

The Nature of Active Sites on Zeolites

IV. The Influence of Water on the Acidity of X and Y Type Zeolites

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The influence of small amounts of water on the acidity of several alkali, alkaline earth, hydrogen, and mixed cation zeolites has been studied by observing changes in the infrared spectrum of chemisorbed pyridine. Water has no marked effect on the acidity of alkali cation X and Y zeolites. With calcium and magnesium, Y zeolites, new hydroxyl groups are formed and there is a marked increase in the Brönsted acidity. Hydroxyl groups associated directly with the cations are identified: these groups are nonacidic. Water can displace pyridine from these cations and form new acidic lattice hydroxyl groups. Calcium and magnesium X zeolites behave differently. Brönsted acid sites were formed on addition of water but were eliminated by evacuation. Water had only a small effect on the pyridine-cation interaction. Water reacts reversibly with hydrogen Y zeolite to convert Lewis acid sites to Brönsted acid sites and vice versa. The Brönsted acid sites formed on rehydration are different from those present on initial calcination. Sodium hydrogen Y and magnesium hydrogen Y zeolites behave as a mixture of the cation and hydrogen Y zeolites. Evidence for the interaction of pyridine with cations giving rise to a band near 1450 cm^{-1} is presented. The changes in acidity are discussed in relation to catalytic activity.

INTRODUCTION

Previously, the effects of cation and calcination temperature on the acidity of Y-type zeolites have been reported (1-4). It was shown that alkali cation zeolites were nonacidic and alkaline earth cation zeolites were Brönsted acids if calcined at a temperature insufficient to cause dehydroxylation. At higher temperatures the alkaline earth forms were both Brönsted and Lewis acids when calcined. For the hydrogen form of the zeolite, it was shown that calcination at increasingly higher temperatures converted Brönsted acid centers into Lewis acid centers. These observations were made on samples which had been calcined in high vacuum and thus were considered to contain negligible amounts of adsorbed water.

It has been shown (5) that the Lewis

acid sites on alumina are not readily converted into Brönsted acid sites by addition of water, whereas those of silica-alumina are converted, the process being reversed by subsequent removal of adsorbed water.

Since most catalytic processes are conducted in non-water-free conditions, it appeared desirable to elucidate the effects of water on the acidity of zeolites. The effects of water are of considerable interest since it has been shown that addition of small amounts of water can enhance the catalytic activity (6-10). Furthermore, such an investigation could possibly yield some insight into the nature of zeolite acidity and activity.

This paper reports the study of the influence of water on the acidity of several mono- and divalent X and Y type zeolites.

Since this work was started, limited reports of the effects of water on zeolite acidity have been reported. Readdition of water to hydrogen Y zeolite calcined at high temperature has been shown to reconvert Lewis acid sites to Brönsted acid sites (2, 3). Also, Eberly (1) has shown similar effects for calcium and magnesium Y zeolites which had been calcined at 427°C.

EXPERIMENTAL

Materials and apparatus. The cation-exchanged Y zeolites were the same samples as used previously (2, 4). Samples of ion-exchanged X zeolite were prepared by exchange of sodium X zeolite ($\text{SiO}_2:\text{AlO}_2$ ratio 2.6:1) with excess 10% aqueous solutions of the desired cation nitrate at 80°C. The exchanged material was washed with distilled water to free it from residual salt. The degree of ion exchange was determined by analysis for sodium by flame spectrometry. Analyses are given in Table 1. Sodium hydrogen Y zeolite was

TABLE 1
ANALYSIS OF ZEOLITES

Cation	Na (%)	Surface area (m^2g^{-1})	Percent exchanged
LiY	1.9	826	81.7
NaY (I)	10.3	901	—
NaY (II)	9.5	885	9.2
KY	0.02	899	99.8
MgY	2.3	801	77.5
CaY	0.7	810	93.6
HY	1.1	860	89.4
NaX	14.4	865	—
MgX	3.4	873	76.6
CaX	0.5	855	97
NaHY	3.3	870	68
MgHY	1.1 (3.2% Mg)	770	58 (Mg)

prepared by partial exchange of the original sodium Y zeolite with ammonium nitrate solution. A second sample of sodium Y zeolite (NaY2) was also studied. This sample had an approximately 10% cation deficiency. Magnesium-hydrogen Y was prepared by partial exchange of ammonium Y with magnesium nitrate solution.

The pyridine, apparatus, and sample preparation techniques were the same as described previously (2). All spectra were

recorded on a Cary-White 90 Spectrophotometer using a spectral slit width of 3 cm^{-1} and a scan speed of $1\text{ cm}^{-1}\text{ sec}^{-1}$. The samples weighed 0.05 to 0.08 g.

Technique. The sample wafers were placed in the furnace end of the cell and evacuated. The temperature was raised to 110°C over 30 min and held until a vacuum of 10^{-4} mm was reached. The temperature was then slowly raised to 400°C and maintained for 6 hr. The sample was cooled to room temperature and its spectrum recorded. Excess pyridine was adsorbed on the sample and allowed to equilibrate for 2 hr. The sample was then evacuated at 250°C for 2 hr, cooled to room temperature, and the spectrum recorded. Water (0.5 mmoles) was then adsorbed on the zeolite overnight and the spectra were recorded after evacuation at room temperature, 150° and 250°C. In further experiments, additional pyridine was added to the zeolite containing adsorbed water and also pyridine and water were co-adsorbed. In a second set of experiments, the zeolites were evacuated at 600° to 630°C instead of 400°C.

