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# The Nature of the Acidic Sites on Mordenite

## Characterization of Adsorbed Pyridine and Water by Infrared Study

MICHEL LEFRANCOIS AND GABRIEL MALBOIS

*Compagnie de Raffinage Shell Berre, Centre de Recherche,*
*76-Grand-Couronne, France*

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The infrared spectrum of pyridine adsorbed on mordenite $H^+$ and exchanged with different cations has been studied at high temperature. Three types of acid sites have been observed. The $H^+$—or incompletely cationized—samples have both Lewis and Brönsted acidities, the Lewis acidity being present even at moderate temperature. A rise in temperature promotes the Lewis acidity while the addition of water completely changes the Lewis acidity into Brönsted acidity. The completely cationized mordenite samples have, besides the Lewis acidity, a third type of acidity which fixes pyridine by a strong hydrogen bond. On these samples, the Brönsted acidity is not present. The strongly cationized mordenite $H^+$ samples have the three types of acid sites. Heavy water has been used for studying the conversion of Lewis sites into Brönsted sites.

## INTRODUCTION

The acidity of catalysts has been the subject of a great number of studies in an effort to relate this acidity to the catalytic activity. The determination of the nature of the acid sites of silica–alumina supported catalysts can be made by infrared spectroscopy of adsorbed pyridine (*1*), which allows a distinction between the protonic Brönsted acid sites, characterized by a band at 1545 $cm^{-1}$ due to the pyridinium ion, and the aprotonic Lewis sites due to the coordinately bonded pyridine and characterized by a band at 1455 $cm^{-1}$. A third band at 1490 $cm^{-1}$ is common to the two acidity types. Basila *et al.* (*2*, *3*) have determined the relative absorption coefficients for these bands. In the present work, the nature of acid centers of samples of "mordenite" zeolite, exchanged with different cations, has been studied.

## EXPERIMENTAL METHODS

### *Materials*

The samples have been prepared from Norton $H^+$ mordenite by ion exchange. The composition of the starting sample is given in Table 1. The specific surface area of this sample was 374 $m^2/g$.

The anions used for ion exchange and the degree of ion exchange of the different samples are listed in Table 2. After ex-

TABLE 1
ANALYSIS OF NORTON $H^+$ MORDENITE SAMPLE

| | |
|---|---|
| $SiO_2$ (% wt) | 82.35 |
| $Al_2O_3$ (% wt) | 11.50 |
| $Na_2O$ (% wt) | 0.36 |
| CaO (% wt) | 0.041 |
| $Fe_2O_3$ (% wt) | 0.05 |
| Si/Al | 6.35 |
| Specific surface area ($m^2/g$) | 374 |

TABLE 2
PREPARATION OF ION-EXCHANGE MORDENITE SAMPLES[a]

| Sample no. | Cation | Anion used for exchange | Cation-exchange (%) |
|---|---|---|---|
| 1 | $H^+$ | | |
| 2 | $Li^+$ | $NO_3^-$ | 15 |
| 3 | | $OH^-$ | 100 |
| 4 | $Na^+$ | $OH^-$ | 26 |
| 5 | | $OH^-$ | 76 |
| 6 | | $OH^-$ | 100 |
| 7 | $K^+$ | $OH^-$ | 32 |
| 8 | | $OH^-$ | 57 |
| 9 | | $Cl^-$ | 60 |
| 10 | | $OH^-$ | 100 |
| 11 | $Cs^+$ | $Cl^-$ | 70 |
| 12 | | $CO_3^{2-}$ | 100 |
| 13 | $Mg^{2+}$ | $NO_3^-$ | 20 |
| 14 | $Ca^{2+}$ | $Cl^-$ | 50 |
| 15 | | $CH_3COO^-$ | 100 |
| 16 | $Ba^{2+}$ | $Cl^-$ | 27 |
| 17 | $Zn^{2+}$ | $CH_3COO^-$ | 77 |

[a] The percentage of exchange was determined by emission spectrometry.

change, the samples were filtered, washed with distilled water, and dried at 120°C for 16 hr.

