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Acid Site Promotion of Mordenite[1]

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The surface acidity of H-mordenite and partially dealuminated H-mordenite has been characterized by gravimetric and spectroscopic measurements of ammonia adsorption. The acidic properties of the mordenite samples are compared with those of other acidic solids. An increase in the number of strongly acidic sites was observed upon dealumination of mordenite up to SiO_2/Al_2O_3 ratios of 16. Evidence is presented for the formation of hydroxyl nests in dealuminated mordenite. The results suggest that Bronsted acid site strength is promoted by the hydroxyl nests, acting through the lattice.

INTRODUCTION

Metal-loaded zeolite catalysts are used in a variety of hydrocarbon conversion reactions. The activity of such catalysts for paraffin conversion depends on both the metal and acid sites. The reactive intermediate in these reactions is thought to be a carbonium ion. The role of Bronsted acid sites in promoting unsaturated hydrocarbons to form carbonium ions is generally agreed upon.

The exact reasons for the greater activity of zeolites compared to other acidic solids is still subject to discussion (*1*). Differences in the rates of these reactions are often discussed in terms of the concentration and strength of the acid sites. For instance, the rate of *n*-hexane cracking using H–Y-zeolite was observed to be 6400 times the rate with amorphous silica–alumina (*2*). However, the concentration of acid sites on the H–Y-zeolite catalyst was only about seven times as great (2.6 vs 0.35 mequiv/g). Of course, the reason for this discrepancy may lie in the greater acid strength of the zeolitic acid sites.

Benesi (*3*) demonstrated the superior catalytic activity of H-mordenite relative to H–Y-zeolite for the low-temperature conversion of *n*-butane and *n*-pentane. Few reports are available concerning the properties of mordenite despite its considerable commercial importance. Therefore, the objective of the present investigation is to provide a characterization of the acidic properties of the zeolite mordenite and its modified forms.

Our previous results on several mordenite samples indicated that the *n*-pentane isomerization activity did not follow the total acidity determined by nonaqueous titration. We, therefore, investigated the type and strength of acid sites on H–M and dealuminated H–M samples.

EXPERIMENTAL

Materials. The mordenite samples employed in this study were prepared by repeatedly exchanging Na-mordenite with

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2 N ammonium nitrate. The samples were then washed with distilled water and calcined at 550°C in dry air. Partial dealumination of samples 2 and 3 was accomplished by dilute mineral acid treatment prior to the wash and calcination. The residual sodium content was ≤ 0.02 wt% in all samples. The samples investigated and their characteristics are presented in Table 1. Since the Benesi technique has been used extensively in the literature for zeolitic and alumina materials, the acidity data of Table 1 are presented as a reference point for the reader. These data, however, are not used for the conclusions of this investigation.

Apparatus and procedure. Gravimetric measurements of ammonia adsorption were made at various temperatures and isosteric heats of adsorption were determined as a function of ammonia uptake. One assumes that the heat of adsorption between the basic ammonia and the acidic surface is proportional to the acid strength of the surface sites.

These measurements were performed with an RG-2000 Cahn electrobalance. The sample (approximately 0.15 g) was suspended in a quartz bucket 50 cm below the balance by nichrome wire. The sample temperature was monitored with an iron–constantine thermocouple located 5 mm from the center of the sample bucket.

Prior to the adsorption measurements, the mordenite sample was treated at 400°C and 10^{-6} Torr. Ammonia adsorption was determined in the pressure range of 5×10^{-3} to 10 Torr and the temperature range of 120 to 350°C.

The reversibility of ammonia adsorbed was demonstrated over the range of conditions employed by approaching a given uptake at a specified temperature and pressure from both the high- and low-pressure sides. Reproducibility in amounts adsorbed was better than 7% for all conditions reported. Buoyancy and thermal correction factors were obtained using glass beads equivalent to the sample in weight.

TABLE 1

Mordenite Samples Examined

Sample	SiO_2/Al_2O_3	Acidity (mequiv/g)[a] >48% H_2SO_4
1	10.0	0.301
2	13.0	0.522
3	16.3	0.800

[a] Determined by Benesi technique (*13*).

The infrared spectra of the samples, before and after ammonia adsorption, were recorded with a Perkin Elmer 283 spectrophotometer in the dual-beam mode. For these measurements, the sample was pressed into a wafer with a density of 6.635 mg/cm². The cell used was an inverse T-shaped cell made of quartz. The catalyst wafer, held in a quartz holder, could be raised to the upper part of the cell where it was treated.