RESULTS

Sodium zeolites. Figure 1 shows the spectra of NaY zeolite at various stages during the adsorption and desorption of pyridine and water in the frequency regions 4000 to 2800 and 1700 to 1400 cm^{-1} . After the zeolite had been calcined at 450°C, no structural hydroxyl groups could be detected. On initial addition of pyridine followed by evacuation at 250°C for 2 hr, absorption bands typical of coordinately bound pyridine are observed (5, 11). In particular, an absorption band at 1438 cm^{-1} due to pyridine adsorbed by interaction with cation is seen (4). No bands are observed due to pyridinium ions which would be indicative of Brönsted acidity. Small amounts of water (0.5 mmoles) were added, allowed to equilibrate, and removed by evacuation for 2 hr at a series of increasing temperatures. When evacuated at room temperature, absorption bands due to the adsorbed water were observed at 3694, 3550, 3340, and 1640 cm^{-1} . The bands due to adsorbed pyridine at 1592, 1489, and 1438

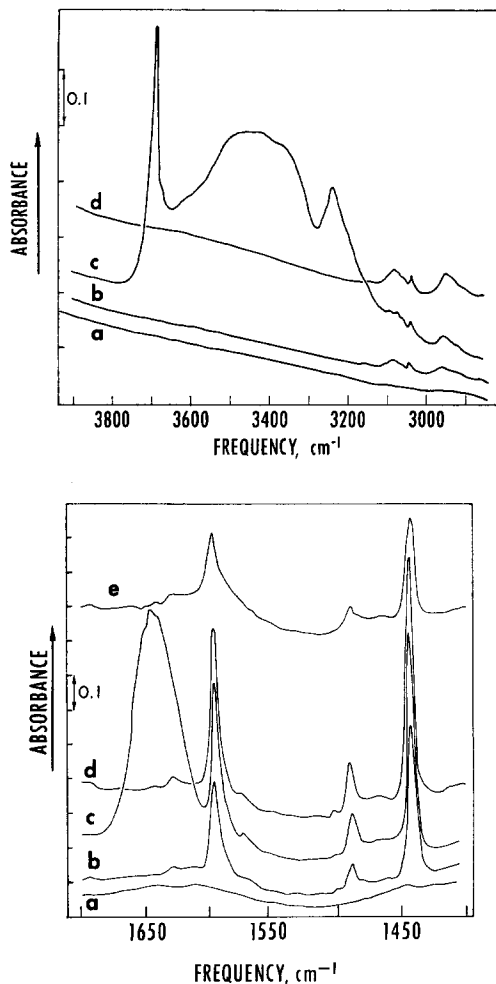


FIG. 1. Spectra of NaY Zeolite after calcination at 400°C: (a) NaY background; (b) pyridine adsorbed followed by evacuation at 250°C; (c) H₂O adsorbed and evacuated at room temperature; (d) evacuated at 150°C; (e) evacuated at 250°C.

cm⁻¹ increased 20% in intensity. No other absorption bands were observed, especially none due to pyridinium ions. Evacuation at 150°C completely removed all bands between 4000 and 3300 cm⁻¹ and the band at 1640 cm⁻¹ while the remainder of the spectrum was unaffected.

On further evacuation at 250°C there was a decrease in the intensity of the bands at 1592, 1489, and 1438 cm⁻¹ due to desorption of the chemisorbed pyridine. The changes in intensity of the bands are listed

in Table 2. Study of NaY zeolite calcined at 625°C yielded identical results. Studies of NaX zeolite after calcination at 450° and 600°C also yielded the same results.

The study of the second NaY sample which had a cation deficiency gave different results. When water was added to the sample after chemisorption of pyridine, a small band due to pyridinium ions was observed. It persisted after evacuation at 250°C but was removed by evacuation at

TABLE 2
ABSORBANCE OF PYRIDINE BANDS ON NaY
AFTER VARIOUS TREATMENTS

Treatment	NaY 400°C absorbance		NaY 625°C absorbance	
	1545 cm ⁻¹	1438 cm ⁻¹	1545 cm ⁻¹	1438 cm ⁻¹
Pyridine added and evac. at 250°C	0	0.24	0	0.45
H ₂ O added: Evac. room temp.	0	0.39	0	0.63
Evacuate 150°C	0	0.41	0	0.68
Evacuate 250°C	0	0.20	0	0.35

400°C. These observations probably represent formation of Brönsted acid sites by interaction of water with Lewis acid sites on the zeolite and are discussed below.

Adsorption of pyridine and water on other alkali cation forms of zeolites produced similar results except that the frequency of the band due to coordinately bound pyridine near 1440 cm⁻¹ varied with the size of the cation as reported previously (4).

Calcium zeolites. Calcium Y zeolite was studied after calcination at both 400° and 600°C. Figure 2 shows the spectra obtained for calcined CaY at 400°C and after adsorption of pyridine and water. As reported previously and in contrast to alkali cation zeolites, structural hydroxyl 400°C. These absorption bands were observed at 3739, 3688, 3642, 3585, and 3540 cm⁻¹. In agreement with other workers (1-3, 12, 13) the 3739-cm⁻¹ band is assigned to Si-OH groups terminating the lattice, the 3640- and 3540-cm⁻¹ bands to Si-OH groups similar to those observed in hydrogen Y zeolite and the 3688-cm⁻¹ band

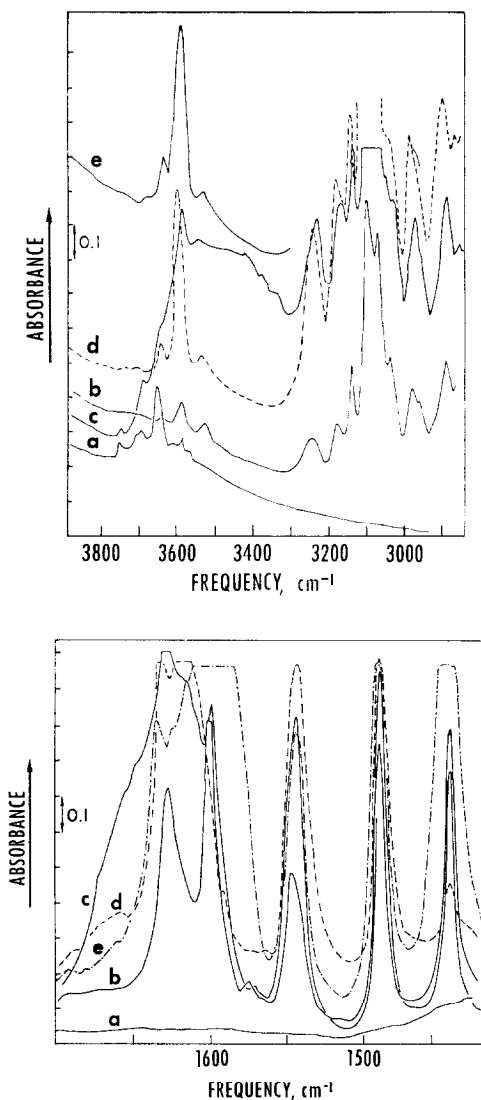


Fig. 2. Spectra of CaY zeolite after calcination at 400°C: (a) CaY background; (b) pyridine adsorbed and evacuated at 250°C; (c) water added and evacuated at room temperature; (d) evacuated at 250°C; (e) further pyridine adsorbed.