### *Cell*

The cell is shown in Fig. 1. It is made of quartz and the windows consist of sodium chloride. The two parts of the cell are connected to each other and the whole cell is connected to the vacuum system and reagent inlets by means of spherical ground joints lubricated with Apiezon L grease. The sample can be heated up to 500°C under vacuum which can reach $10^{-6}$ Torr. A vacuum of $2.10^{-5}$ Torr can be maintained for several hours at 400°C in the cell isolated from the vacuum system.

### *Sample Preparation*

The exchanged mordenite was ground in an agate mortar to a powder with an average grain diameter of 3 $\mu$. Fifteen mg of the powder were compacted under a pressure of 2 ton/cm$^2$ to obtain a disc of 20 mm diameter and 5 mg/cm$^2$ thickness.

Pyridine (Eastman o.c;) and water were purified by the freeze–pump–thaw technique.

### *Spectroscopic Technique*

The infrared apparatus used in these experiments was a double-monochromator Beckman IR4 spectrometer with NaCl prisms. The spectral slit was 4 cm$^{-1}$ at

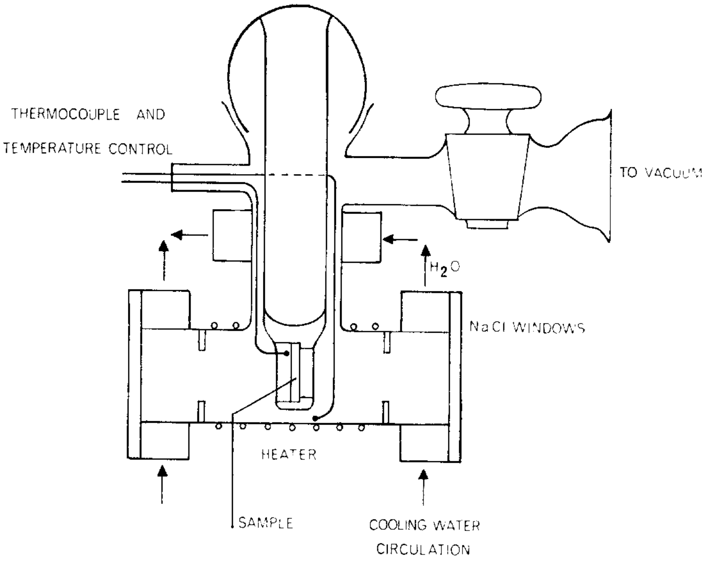

FIG. 1. Design of infrared cell.

1450 cm$^{-1}$ and the scan speed 16 cm$^{-1}$/min. The discs transmitted about 30% of the incident infrared energy at 1450 cm$^{-1}$ after dehydration. An optical attenuator was used in the reference beam.

### *Determination of Acidity at 300°C*

The sample was pretreated by heating under vacuum at 400°C for 2 hr, then cooled down to 300°C. The spectrum was recorded before adsorption, then pyridine was introduced under its vapor pressure at 20°C and allowed to remain in contact with the sample for 30 min; after evacuation for 2 hr, the adsorption spectrum was recorded. Water (either light or heavy according to the case) was introduced under its vapor pressure at 20°C for 30 min. The hydration spectrum was recorded and, after evacuation at $10^{-6}$ Torr for 30 min, a last spectrum was recorded.

### *Determination of Acidity as a Function of Temperature*

The sample was heated for 2 hr at 200°C under vacuum ($10^{-6}$ Torr) and the reference spectrum was recorded. Pyridine was introduced under its vapour pressure at 20°C for 15 min; after evacuation for 30 min, the absorption spectrum was recorded, then the sample was heated to a higher temperature. Pyridine was introduced again (15 min of contact with the sample) and after evacuation for 30 min, the spectrum was recorded. These operations were repeated at each predetermined temperature level (200, 300, 400, and 450°C).

