridine discerned by TPD as having adsorbed onto mordenite were substantially reduced at high exchange levels. However, as seen in Fig. 5, at 873 K the amounts of pyridine measured in IR experiments approached, and sometimes ex-

ceeded, the values given by TPD. If acid sites at 873 K in TPD studies can also be assumed to be predominantly of Lewis nature, this shows that the adverse effect of compacting IR wafers is no longer significant given the difficulties encountered in adsorbing onto Lewis sites. Furthermore, it is not likely that much new pyridine adsorbed onto IR wafers after calcination at 873 K; indeed, very little pyridine adsorbed onto Lewis sites of NH$_4$(64)NaM freshly calcined at 773 K for 4 h. Similarly the strong presence of Lewis sites upon dehydroxylation may explain why HM calcined at 773 K adsorbed no pyridine at 313 K during TPD while IR spectra of HM calcined at temperatures between 313 and 573 K showed a BPy band after pyridine adsorption at 303 K. Unfortunately it was not possible to determine the LPy band absorbance unless calcination took place above 573 K as it was eclipsed by a broad band at 1445 cm^{-1} for calcination between 313 and 573 K. Karge (13) also observed BPy and LPy bands on HM calcined at 673 K after pyridine adsorption at room temperature. Data obtained in an attempt to adsorb pyridine at 313 K onto HM freshly calcined at 773 K for 17 h and onto NH$_4$(64)NaM calcined at 673 K for 4 h were not conclusive because residual pyridine in the IR cell adsorbed onto the mordenite samples during calcination. Adsorption at 313 K did not enhance the above band intensities recorded immediately after calcination.

Jacobs and Beyer (17) suggest that the reappearance of pyridinium ions after rehydration in the presence of pyridine does not necessarily mean that the original Brønsted sites are restored. Hence in rehydration tests reference is made to the reappearance of the 1546 cm^{-1} band rather than to BPy absorbance. Karge (16), by rehydrating HM previously calcined at 973 K, showed that dehydroxylation was irreversible. Cannings (8) calcined HM at successively higher temperatures, alternating with rehydration, and found that after pyridine and

water vapor dosing (each at 3 Torr) at 298 K for 16 h on HM calcined at 873 K, the 1546 cm^{-1} band absorbance was 32% of that measured following calcination at 573 K. The degree to which the 1546 cm^{-1} band intensity was restored after rehydrating HM dehydroxylated at 873 K was somewhat higher in this work. At higher temperatures, the formation of pyridinium ions upon rehydration became increasingly difficult, and at 982 K a 1546 cm^{-1} band was essentially absent.

The data obtained in this work are at variance with Karge's results (9) in that the BPy absorbances began falling above 573 K whereas Karge found that the BPy absorbance of NH$_4$M (Si/Al = 4.6) did not start to decrease until approximately 750 K. Karge also found that the LPy absorbance of HM increased slightly over the region 750–850 K and remained high until 973 K, while in this work the LPy absorbance had fallen significantly by 973 K. This discrepancy may be eliminated by extending the contact time of pyridine with the catalyst in this work. Confining our attention to degrees of exchange equal to or above 55%, the drop in BPy band intensities below 750 K was accompanied by rises in LPy band intensities, most prominently in the case of NH$_4$(55)NaM and NH$_4$(97)NaM. Within the pyridine adsorption time of 30 min, pyridine which managed to penetrate inside the main channel of mordenite was most probably a fraction of the amount which could occupy the entire pore volume. The above-mentioned decrease in BPy absorbance and increase in LPy may indicate that for adsorption onto sites for which no serious adsorption or diffusional activation energy barrier exists, there is preferential adsorption onto Lewis sites. This may explain the data obtained by Karge (9) in which increasing the pyridine adsorption time from 2 to 17 h enhanced BPy absorbances more than LPy absorbances in all the cases with no or little dealumination. This may also explain why, when pyridine uptake is lim-

ited as in this work, so few Brønsted, and significantly more Lewis, sites were detected on HM prior to the onset of dehydroxylation.