to Al-OH groups. The band at 3585 cm^{-1} is tentatively assigned to CaOH groups and will be discussed in more detail at a later point. On adsorption of pyridine and removal of excess by evacuation at 250°C, the pyridine interacts only with the 3640- cm^{-1} band. As reported previously, new bands are formed between 3300 and 2800 cm^{-1} typical of pyridinium ion and

coordinately bound pyridine. Below 1700 cm^{-1} , bands typical of pyridinium ion (1545 cm^{-1}) and coordinately bound pyridine (1443 cm^{-1}) are observed. Figure 2 and Table 3 also show the effects of removal of water as a function of temperature.

On initial addition of water the absorption band due to pyridinium ions at 1545 cm^{-1} increases by a factor of 4, that at 1450 cm^{-1} due to coordinately bound pyridine decreases by 15%, while the band at 1490 cm^{-1} doubles in intensity. On removal of part of the adsorbed water by evacuation at 150°C the pyridinium ion band doubles while the coordinately bound pyridine bands decrease by a factor of 3. Further evacuation slightly decreases the pyridinium ion band intensity and the coordinately bound pyridine decreases by two-thirds. In contrast to silica-alumina (5, 11) and hydrogen Y zeolite, removal of the water does not decrease the intensity of the pyridinium ion band and increase that of the coordinately bound pyridine. Intensity data are listed in Table 3.

In the hydroxyl stretching region, on addition of water a broad unresolved band between 3700 and 3200 cm^{-1} was formed. On removal of the excess water by evacuation at 150°C discrete absorption frequencies were observed at 3638, 3585, and 3530 cm^{-1} . In marked contrast to the initial spectrum of the hydroxyl groups the band at 3585 cm^{-1} is five times as intense as that at 3638 cm^{-1} , suggesting a particular type of hydroxyl group is formed on readdition of water. Little change in the hydroxyl group region of the spectrum was observed on evacuating at 250°C. In order to see whether the 3585- cm^{-1} hydroxyl group was acidic or not, more pyridine was added to the sample after the 250°C evacuation. Although sufficient pyridine was added to give rise to physical adsorption as well as chemisorption, no interaction with the 3585- cm^{-1} hydroxyl band was observed. No change was observed either when the excess pyridine was removed as a function of temperature. The intensity data are given in Table 3.

To further investigate the formation of

TABLE 3
ABSORPTION OF PYRIDINE BANDS ON CaX AND Y AFTER VARIOUS TREATMENTS

Treatment	CaY 430°C Absorbance		CaY 600°C Absorbance		CaY 400°F H ₂ O added first Absorbance		CaX 400°F Absorbance	
	1545 cm ⁻¹	1443 cm ⁻¹	1545 cm ⁻¹	1443 cm ⁻¹	1545 cm ⁻¹	1443 cm ⁻¹	1545 cm ⁻¹	1443 cm ⁻¹
Pyridine added:								
Evac. at 250°C	0.27	0.74	0.13	0.61	—	—	0.04	1.48
H ₂ O added:								
Evac. room temp.	0.83	0.60	0.60	0.19	0.42	1.43	0.44	1.18
Evac. at 150°C	1.25	0.20	0.70	0.17	0.59	0.73	0.48	0.87
Evac. at 250°C	1.18	0.08	0.45	0.15	0.80	0.31	0.20	1.16
Evac. at 350°C	—	—	0.36	0.12	—	—	0.00	0.70

the 3585-cm⁻¹ band, CaY zeolite was calcined under vacuum at 420°C and then a small amount of water added to it. The spectra are shown in Fig. 3. After calcination the CaY zeolite had absorption bands at 3740, 3684, 3642, 3584, 3560, and 3525 cm⁻¹. On addition of water a broad intense

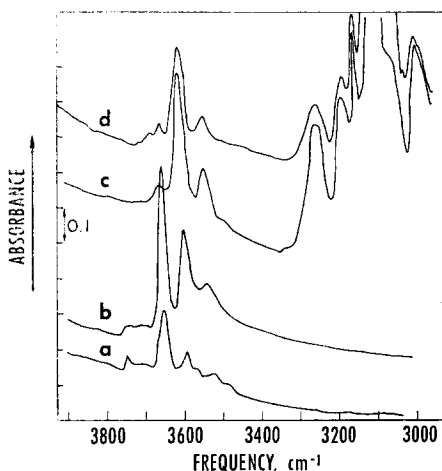


FIG. 3. Spectra of CaY zeolite calcined at 400°C: (a) CaY background; (b) water added and evacuated at 250°C; (c) pyridine added and evacuated at room temperature; (d) evacuated at 250°C.

absorption occurred but on removal of water at a series of increasing temperatures, discrete hydroxyl groups were observed. The spectra were similar after evacuation at 250° and 350°C. However they differed from the original in that the bands at 3642 and 3584 cm⁻¹ were three times as intense. On addition of pyridine the 3584-cm⁻¹ band

was unaffected while the 3642-cm⁻¹ band decreased to one-eighth of its original intensity. In the 1700 to 1400 cm⁻¹ region, the spectrum indicated that the relative population of Lewis and Brönsted acid sites was the same as that for the samples rehydrated after chemisorption of pyridine.