## RESULTS

### *Determination of the Acidity at 300° of H$^+$ Mordenite Samples*

The spectra of pyridine adsorbed on the H$^+$ mordenite sample at 300°C (sample No. 1 in Table 2) are represented in Fig. 2, together with the reference spectrum recorded before pyridine adsorption and after evacuation for 2 hr at 400°C; the latter shows a large absorption band at about 1630 cm$^{-1}$ due to residual water. The spectrum of the sample with pyridine adsorbed at 300°C shows bands at 1455, 1490, 1545,

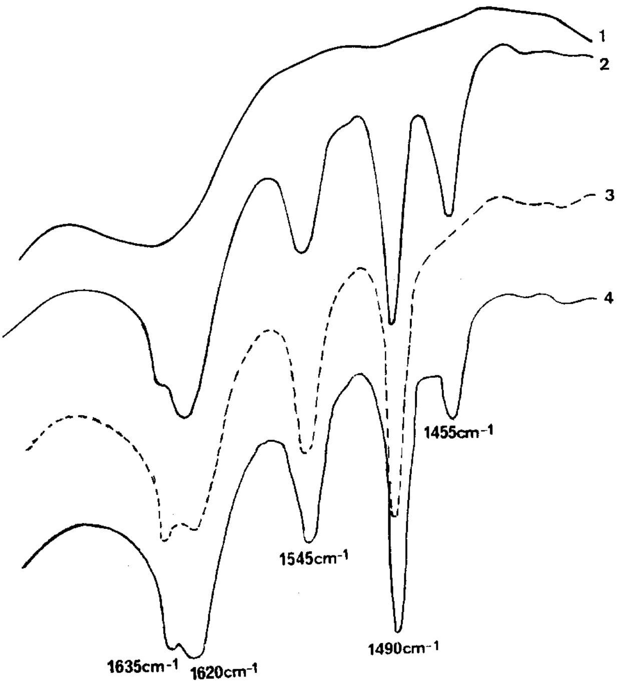

FIG. 2. Spectra of pyridine on 100% H$^+$ mordenite: (1) before pyridine adsorption (reference spectrum); (2) after pyridine adsorption; (3) after pyridine adsorption + $H_2O$; and (4) after pyridine adsorption + $H_2O$ + evacuation.

1620, and 1635 cm$^{-1}$. The band at 1455 cm$^{-1}$ completely disappears after water addition while the intensity of the bands at 1545 and 1635 cm$^{-1}$ increases. After water evacuation under high vacuum, part of the initial intensity of the 1455 cm$^{-1}$ band is restored while the intensity of the 1545 and 1635 cm$^{-1}$ bands decreases. After additions of heavy water under the same conditions (Fig. 3), the spectrum no longer has any band at 1455, 1545, and 1620 cm$^{-1}$ while the band at 1490 cm$^{-1}$ increases considerably. After evacuation, the 1455 cm$^{-1}$ band partly reappears. Last of all, after admission of ordinary water and evacuation, the spectrum shows a new band at 1462 cm$^{-1}$ while the 1455 cm$^{-1}$ band disappears and the 1620 and 1545 cm$^{-1}$ bands appear again.

### *Determination of the Acidity at 300°C of 100% Cationized Mordenite Samples*

The adsorption of pyridine on mordenite samples cationized with $Li^+$, $Na^+$, $K^+$, $Cs^+$, and $Ca^{2+}$ (samples Nos. 3, 6, 10, 12, and 15 in Table 2) has been studied under the same conditions. The spectra of $Li^+$ and $Na^+$ exchanged samples are represented in Fig. 4. Even after dehydration during 2 hr at 400°C under high vacuum, molecular water remains in the sample as shown by the broad band near 1635 cm$^{-1}$ in Fig. 4. The adsorbed pyridine spectrum shows bands at 1445, 1490, 1590, or 1600 cm$^{-1}$. The 1445 cm$^{-1}$ band has a shoulder at 1455 cm$^{-1}$. After addition of water, this shoulder disappears while a small band appears at 1545 cm$^{-1}$. After evacuation, the 1455 cm$^{-1}$ shoulder reappears.