Because of the extended time needed for pyridine to interact fully with mordenite acid sites in IR experiments, the ratio of Lewis to Brønsted sites at each calcination temperature for different degrees of exchange cannot be deduced. At a calcination temperature of 573 K the amount of Lewis acidity on NH$_4$NaM was very small. Hence it may be assumed that diffusional limitations inside the main channel were also small. The average pore filling, however, was about 50–70%, and there was essentially no increase in the amount of Brønsted acidity with increasing exchange level. This suggests that the resistance to pyridine uptake lay in partial pore mouth blockage and/ or reduction in intercrystalline pore volume. Another possibility, namely that some pore mouths were completely blocked while others were freely accessible to pyridine, and those accessible to pyridine were completely filled, is untenable for the following reason. In the case of NH$_4$(55)NaM, the number of Brønsted sites before dehydroxylation corresponds approximately to the number of pyridine molecules which can occupy the main channel. If after calcination at 573 K, 30–50% of the main channels are completely inaccessible to pyridine, and the remaining channels have 100% pore filling, the maximum number of Lewis sites detected after calcination at higher temperatures cannot exceed one-half the maximum Brønsted sites, provided one pyridine molecule adsorbs onto one Lewis site corresponding to one or more aluminium. Table 1 shows, however, that the maximum number of Lewis sites is about two-thirds of the maximum Brønsted acidity.

Decreases in total number of acid sites, as indicated by pyridine, after pretreatment at higher temperatures are most probably due to diffusional limitations inside the

main channel. At these temperatures what this study provides is an indication, given enough pyridine to achieve potential pore filling of 50–70%, of the ratio of Brønsted to Lewis sites for a contact time of the order of 30 min to 2 h. Although Karge (9) showed that increasing the contact time from 2 to 17 h at 573 K increased considerably the amount of pyridine adsorbed, in a typical reactor the residence time of molecules is much shorter, and hence this study provides information on catalytically relevant acid sites which can be accessed without encountering significant mass transfer resistance inside the zeolite channel for those reactions which involve molecules of diffussivity similar to that of pyridine.

It is interesting to compare the estimated values of Brønsted and Lewis sites given in Table 1 with reaction data of Minachev et al. (18) and of Ratnasamy et al. (19). Minachev et al. (18) calcined $NH_4(25, 48, 63, 83)$ NaM (prepared by treating NaM with NH_4 NO_3) at 793 K in flowing air (time unspecified) and examined isomerization of cyclohexane at 573 K and 30 atm as a function of percentage exchange. They found that the activity increased linearly with increasing ammonium ion content. Ratnasamy et al. (19) calcined $NH_4(0, 36, 61, 71, 100)$NaM (prepared by treating NaM with NH_4Cl) in static air at 823 K for 6 h and passed o-xylene over the sample at 623 K. The conversion of o-xylene increased linearly with exchange level but there were two slopes, the steeper of which was obtained above an ammonium ion content of 61%. Moreover, selectivity toward disproportionation increased nonlinearly with percentage exchange. They attributed enhanced activity and occurrence of disproportionation to the formation of strong sites (in the form of extraframework oxoaluminium species). Pyridine TPD studies of NH_4NaM indicated (1), however, that it was questionable if o-xylene could reach the strong sites accessed by ammonia during ammonia adsorption studies. One difficulty encountered in correlating the IR results with the above activity data is the uncertainty in regard to the degree of dehydroxylation owing to different calcination procedures. Calcinations in static air, in flowing air, and by evacuation most probably yield different amounts of Lewis sites. From the evidence found in the literature, calcination in static or flowing air probably delays dehydroxylation, although to a lesser extent in flowing air (13). Hence calcination in static air at 823 K for 6 h may correspond, for example, to successive evacuation for 2 h each to a temperature of 773 K. Bearing in mind the limitations of comparing mordenite pretreated under different conditions and of estimating numbers of acid sites using IR analysis, two linear relationships between acidity and percentage exchange may be linked to the observed activity trends: the number of Brønsted sites at 773 K and of Lewis sites at 823 K. Both have shortfalls at an exchange level of 97%. It is possible that these Brønsted sites which are accessible to pyridine, and not Lewis as suggested by Ratnasamy et al. (19), are primarily responsible for catalytic activity, and that they are stronger than Brønsted acidity which is present at lower calcination temperatures because Lewis sites are enhancing the strength of these residual Brønsted sites. Further work involving in situ reaction in an IR cell needs to be carried out before any conclusions may be drawn.

CONCLUSIONS

The extent of dehydroxylation was found to be very sensitive to the catalyst geometry and pretreatment procedure. Pore diffusional limitations became significant in the presence of Lewis sites. In the context of limited adsorption equilibration time, there was some evidence of linearity between Brønsted/Lewis sites detected and ammonium ion content in the neighborhood of 800 K.

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