On calcination at 600°C, the results were basically similar. Naturally, fewer structural hydroxyl groups were detected and the concentration of Brönsted acid sites was less. A weak shoulder was observed on the 1444-cm⁻¹ band at about 1450 cm⁻¹, probably indicating Lewis acid sites formed by dehydroxylation. On addition of water, an increase in Brönsted acidity and decrease in pyridine adsorbed on calcium ions was seen, similar to that observed with the 400°C calcined sample. On evacuation of adsorbed water at 250°C, a distinct band at 1451 cm⁻¹ due to Lewis acid sites was observed.

Completely different results were observed for calcium X zeolite both after calcination at 400° and 600°C. After calcination at 400°C, hydroxyl groups were observed at 3690, 3610, and 3510 cm⁻¹. On addition of pyridine the hydroxyl groups became involved in hydrogen bonding and bands due to chemisorbed pyridine and pyridinium ions were observed between 3300 and 2800 cm⁻¹. A weak band was observed at 1545 cm⁻¹ due to pyridinium ions and a strong band at 1443 cm⁻¹ due to coordinately bound pyridine. On addition of water followed by evacuation at 150°C there resulted a tenfold increase in intensity

of the 1545-cm^{-1} band and about 10% decrease in intensity of the 1443-cm^{-1} band. This band was also somewhat narrower. Evacuation at somewhat higher temperatures gradually restored the intensity of the 1443-cm^{-1} band and simultaneously decreased the intensity of the Brönsted acid band. Evacuation at 350°C restored the band intensities to the same ratio they had initially been on the dehydrated zeolite. The cycle could be repeated by

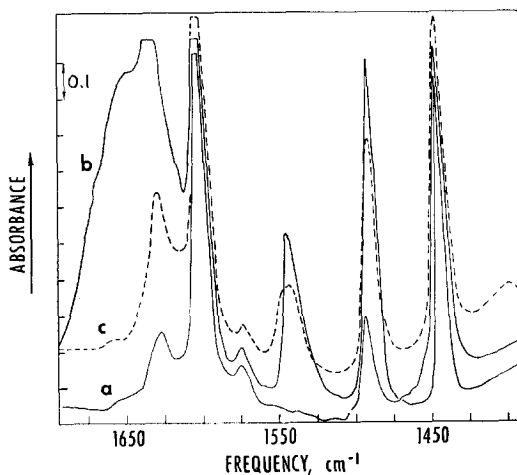


FIG. 4. Spectra of CaX zeolite: (a) pyridine adsorbed and evacuated at 250°C ; (b) water added and evacuated at room temperature; (c) evacuated at 250°C .

retreatment with water. No new hydroxyl bands were observed in the 3800 to 3300 cm^{-1} region. Similar results were obtained with CaX calcined at 610°C . Typical spectra for CaX are shown in Fig. 4.

Magnesium zeolite. Magnesium Y zeolite was studied after calcination at about 400°

and 600°C . In most parts, the results were similar to those obtained with CaY zeolite. The 1545- and 1450-cm^{-1} band peak heights are listed in Table 4. The zeolite on initial calcination at 430°C had absorption bands in the hydroxyl stretch region at 3740 , 3690 , 3639 , and 3610 cm^{-1} . On addition of pyridine, as in the case of CaY, these groups became involved in hydrogen bonding. Addition of water after removal of the excess pyridine resulted in the appearance of a band at 3595 cm^{-1} compared to 3588 cm^{-1} in the case of CaY. In all other respects the behavior was similar to CaY. Results on samples calcined at 600°C were analogous to those of CaY calcined at high temperature. The intensity data are summarized in Table 4.

With magnesium X zeolite, results obtained were similar to those found for calcium X.

Hydrogen Y zeolite. Marked differences were observed in the effects of water on the acidity of hydrogen zeolite depending on the temperature of calcination of the zeolite. It has previously been shown (2, 3, 14) that the acidity of hydrogen Y zeolite varies with the pretreatment temperature. Low temperature ($<500^\circ\text{C}$) calcination produces high concentration of Brönsted acidity while increasing the calcination temperature converts Brönsted acid sites into Lewis acid sites.

Figure 5 shows the spectra of hydrogen Y zeolite after calcination at 390°C . In the spectrum of HY after calcination, the three characteristic absorption bands due to hydroxyl groups are seen at 3742 , 3643 , and 3540 cm^{-1} . On adsorption of excess pyridine

TABLE 4
ADSORPTION OF PYRIDINE ON MGY AND HY AFTER VARIOUS TREATMENTS

Treatment	MgY 400°C Absorbance		MgY 600°C Absorbance		HY 430°C Absorbance		HY 650°C Absorbance	
	1545 cm^{-1}	1446 cm^{-1}	1545 cm^{-1}	1446 cm^{-1}	1545 cm^{-1}	1451 cm^{-1}	1545 cm^{-1}	1451 cm^{-1}
Pyridine added:								
Evac. at 250°C	0.31	0.71	0.15	0.41	0.56	0.04	0.17	0.96
H ₂ O added:								
Evac. room temp.	0.66	0.50	0.34	0.28	0.17	0.03	0.38	0.38
Evac. at 150°C	0.73	0.50	0.44	0.12	0.61	0.04	0.41	0.49
Evac. at 250°C	0.60	0.45	0.40	0.12	0.50	0.02	0.20	0.95

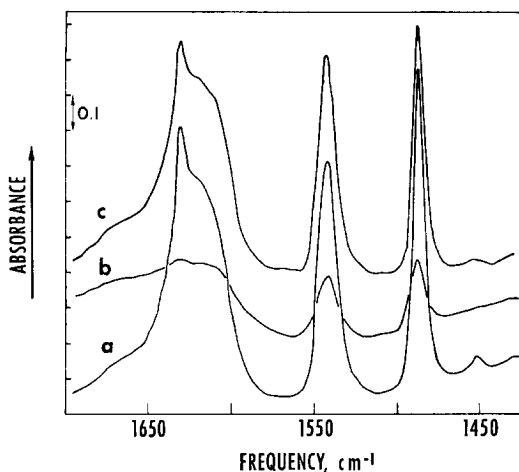


FIG. 5. Spectra of HY zeolite after calcination at 400°C: (a) pyridine adsorbed and evacuated at 250°C; (b) water added and evacuated at room temperature; (c) evacuated at 250°C.