The introduction of heavy water (Fig. 5) results in a new band at 1420 cm$^{-1}$.

While all the 100% cationized samples have absorption bands at the same wavelengths, the intensity of these bands decreases gradually and appreciably as the atomic number of the exchanged cation increases.

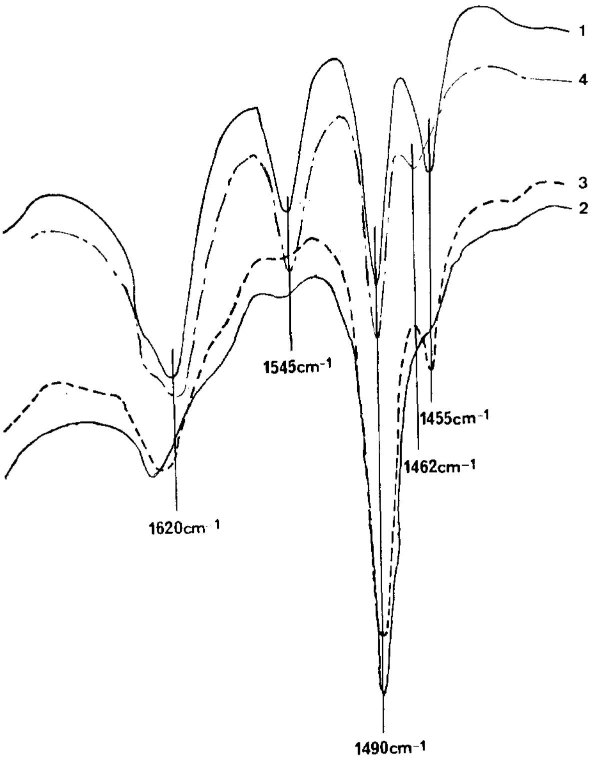

FIG. 3. Spectra of pyridine on 100% $H^+$ mordenite: (1) after pyridine adsorption; (2) after pyridine adsorption + $D_2O$; (3) after pyridine adsorption + $D_2O$ + evacuation; and (4) after pyridine adsorption + $H_2O$ + evacuation.