Following a 325°C evacuation to 10^{-6} Torr and room temperature adsorption of ammonia, the sample was evacuated at various temperatures to determine the strength and relative amount of Bronsted and Lewis sites present. The spectra, obtained at room temperature, were recorded in the range of 4000 to 1000 cm^{-1}.

The reproducibility of the infrared peak area for Bronsted sites was greater than 4%, and that for Lewis sites was greater than 1%. The differences observed between samples 2 and 3 were considerably greater than the above reproducibilities.

RESULTS

The ammonia adsorption isotherms for samples 1 and 2 are presented in Figs. 1 and 2, respectively. Both sets of isotherms are typical of materials with a wide range of acid site strengths. An important aspect, evident from these figures, is that the partial dealumination of mordenite results in an increased ammonia uptake. Thus,

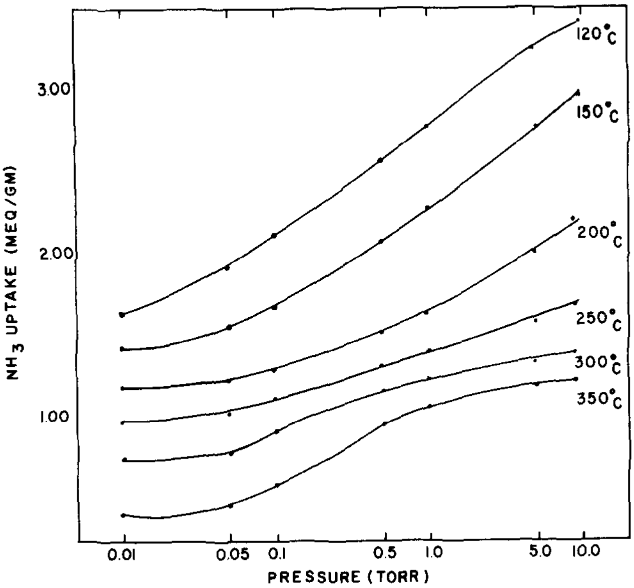


Fig. 1. Ammonia adsorption isotherms for H-mordenite sample 1.

even though the content of alumina tetrahedra in sample 2 is less than in sample 1, the number of acid sites appears to be greater in sample 2.

Considering the adsorption data at 1 Torr, sample 2 and Y-zeolites (*4*) have similar ammonia uptakes at 220°C. However, sample 2 has a greater uptake at higher temperatures and a lower uptake at lower temperatures. A similar comparison can be made between sample 1 and Y-zeolite. These points are illustrated by the comparative isotherms in Fig. 3. This suggests that mordenite has a larger fraction of strongly acidic sites than do Y-zeolites.

Isosteric heats of adsorption were obtained by applying the Clausius/Clapeyron

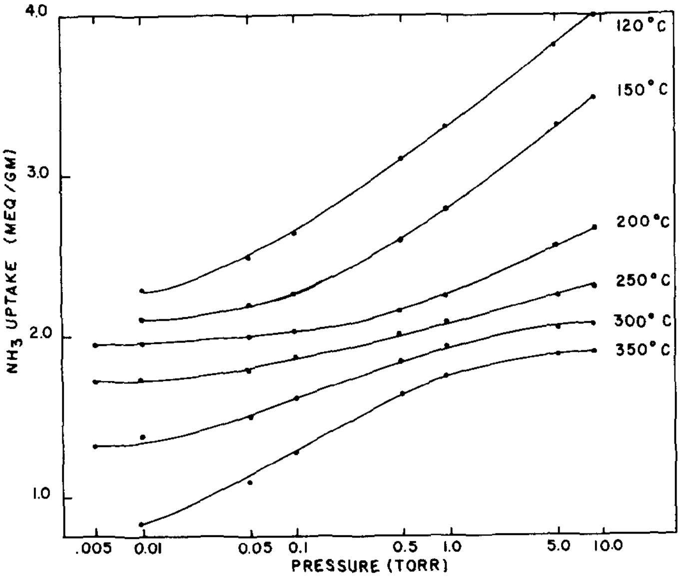


Fig. 2. Ammonia adsorption isotherms for H-mordenite sample 2.