followed by evacuation at 250°C, it is seen that the pyridine has interacted with the 3643-cm⁻¹ band and that a spectrum with bands at 3240, 3170, 3130, and 1545 cm⁻¹ indicative of pyridinium ions (1, 2) is produced. The band at 3540 cm⁻¹ is unaffected. Only a very weak band is observed at 1451 cm⁻¹, indicating that very few Lewis acid sites are present. These results are consistent with previous observations (2, 3, 14). On addition of water, the discrete band at 3540 cm⁻¹ disappears and a broad band between 3000 and 2800 cm⁻¹ due to hydrogen bonding of free hydroxyl groups to the water is observed. An overall decrease in the intensity of the spectrum in the 1700 to 1400 cm⁻¹ region is seen. On evacuation of the water several changes in the spectrum occur. The intensity changes in the spectrum are given in Table 4. Removal of the water by evacuation at 150°C removes most of the hydrogen-bonding interaction in the 3700 to 2800 cm⁻¹ region. The intensity of the 1545- and 1487-cm⁻¹ bands are about 10% greater than in the original spectra of adsorbed pyridine while the weak band at 1451 cm⁻¹ is restored. On further evacuation at 250°C, the band intensities are changed to slightly less than their original values, probably reflecting some desorption of chemisorbed

pyridine. Further evacuation at higher temperatures desorbs more of the pyridine until at 600°C practically all of the pyridine has been desorbed.

When the hydrogen Y zeolite was calcined at higher temperature, for example 600°C, different results were obtained. The spectra of hydrogen Y after calcination and removal of excess pyridine at 250°C are shown in Fig. 6. Discrete hydroxyl groups are observed between 3800 and 3500 cm⁻¹. The spectra are similar to those reported previously (2). In contrast to the spectra of pyridine adsorbed on hydrogen Y calcined at 390°C, the absorption band at 1451 cm⁻¹ due to pyridine on Lewis acid sites is much more intense and that at 1545 cm⁻¹ due to pyridine adsorbed on Brönsted acid sites is much weaker. On addition of water, the hydroxyl groups hydrogen-bond to the water and a broad band is observed between 3700 and 2600 cm⁻¹. The bands near 1450 and 1490 cm⁻¹ are considerably reduced in intensity while that at 1545 cm⁻¹ is doubled. On removal of the excess water by evacuation at 150°C, the intensity of the 1545-cm⁻¹ band increases threefold compared to that observed after only pyridine had been added. On further evacuation of the adsorbed water at increasing temperatures, the 1545-cm⁻¹ band gradually

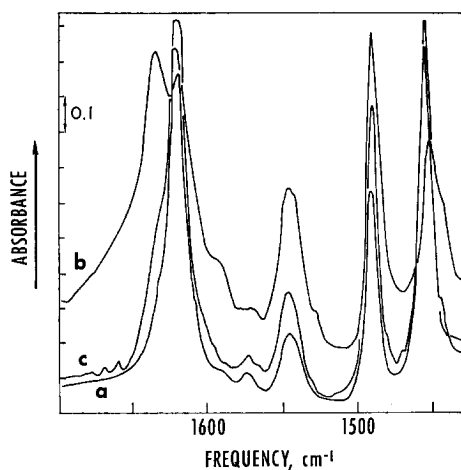


FIG. 6. Spectra of HY zeolite after calcination at 600°C: (a) pyridine adsorbed and evacuated at 250°C; (b) water added and evacuated at room temperature; (c) evaluated at 250°C.

decreased in intensity while the 1451-cm⁻¹ band increased. These changes are shown in Fig. 6.

Sodium hydrogen and magnesium hydrogen Y zeolites. These two forms of the zeolite were studied in order to examine simultaneously the behavior of the two different types of coordinately bound pyridine. Figure 7 shows the spectra of pyridine

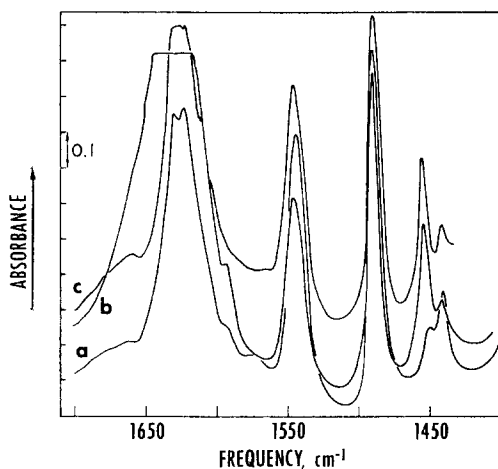


FIG. 7. Spectra of NaHY zeolite calcined at 400°C: (a) pyridine adsorbed and evacuated at 250°C; (b) water adsorbed and evacuated at room temperature; (c) further evacuation at 250°C.

chemisorbed on NaHY calcined at 400°C before, during, and after the removal of small amounts of water. Absorption bands were observed in the spectrum of the NaHY after calcination at 400°C at 3730, 3644, and 3550 cm⁻¹ as in HY zeolite. On addition of pyridine and removal of excess by evacuation at 250°C, the 3640-cm⁻¹ band

disappeared and the usual bands due to 3300 and 2800 cm⁻¹. In the 1700 to 1400 cm⁻¹ region, the expected band at 1545 cm⁻¹ due to pyridinium ions is seen while near 1450 cm⁻¹, two bands are observed, one at 1452 and the other at 1439 cm⁻¹. Two bands have previously been observed at 1455 and 1445 cm⁻¹ by Liengme and Hall for a sodium Y zeolite which had been 45% ion-exchanged with ammonium ions (14). These bands are attributed to pyridine adsorbed on tricoordinated aluminum atoms (Lewis acid sites) and on the sodium cations. On addition of water hydrogen bonding occurs in the 3000-cm⁻¹ region. In the 1700 to 1400 cm⁻¹ region the intensity of the 1545-cm⁻¹ band increases by 40% while that of the 1452-cm⁻¹ band decreases by 66% and that of the 1439-cm⁻¹ band increases by 50% (Table 5). On removal of water by evacuation at increasing temperatures, the intensity of the pyridinium ion band decreases to close to its original value and that of the 1452-cm⁻¹ band increases to its initial value. The 1439-cm⁻¹ band also decreases to its initial intensity. Similar results were observed for NaHY calcined at 600°C, the spectrum showing more dehydroxylation. It is interesting to note that the NaHY system has a great population of Lewis acid sites in relation to Brönsted acid sites compared to HY for the same temperature of calcination (compare Figs. 5 and 7).