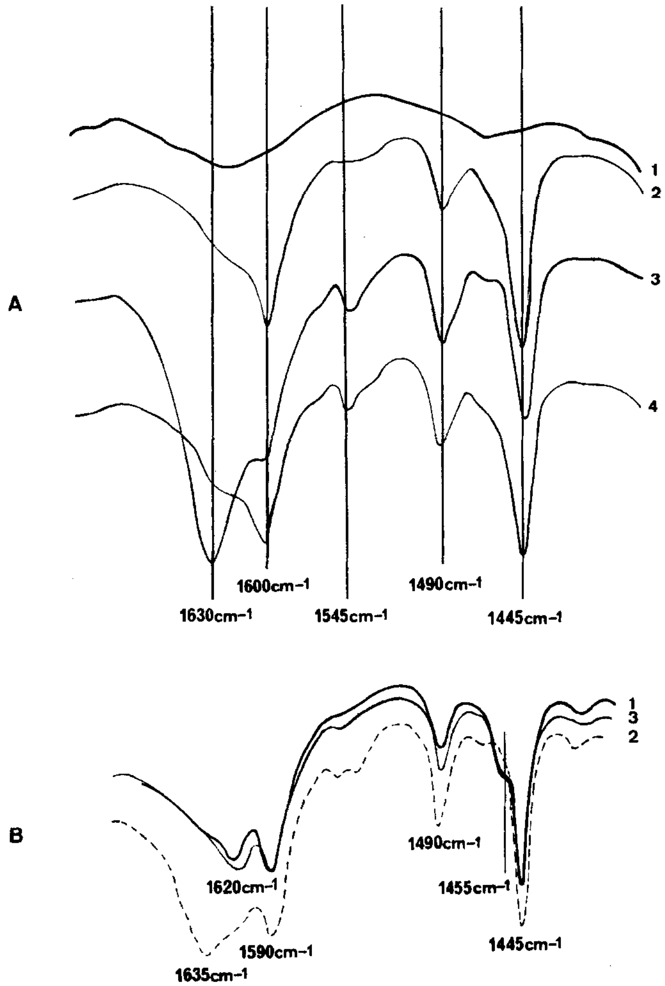

FIG. 4. Spectra of pyridine on 100% cationized mordenite: (A) $Li^+$ 100%: (1) before pyridine adsorption (reference spectrum); (2) after pyridine adsorption; (3) after pyridine adsorption + $H_2O$; and (4) after pyridine adsorption + $H_2O$ + evacuation. (B) $Na^+$ 100%: (1) after pyridine adsorption; (2) after pyridine adsorption + $H_2O$; and (3) after pyridine adsorption + $H_2O$ + evacuation.

### *Determination of the Acidity at 300°C of Incompletely Cationized $H^+$ Mordenite Samples*

The spectra of pyridine adsorbed on $H^+$ mordenite samples cationized to a moderate degree (sample Nos. 2, 4, 7, 8, 9, 11, 13, 14, 16, and 17 in Table 2) are qualitatively identical to the spectrum of the 100% $H^+$ mordenite sample. The spectrum is sensibly different when the ion-exchange degree is high. Figure 6 illustrates the evolution of the phenomenon with the exchange degree for the $Na^+/H^+$ samples. At 26% $Na^+$ exchange, the nature of sites is not modified; at 76%, the 1540 $cm^{-1}$ band has appreciably decreased while a new band appears at 1445 $cm^{-1}$. At 100% $Na^+$ exchange, the 1545 $cm^{-1}$ band has disappeared while intense bands at 1445 and 1590 $cm^{-1}$ and a shoulder at 1455 $cm^{-1}$ can be noted.

### *Variation of the Acidity of Mordenite Samples with Temperature*

Figure 7 shows the evolution of the spectrum of pyridine adsorbed on the 100% $Na^+$ exchanged sample. At 200°C, the 1445, 1490, and 1590 $cm^{-1}$ bands are strong. When the temperature increases, these three

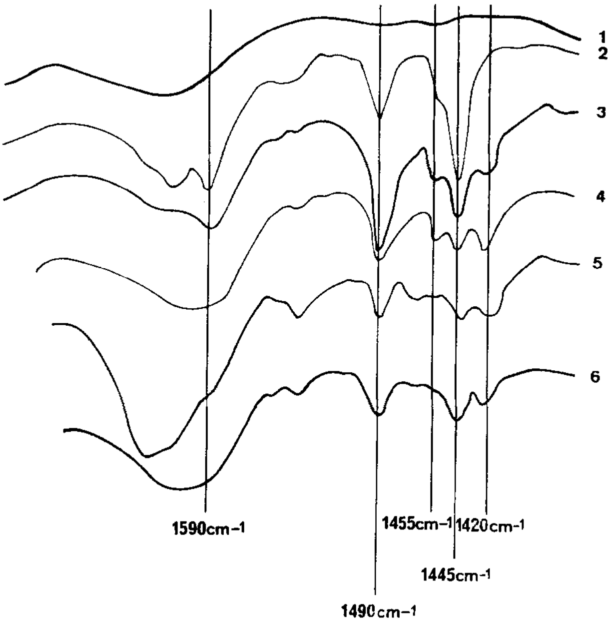

FIG. 5. Spectra of pyridine on 100% $Na^+$ mordenite: (1) before pyridine adsorption (reference spectrum); (2) after pyridine adsorption; (3) after pyridine adsorption + $D_2O$; (4) after pyridine adsorption + $D_2O$ + evacuation; (5) after pyridine adsorption + $D_2O$ + evacuation + $H_2O$; and (6) after pyridine adsorption + $D_2O$ + evacuation + $H_2O$ + evacuation.

bands are appreciably weakened while the 1620 $cm^{-1}$ band seems unaffected. The shoulder at 1455 $cm^{-1}$ grows with temperature.