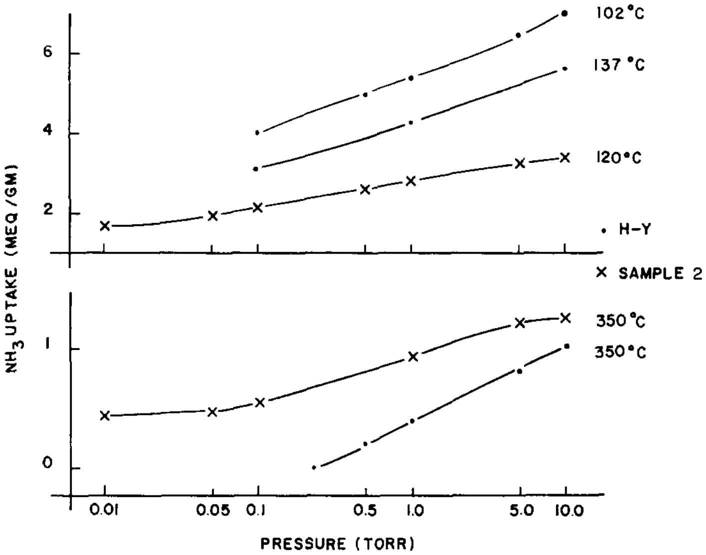


FIG. 3. Comparison of ammonia adsorption isotherms for H-mordenite sample 2 and the H-Y-zeolite sample.

equation to the equilibrium values of temperature and pressure required to maintain a given adsorbate coverage. These results are plotted in Fig. 4 for samples 1 and 2, H-Y-zeolite (*4*), η-Al_2O_3, and an amorphous SiO_2-Al_2O_3 (*5*) with a composition similar to that of the zeolites.

The zeolite samples are observed to have a wide range of acid site strengths and a large number of sites with strengths of approximately 20 kcal/mole. Moreover, sample 2, with a SiO_2/Al_2O_3 ratio of 13, has a large number of acid sites with strengths $\geq$42 kcal/mole. Thus, the effect

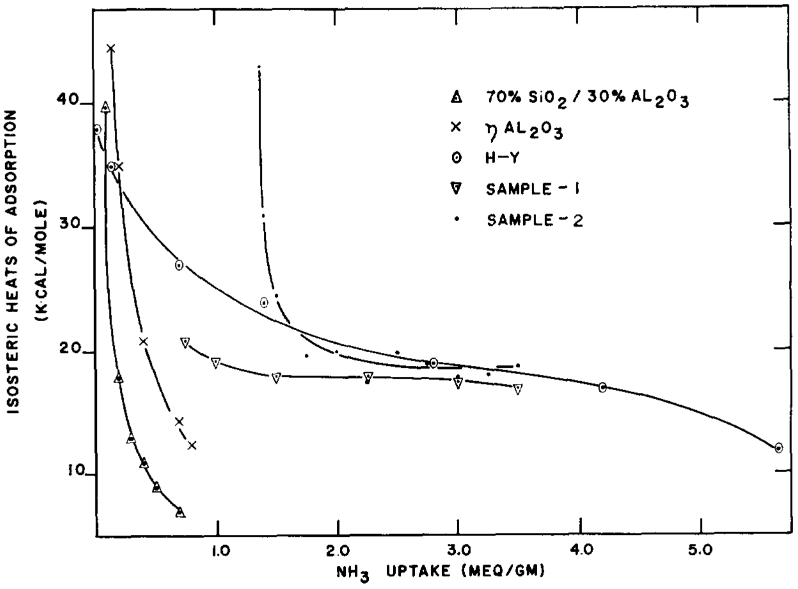


FIG. 4. Isosteric heat of ammonia adsorption vs ammonia uptake.

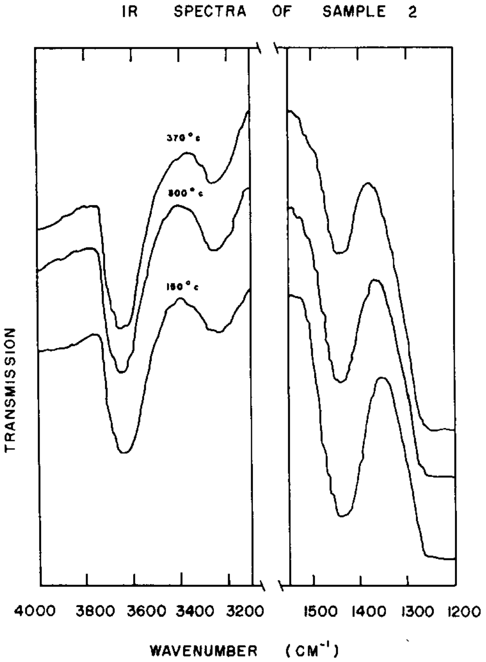


FIG. 5. Infrared spectra of sample 2 after NH_3 adsorption.