In the magnesium hydrogen Y system, after calcination at 400°C the spectra of the zeolite initially shows bands due to hydroxyl groups at 3742, 3644, and 3550 cm⁻¹. As with NaHY, on addition of excess

TABLE 5
ADSORPTION OF PYRIDINE ON NAHY AND MGHY AFTER VARIOUS TREATMENTS

Treatment	NaHY 400°C Absorbance			NaHY 600°C Absorbance			MgHY 400°C Absorbance			MgHY 570°C Absorbance		
	1545 cm ⁻¹	1451 cm ⁻¹	1438 cm ⁻¹	1545 cm ⁻¹	1451 cm ⁻¹	1438 cm ⁻¹	1545 cm ⁻¹	1451 cm ⁻¹	1446 cm ⁻¹	1545 cm ⁻¹	1451 cm ⁻¹	1446 cm ⁻¹
Pyridine added:												
Evac. 250°C	0.47	0.38	0.15	0.40	0.61	0.19	0.49	0.26	0.37	0.25	0.22	0.31
H ₂ O added:												
Evac. room temp.	0.61	0.14	0.23	0.66	0.18	0.20	0.63	0.04	0.20	0.34	0.05	0.30
Evac. 150°C	0.69	0.25	0.12	0.62	0.35	0.15	0.49	0.12	0.25	0.38	0.15	0.20
Evac. 250°C	0.58	0.36	0.13	0.52	0.39	0.17	0.41	0.19	0.32	0.23	0.19	0.25

pyridine, the three hydroxyl groups interact and absorption bands due to chemisorbed pyridine are observed between 3300 and 2800 cm^{-1} . However, after evacuation at 250°, pyridine only interacts with the 3644- cm^{-1} band. Again a strong band due to pyridinium ion is observed at 1545 cm^{-1} and two bands due to coordinately bound pyridine at 1451 and 1446 cm^{-1} were observed. On addition of water, the band due to pyridinium ions increased in intensity by 40% while the band at 1451 cm^{-1} decreased by two-thirds and the band at 1446 cm^{-1} was unchanged. On removal of water by evacuation up to 250°C the intensity of the pyridinium ion band decreased while that of the 1451 cm^{-1} increased to the original intensity.

On further evacuation at higher temperatures, the chemisorbed pyridine was desorbed. In marked contrast to CaY and MgY no new absorption bands in the hydroxyl stretch region (3800–2800 cm^{-1}) appeared on the addition of water.

Similar results were obtained when the samples was calcined at 450° and 600°C except that the 1451- cm^{-1} band was increased in intensity and the 1545- cm^{-1} band decreased, reflecting the increased dehydroxylation with increased temperature and the conversion of Brönsted acid sites to Lewis acid sites.

DISCUSSION

The use of pyridine chemisorption to characterize the acidity of oxide surfaces has been reported by several workers (1–5, 11, 14). Absorption bands in the infrared spectrum near 3240, 3180, 1545, and 1490 cm^{-1} can be assigned to pyridine adsorbed on Brönsted acid sites (pyridinium ions) and bands at about 1620, 1490, and 1455 and 1435 can be assigned to pyridine adsorbed on Lewis acid sites (coordinately bound pyridine). The band near 1545 cm^{-1} is the most suitable band for characterizing Brönsted acidity while that near 1450 cm^{-1} is most characteristic of Lewis acidity. However, as shown previously (4), an absorption band near 1450 cm^{-1} can arise through simple interaction of pyridine with cations in the structure. Such bands

have frequencies in the range 1446 to 1438 cm^{-1} whereas pyridine adsorbed on true Lewis acid sites gives rise to a band at 1450–1451 cm^{-1} .

In the previous study of the acidity of anhydrous zeolites it was shown that Brönsted acidity was observed in zeolites containing polyvalent cations and hydrogen ions or hydroxyl groups formed by interaction of hydrogen ions with the lattice. These forms were also shown to contain hydroxyl groups whereas the alkali cation forms did not and a relationship between Brönsted acidity and hydroxyl group content was established. Furthermore, activity studies indicated that the acidic hydroxyl groups were the active centers. It was also shown that, on calcination at higher temperatures, Lewis acid sites were present. These Lewis acid sites were formed by dehydroxylation of the lattice resulting in the formation of tricoordinated aluminum atoms and were of about the same strength as Lewis acid sites on alumina. A second absorption band was observed in the "Lewis acid region" of the spectrum which was attributed to interaction of the pyridine with the exchangeable cations. This conclusion was supported by the observation that the frequency and intensity of the absorption band varied with the cation and that it was also unaffected by calcination temperature. With this tentative concept of the nature of zeolite acidity, it is possible to consider the influence of water on the acidity.

The results of the study of water on the acidity of zeolites show that there are considerable differences in the surface chemistry of exchanged zeolites. For the alkali metal Y zeolites, as typified by the sodium form, the dehydrated zeolite is nonacidic. As reported previously (4), no hydroxyl groups are detected in the spectra of the zeolite. Pyridine is seen to interact with the surface only by coordination with the cations. No Brönsted acidity is observed.