The 100% $H^+$ or incompletely cationized samples behave exactly in the same way as shown in Fig. 8. A rise in pyridine adsorption temperature reduces the intensity of the 1490, 1545, and 1635 $cm^{-1}$ bands while it favors the 1455 and 1620 $cm^{-1}$ bands.

### *Determination of the Relative Molecular Extinction Coefficients*

Basila *et al.* (*2*) have determined the relative absorption coefficients at 1450 and 1545 $cm^{-1}$ by selectively eliminating the 1545 $cm^{-1}$ band, due to Brönsted sites, on potassium-exchanged silica–alumina. They have obtained $\epsilon_{1450}/\epsilon_{1545} = 8.8$. A new evaluation of the absorption coefficients (*3*) has led them to give a value of 6.0 ± 0.9 to the $\epsilon^B{}_{1490}/\epsilon^L{}_{1490}$ ratio of extinction coefficients for the 1490 $cm^{-1}$ band of Brönsted and Lewis sites. Hugues and White (*4*) have estimated this ratio to be equal to 5.8 in pyridine adsorbed on Y zeolite. Cannings (*5*) indicates a conversion factor of 2.61 for the interconversion of Lewis to Brönsted sites, on contacting with water, for the 1455 and 1546 $cm^{-1}$ bands.

The fact that the addition of water to $H^+$ mordenite samples results in a complete removal of the $A_{1455}$ band of the Lewis acidity at 1455 $cm^{-1}$, while the intensity of the $A_{1545}$ band of the Brönsted acidity at 1545 $cm^{-1}$ and $A_{1490}$ band at 1490 $cm^{-1}$ increases, makes it possible to determine the relative concentrations of Lewis sites $(L)$ and Brönsted sites $(B)$ and the relative absorption coefficients when assuming that each Lewis site is converted into a Brönsted site. The relative Brönsted site concentration is given by:

$$\frac{(B)}{(L)+(B)} = \frac{A_{1545}\text{ before hydration}}{A'_{1545}\text{ after hydration}} = 0.55.$$

It is possible to determine:

$$\frac{\epsilon^L{}_{1455}}{\epsilon^B{}_{1545}} = \frac{A^L{}_{1455}\cdot(B)}{A^B{}_{1545}\cdot(L)} = 1.54,$$