of dealumination on mordenite is apparently unlike that found for Y-zeolites. Dealumination of mordenite results in a considerable transformation in the surface acid site characteristics. A large number of high strength acid sites are now present on the dealuminated mordenite. Dealumination of Y-zeolites, on the other hand, has been reported to result in the removal initially of 30–35% of Al atoms associated with weak acid sites and then the removal of Al atoms associated with strong acid sites (*6–8*). The observed isooctane cracking activity did not vary for H–Y-zeolite samples in which up to 33% of the Al atoms had been extracted. With further dealumination, a decrease in activity was observed (*6*). In agreement with the present acidity measurements, the *n*-hexane cracking activity of mordenite was observed to increase with increased dealumination (*9*).

Samples 2 and 3 were examined by infrared spectroscopy to obtain information about changes in the Bronsted and Lewis acidity upon further dealumination. Following a 325°C evacuation and room temperature adsorption of ammonia, the sample was evacuated at various temperatures to determine the strength and relative amount of Bronsted and Lewis acid sites present. The spectra of sample 2 are presented in Fig. 5. The absorption band at 1435 cm^{-1} is characteristic of ammonia adsorbed on Bronsted sites, while the bands at 3340 and 3280 cm^{-1} are characteristic of ammonia adsorbed on Lewis sites. The relative amount of ammonia adsorbed on the respective site types was determined from the peak areas and is plotted in Fig. 6 as a function of temperature.

Since the ir measurements were made after evacuation at various temperatures, the results reveal information about the strength of the acid sites, Upon increasing the temperature, weakly held ammonia will desorb and only the ammonia on the stronger sites will remain.

A comparison of these two samples at 150°C reveals that sample 3 has fewer Bronsted sites and somewhat more Lewis acid sites than sample 2. Furthermore,

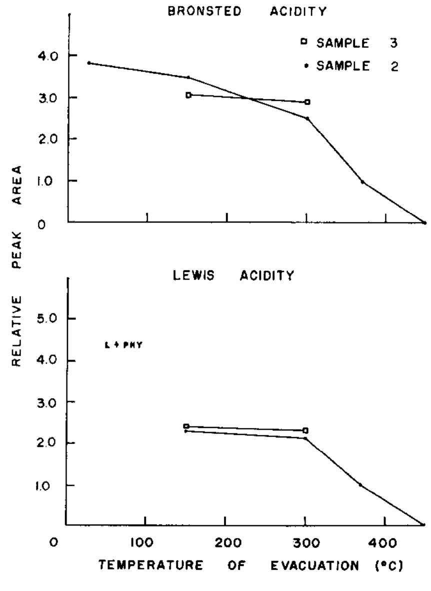


FIG. 6. Acid sites measured by ir peak area after NH_3 adsorption vs temperature.

sample 3 has not lost significant ammonium ions (adsorbed on Bronsted sites) upon increasing the temperature from 150 to 300°C. Over the same range, sample 2 loses considerable ammonium ions. Indeed, sample 3 has more ammonium ions at the 300°C temperature than does sample 2. A similar, although less pronounced, occurrence is observed for the ammonia adsorbed on Lewis sites upon heating to 300°C, i.e., sample 2 loses more Lewis adsorbed ammonia than does sample 3.

It is concluded from these results that sample 3 (SiO_2/Al_2O_3 = 16.3) has more strong Bronsted and strong Lewis acid sites than does sample 2 (SiO_2/Al_2O_3 = 13.0). Thus, further dealumination up to a SiO_2/Al_2O_3 ratio of 16.3 results in a further increase in strong acid sites.

A further comparison of samples 2 and 3 is presented in Fig. 7. These spectra, in the hydroxyl absorption region, were obtained after the samples were outgassed at 326°C and before dosing with ammonia. The important difference between these two spectra is that the hydroxyl absorption in the region of 3640–3700 cm^{-1} is greater for sample 3 than for sample 2.