The addition of water led to the formation of no new structural hydroxyl groups. Although sharp and broad bands at 3694 and 3550 cm^{-1} were observed in the spec-

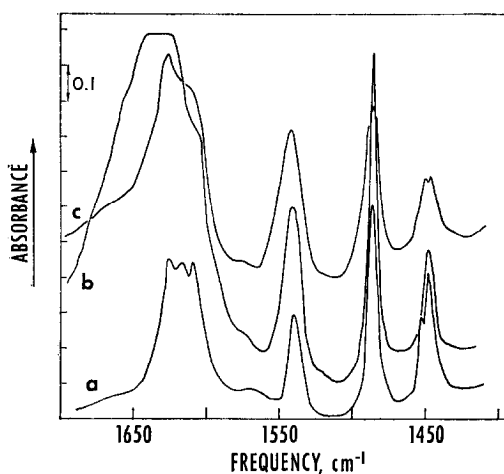
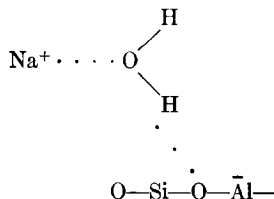


FIG. 8. Spectra of MgHY zeolite calcined at 570°C: (a) pyridine adsorbed and evacuated at 250°C; (b) water adsorbed and evacuated at room temperature; (c) further evacuation at 250°C.

trum these could be completely removed by evacuation at 150°C. This observation is similar to that of Bertsch and Habgood (15) for water adsorbed on sodium X zeolite and is probably due to simultaneous interaction of the water with the lattice and cation, thus



The hydrogen-bonded hydrogen is considered to give rise to the broad band and the free hydrogen to the sharp hydroxyl band. Interaction with the cation is supported by the shift in frequency of the sharp hydroxyl band with change of cation (16) similar to that observed for alkali ion X zeolites (15). The frequency of the sharp band decreases with larger cation radius and weaker electrostatic field (16). The formation of these hydroxyl absorption bands in the presence of pyridine, similar to those formed in the absence of pyridine (15, 19), suggests that the M^+OH or M^+OH_2 groups are nonacidic.

No formation of Brönsted acid sites was

observed on addition of water and its subsequent stepwise removal. This is not unexpected since no Lewis acid sites were observed in the dehydrated system. The band at 1438 cm^{-1} is attributed to direct interaction of the pyridine with the cation rather than to Lewis acidity. The increase in the intensity of the 1438- cm^{-1} band with addition of water is probably due to additional interaction of the pyridine with the cations brought about by the water increasing the mobility of the cations. Study of NaY zeolite dehydrated at 600°C and of NaX zeolite dehydrated at 400° and 600°C gave similar results. Identical results would be expected if the pyridine is indeed simply reacting with the exchangeable monovalent cations, which would be expected to be uninfluenced by dehydration temperature. The study of lithium and potassium Y zeolites gave the same results, except that the frequency of the coordinately bound pyridine near 1440 cm^{-1} varied with the cation as shown previously (4).

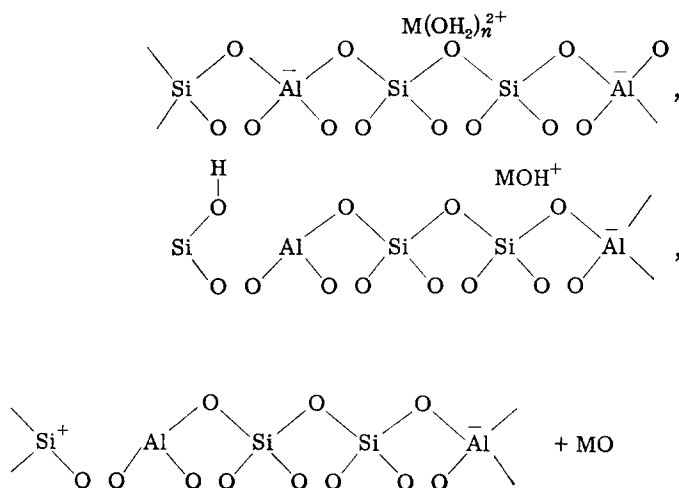
For the sodium Y form having a cation deficiency, addition of water produced Brönsted acidity when the zeolite was calcined at 600°C. The Brönsted acidity is thought to be produced by interaction of water with true Lewis acid sites formed by dehydroxylation involving hydroxyl groups located at cation deficient sites. On removal of the adsorbed water at 400°C but not at 250°C, the Brönsted acidity was eliminated. This phenomenon will be discussed in further detail at a later point.

The results obtained for HY zeolite are essentially similar to those reported previously (2, 3). When the zeolite is calcined at low temperature, little dehydroxylation of the structure takes place and hence, as indicated by the spectrum of chemisorbed pyridine, few Lewis acid sites are formed. Hence, as observed, only a small increase, if any, in intensity of the Brönsted acid site concentration would be expected on addition of water. At higher temperatures, more dehydroxylation occurs and, as shown by the spectrum of the initially chemisorbed pyridine, fewer Brönsted acid sites remain on the surface

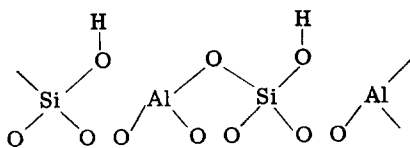
and more Lewis acid sites are present. In this case addition of water has a marked effect on the distribution of Lewis and Brönsted acid sites. As with silica-alumina cracking catalysts, removal of the water reconverts the Brönsted acid sites to Lewis acid sites. In a previous study (2), it was shown that in the initial calcined hydrogen Y zeolite, the Brönsted acidity is associated with the hydroxyl groups giving rise to the 3640-cm⁻¹ band. In contrast, on readdition of water, no discrete hydroxyl bands are formed and hence, the recon-

that the reformed hydroxyl groups are in different locations on the lattice before and after the treatment. This scheme does, however, differ from silica-alumina in that two Brönsted acid sites are converted to one Lewis acid site.

The influence of water on the acidity of divalent cations is much less clear. It has been suggested previously (4) that the structure of the divalent cation zeolites is one of or a mixture of the following three structures, according to dehydration temperature:

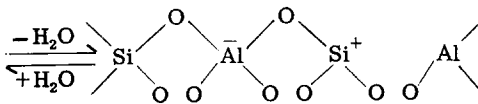


stituted Brönsted acidity in zeolites which have been calcined at high temperature must be somewhat different to that found in zeolites calcined at lower temperatures, as previously suggested by Hughes and White (3). The interconversion of Brönsted and Lewis acid sites by addition and removal of water almost certainly is similar to that previously suggested for silica-alumina (11) and can be represented diagrammatically as



Uytterhoeven *et al.* (12) have proposed such a structure. Since the 3640-cm⁻¹ band is not reformed on rehydration, it is likely

When calcined at a temperature insufficient to produce substantial dehydroxylation, it would be expected that Brönsted acidity but no Lewis acid would be observed. Interaction of pyridine with the cation would also be expected. Thus no marked effect of water would be expected. At higher calcination temperatures, some Lewis acidity would be expected due to dehydroxylation and hence water effects would be expected.