which is the conversion factor of a Lewis

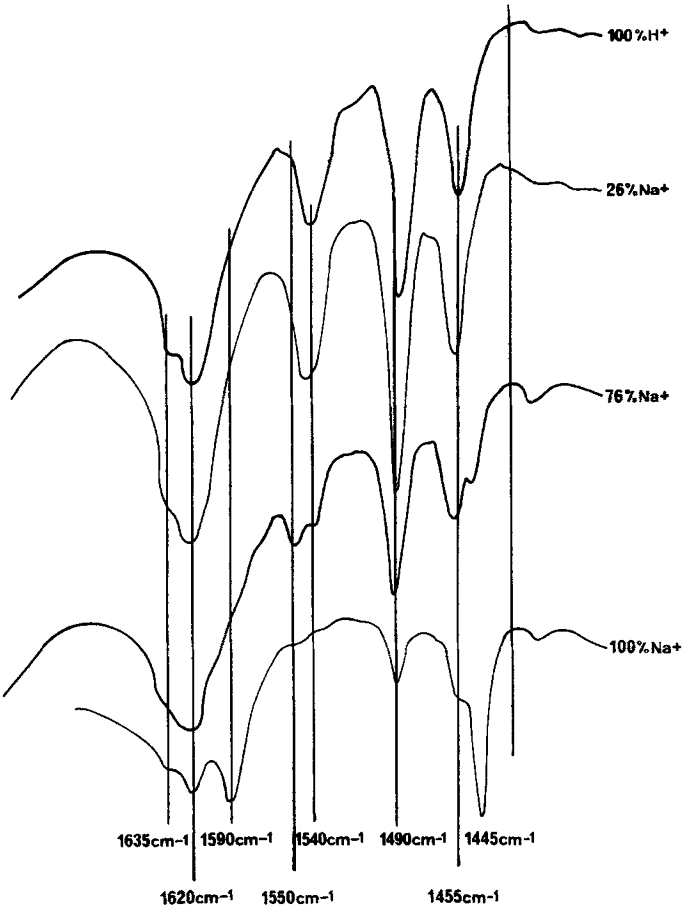

FIG. 6. Spectra of pyridine on $Na^+/H^+$ mordenite: influence of cation exchange rate.

site into a Brönsted site. The Lewis acidity completely disappears on hydration, therefore:

$$\frac{\epsilon^B{}_{1490}}{\epsilon^B{}_{1545}} = \frac{A'_{1490}}{A'_{1545}},$$

from which:

$$A^L{}_{1490} = A^{L+B}{}_{1490} - A^B{}_{1545} \cdot \frac{\epsilon^B{}_{1490}}{\epsilon^B{}_{1545}},$$

and finally:

$$\frac{\epsilon^B{}_{1490}}{\epsilon^L{}_{1490}} = \frac{A^B{}_{1490}}{A^L{}_{1490}} = 5.2.$$

This value approximates to that given by Basila and Kantner (*3*) and Hugues and White (*4*).

## DISCUSSION

Results of the adsorption of pyridine on mordenite at high temperature show that there are three types of adsorption sites (Table 3). The infrared absorption bands in the 1400–1700 $cm^{-1}$ region for pyridine adsorbed on silica–alumina and alumino-silicates have been observed by Parry (*1*) and used by different authors for studying the acidity of silico–aluminates (*2–14*), but the nature of acid sites on zeolites has not been completely elucidated. It has been shown that, even at high temperature, hydroxyl groups remain on zeolites (*6*, *7*, *15–18*) and the spectra of mordenite before pyridine adsorption show the characteristic band of water at about 1635 $cm^{-1}$ on all the samples even after evacuation at 400°C for several hours. Carter *et al.* (*15*) have shown that, on "near faujasite" type zeolites, residual OH forms sites identical either to alumina sites or to silica ones; they belong to Brönsted acid centers (*6*, *7*,

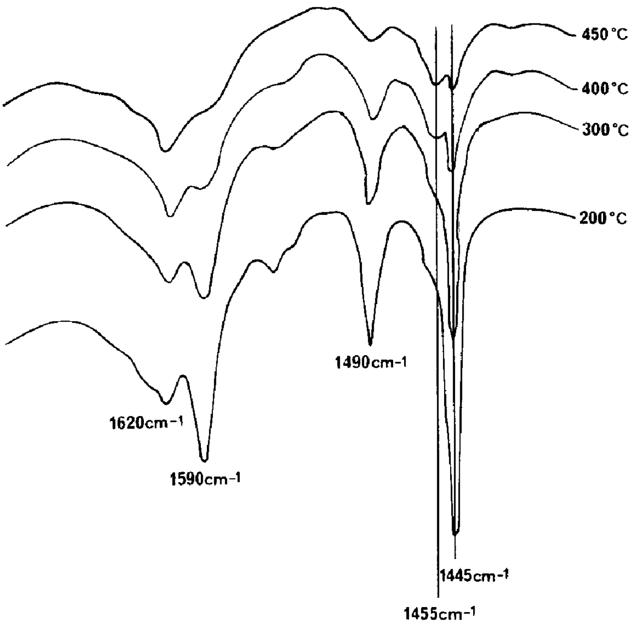

FIG. 7. Spectra of pyridine on 100% $Na^+$ mordenite: influence of pyridine adsorption temperature.