In previous studies of hydrogen mordenite (*10*), it has been observed that the 3610 cm^{-1} hydroxyl band interacts with basic molecules such as pyridine, whereas the 3650 cm^{-1} hydroxyl band does not. During our measurements with ammonia adsorption, the same phenomenon was observed. Accordingly, the increased hydroxyl absorption of sample 3 corresponds to nonacidic hydroxyls. Further, it is expected that a hydroxyl attached to a Si ion (Si–OH) would be more strongly bonded (absorb at higher wavenumber) than a hydroxyl shared between a Si ion and an Al ion. Thus, the nonacidic nature and higher wave number of the increased band observed for sample 3 is in accordance with an increase of Si–OH (hydroxyl nest) in sample 3. It is therefore concluded that the increased absorption of sample 3 (SiO_2/Al_2O_3 = 16.3) relative to sample 2 (SiO_2/Al_2O_3 = 13.0) is strong evidence for the formation of hydroxyl nests upon dealumination of mordenite. While their data were not presented, Kranich *et al.* (*11*) stated that they also observed evidence for the formation of hydroxyl nests upon dealumination of mordenite samples.

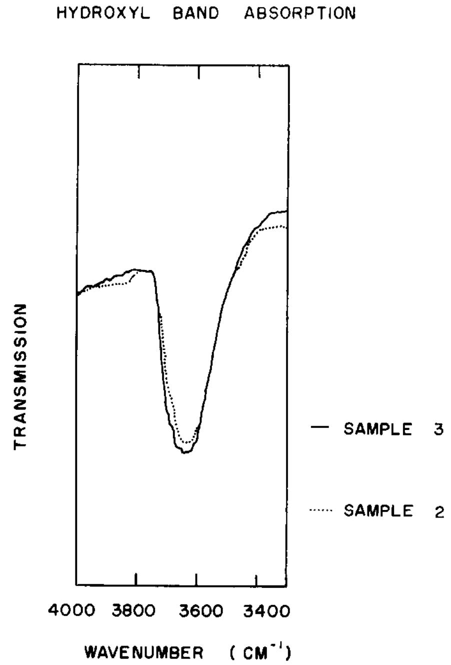


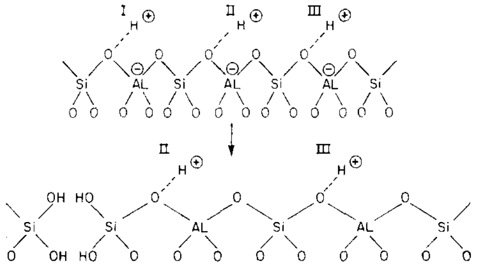
Fig. 7. Hydroxyl band absorption spectra.

DISCUSSION

Since H–Y-zeolite has a larger number of acid sites, it has been suggested that the greater activity of H-mordenite is related to the relatively stronger Bronsted acidity as the Si/Al ratio increases. The adsorption isotherms of the present investigation indicate that both mordenite samples (1 and 2) have a larger fraction of strongly acidic sites than do H–Y-zeolites.

The present results also show that partial dealumination of mordenite, up to SiO_2/Al_2O_3 ratios of 16.3, results in an increased number of strong acid sites (both Lewis and Bronsted). Thus, the effect of dealumination on mordenite is apparently unlike that found for Y-zeolites. As previously discussed, Beaumont and Barthomeuf (*6–8*) have, on the basis of activity and acidity measurements, proposed that the weaker acid sites in Y-zeolite are the first to be removed during dealumination, followed by removal of the stronger acid sites. Dealumination of mordenite, on the other hand, increases the number of strong acid sites (present results) and increases the *n*-hexane cracking activity (*9*).

We suggest the possibility that the hydroxyl nest left behind by dealumination acts through the lattice to polarize the hydroxyl electron cloud away from the proton (site II in the following diagram), making it more acidic. This would account for the increased number of strongly acidic Bronsted sites present upon dealumination of mordenite.



In the present investigation, the observed increase of Si–OH and increase in the number of strong Bronsted acid sites for sample 3 relative to sample 2 is strong supporting evidence for this suggestion.

One possible reason for the previous lack of observance of an increase in the 3650 cm^{-1} band upon dealumination by some authors may be caused by the temperature of evacuation prior to ir examination. According to the results of Karge (*10*), the 3650 cm^{-1} hydroxyl band of mordenite decreases considerably at temperatures greater than 325°C. Accordingly, the evacuation of 325°C in the present investigation should not have altered the original 3650 cm^{-1} hydroxyl absorption. In contrast, Eberly *et al.* (*12*) used an evacuation temperature of 427°C and did not observe the increase in this absorption band.

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