On initial adsorption of pyridine the observations agree well with predictions. For CaY absorption bands are observed

at 1545 cm^{-1} , indicating Brönsted acidity and at 1443 cm^{-1} , indicating pyridine-cation interaction. On calcination at 600°C , but not at 400°C , a band at 1451 cm^{-1} indicating Lewis acidity is observed. However, on addition of water to CaY calcined at 400°C , a marked increase in Brönsted acidity is observed and a decrease in intensity of the band indicating pyridine-cation interaction. On removal of the water by evacuation at increasing temperatures, the reversal of this phenomenon is not found. Simultaneously a new band is observed in the infrared spectrum at 3585 cm^{-1} . Addition of more pyridine showed this type of hydroxyl group to be non-acidic to pyridine. Addition of water to the 400°C calcined CaY before pyridine resulted in the formation of the 3585-cm^{-1} band and also an increase in intensity of the band at 3644 cm^{-1} . Addition of pyridine removed the 3642-cm^{-1} band but not the 3585-cm^{-1} band, thus confirming the acidity of the 3642-cm^{-1} type hydroxyl groups and the nonacidity of the 3585-cm^{-1} type. These observations are thought to be consistent with the dissociation of the re-added water to give lattice hydroxyl groups (3642-cm^{-1} band) and interaction of hydroxyl groups with the cation (3585 cm^{-1}). This latter assignment is supported by studies of pyridine adsorption on rare earth X and Y zeolites (16) which show the adsorption band near 3520 cm^{-1} to represent nonacidic hydroxyl groups. This band has been attributed to hydroxyl groups associated directly with the cation (18). The hydroxyl groups are believed to displace the chemisorbed pyridine from the cation resulting in the decrease in intensity of the 1443-cm^{-1} band. This is confirmed by the 1443-cm^{-1} band not being restored by further addition of pyridine if the zeolite has only been evacuated at 250°C after the addition of water but by the band being restored by pyridine addition after calcination at 450°C which would be expected to remove the adsorbed water. What the exact structure of the zeolite is before addition of the water and what the nature of the newly formed lattice hydroxyl groups are is not clear at this

time. However, since the frequency is 3642 cm^{-1} , it seems that these acidic hydroxyl groups are similar to those of hydrogen Y zeolite.

In the study of MgY zeolite, the only noticeable differences are that the pyridine-cation band is at 1446 cm^{-1} and the hydroxyl groups formed on readdition of water are a band at 3595 cm^{-1} . The shift of the pyridine-cation interaction band to higher frequency has been attributed to the greater interaction in the stronger electrostatic field (4) while the shift of the hydroxyl band to higher frequency is probably also due to the electrostatic field change. Shifts of frequency have been observed for X zeolite (15) and Y zeolite (16) with changes in cation radius and field.

The only differences observed with the Ca and MgY zeolites calcined at higher temperatures was the formation of Lewis acid sites initially which could be converted to Brönsted acid sites by addition of water.

The reasons why CaX and MgX zeolites behave differently from the Y zeolites is not clear at this time. A possible explanation is that the interaction of water with the cations in the X zeolite is considerably weaker than in Y zeolites and consequently less complete and more readily reversed. The type of interaction of water with the zeolite which causes the large reversible change in Brönsted acidity on adsorption and desorption is also not understood. However, since it is highly reversible, the interaction probably involves formation and decomposition of acidic hydroxyl groups.

The cation hydrogen Y zeolites yield the expected results. For both the sodium and magnesium forms studied, the Lewis acid sites formed by dehydroxylation could be reversibly converted into Brönsted acid sites as in the case of the pure hydrogen Y zeolite. In contrast to Ca and MgY zeolites, the cation portion of the MgHY zeolites behaved more like Ca and MgX zeolites. The band at 1446 cm^{-1} was hardly changed in intensity. This possibly indicates that the magnesium ions are located differently

from those in MgY zeolite or else that the hydrogen ions are occupying the crystallographic locations of the magnesium ions which interact with water. In the case of the NaHY zeolite, the sodium ions behave as in pure NaY zeolite.

In both zeolites the ratio of the 1451-cm⁻¹ band to the 1446- or 1436-cm⁻¹ band varies considerably with calcination temperature. The 1451-cm⁻¹ band intensity increases markedly with calcination temperature while the 1446- or 1439-cm⁻¹ band remains constant. This confirms previous observations (4) that only the 1451-cm⁻¹ band indicates true Lewis acidity (interaction of pyridine with tricoordinated aluminum) and that bands at lower frequencies are due to pyridine-cation interactions.

Previously (2, 4) it was suggested that for cracking and alkylation reactions, the active centers on zeolitic catalysts were Brönsted acids. The increase in Brönsted acidity on addition of water found for divalent cation and hydrogen forms of X and Y zeolites when compared with the increase in catalytic activity of these zeolites on addition of small amounts of water and proton donors (6, 8, 10, 17) provides more evidence for the Brönsted acid sites being active centers and is further evidence against Lewis acid centers being the active sites. Similar results have been obtained for rare earth X and Y zeolites and other multivalent cation zeolites (16). The alkali metal zeolites were found to have no Brönsted acid sites before or after addition of water. Similarly, these zeolites are not active catalysts at moderate temperatures and are not activated by water (4, 16).

In conclusion, it has been shown that small amounts of water when added to dehydrated zeolites can transform Lewis acidity into Brönsted acidity. Removal of water restores the Lewis acidity. In the case of Mg and CaY zeolites water interacts with the cation forming MOH groups

which are nonacidic and new acidic structural hydroxyl groups. NaHY and MgHY behave as a mixture of the HY and the cation Y. The results further support the role of Brönsted acid sites as active centers in cracking reactions.

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