TABLE 3

DISTRIBUTION OF THE CHARACTERISTIC BANDS OF THE THREE TYPES OF ACIDITY

| Nature of site | Absorption bands ($cm^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| *L*Py | | 1620 | | | 1490 | 1455 | |
| *B*Py | 1635 | 1620 | | 1545 | 1490 | | |
| HPy | | | 1600–1590 | | 1490 | | 1445 |

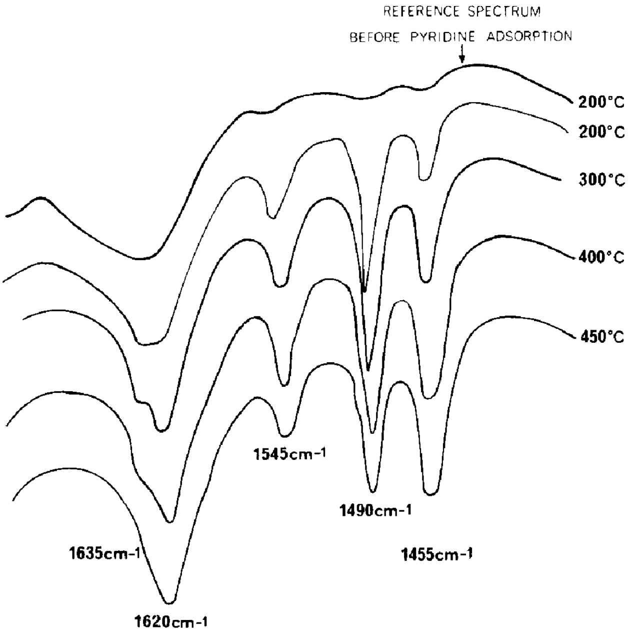

FIG. 8. Spectra of pyridine on 100% $H^+$ mordenite: influence of pyridine adsorption temperature.

*11, 13, 19*). These Brönsted sites (*B*Py) show bands at 1490, 1545, 1620, and 1635 $cm^{-1}$. The 1545 $cm^{-1}$ band is typical of this site, the corresponding species is the pyridinium ion ($PyH^+$). It is otherwise assumed that tri-coordinated aluminium atoms with an electron-free orbit constitute the Lewis acid centers. Those Lewis sites (*L*Py) show bands at 1455, 1490, and 1620 $cm^{-1}$, the pyridine being coordinated to an aluminium atom; the 1455 $cm^{-1}$ band is typical of this site. The third type of site corresponding to hydrogen-bonded pyridine (HPy) on the silico–alumina solid (*1*) shows bands at 1445, 1490, and 1590 $cm^{-1}$; it has already been observed on Na X (*13, 17*), H, Na Y (*14, 20*), and Na mordenite (*5*). The third type of acid site (HPy) is only present on strongly cationized samples. The bands corresponding to this type (1445 and 1590 $cm^{-1}$) are probably due to a strong interaction between the cation and the pyridine molecule, by attraction of the cation into the electrostatic field (*8*). Liengme and Hall (*14*) suggest a second type of Lewis site and attribute the 1445 $cm^{-1}$ band to the 19 *b* vibration of pyridine coordinately bonded to the residual $Na^+$ cations on dehydroxylated Y-type zeolite. This pyridine-cationized mordenite band is strong enough to be still present even after evacuation at 450°C.

It is noteworthy that, the infrared spectrum being taken at the operating temperature, the apparent intensity of the bands observed is much lower than if the spectrum had been recorded after cooling, even with simultaneous evacuation.

Even under these conditions, the 1620 and 1455 $cm^{-1}$ characteristic bands of pyridine, coordinately bonded to the aluminum atoms on the $H^+$ mordenite samples, appreciably increase with the temperature, thus showing the increase of the number of Lewis sites by dehydration of $H^+$ mordenite.

As a conclusion, the adsorption of pyridine at high temperature on mordenite samples shows that there are three types of sites: the Lewis sites, completely converted into Brönsted sites by addition of water and whose concentration increases with the temperature of the thermal treatment, the Brönsted sites, and a third type of site only present on strongly cationized samples.

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