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The Nature of the Acid Sites on Cationized Zeolites

Characterization by Infrared Study of Adsorbed Pyridine and Water

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Infrared spectral studies of pyridine adsorbed on cationized zeolites prepared from Linde 13-X by ion exchange with salt solutions of K, NH_4, Mg, Ca, Sr, Zn, La(III), Ce(III), and Mn are presented in this paper.

The OH stretching frequency was studied in connection with the adsorption of water and pyridine.

NH_4-X, La-X, and Ce-X have both Brönsted and Lewis acid sites, and the larger portion of the Lewis acid is strong enough to be converted into Brönsted acid by the addition of water. On Ca-X and Sr-X, only Lewis acid is present after evacuation at 450°C and it can be converted into Brönsted acid by water. On Zn-X, Mg-X, and Mn-X, the larger portion of acid is of a weak Lewis type and not all of the Lewis acid can be converted into Brönsted acid by water. Only weak Lewis acid is present on Na-X.

More than three OH stretching frequencies were observed on all of the zeolites and the nature of each OH group is discussed.

INTRODUCTION

It is important to determine the nature of acid sites on catalysts for the study of the catalytic activity of solid acid catalysts. Infrared study of adsorbed pyridine is of great advantage in distinguishing between Brönsted acid and Lewis acid sites on solid catalysts. Pyridinium ion which is formed through the adsorption of pyridine on Brönsted acid is characterized by a band near 1540 cm^{-1} and coordinately bonded pyridine which is formed by the interaction with Lewis acid is characterized by a band near 1450 cm^{-1}. Parry (*1*) and Basila *et al.* (*2*, *3*) have characterized the acid forms of silica, alumina, and silica-alumina. Recently Liengme and Hall (*4*) and Hughes and White (*5*) have reported on NH_4^+ ion-exchanged zeolite Y.

On the nature of OH groups on the surface of zeolites, many reports have been published (*5–12*).

The present study reports on the nature of acid sites on wide varieties of ion-exchanged zeolites by infrared measurement of the adsorbed pyridine and of OH stretching vibrations. The effect of the addition of water on the nature of the acid is also examined.

EXPERIMENTAL

Catalyst preparation. Linde 13X (Na-X) with no binder was ion-exchanged in the following way: The saturated solution of the chloride or acetate of the exchanging cation was passed through the Na-X column. Six times of exchanging cation equivalents for the exchange capacity of the Na-X was employed. The exchanged zeolites were then washed thoroughly with decationized water and dried at 120°C followed by calcination at 450°C in the air, except for NH_4-X.

The degree of ion exchange was calculated from the sodium content of Na-X and that of the solution after ion exchange. Sodium concentration was determined by flame photometry. The degree of ion exchange is listed in Table 1.

Infrared spectrum measurement. Zeolite was formed into a thin disc about 10 × 18 mm by pressing the powder. The "thickness" of the disc was 5–20 mg/cm^2.

The disc was pretreated by evacuation at 450°C for 2 hr in the infrared cell equipped with KBr windows. In the case of NH_4X, since the crystalline structure was completely destroyed at 450°C, the evacuation was carried out at 270° or 300°C. About half of the crystalline structure, however, was destroyed by evacuation at this temperature.

After the pretreatment and recording the background spectrum, the disc was exposed to pyridine vapor of about 0.1 mm at 100°C for 15 min. Then the spectrum was recorded after evacuation for 1 hr at various elevated temperatures.

TABLE 1
ION-EXCHANGED ZEOLITES

Zeolite	Anion of exchanging solution	Exchange degree (%)
K-X	CH_3COO^-	62.0
NH_4-X	CH_3COO^-	81.9
Ca-X	CH_3COO^-	—
Sr-X	Cl^-	—
Zn-X	Cl^-	90.6
Mg-X	Cl^-	78.6
La-X	Cl^-	91.6
Ce-X	CH_3COO^-	—
Mn-X	CH_3COO^-	74.9

An experiment was carried out to test the effect of the added water as follows: The disc which had been pretreated was exposed to pyridine vapor and evacuated at various elevated temperatures for 1 hr as above, then exposed to water vapor at about 0.1 mm for 15 min, followed by evacuation for 30 min. In some cases, additional water was adsorbed.

In the case of measuring in the OH stretching region, the temperature of the disc was gradually lowered from 450° to 100° in the presence of water vapor at about 0.1 mm, then the spectrum was recorded after evacuation at various elevated temperatures for 1 hr.

All spectra were recorded after cooling the disc to room temperature. The spectrophotometer used in these experiments was Japan Spectroscopic Co. IR-G spectrophotometer. The uncertainty of frequency observed with this spectrophotometer seems to be within 3 cm^{-1}.

RESULTS

1. *Pyridine on Zeolites*

Pyridine on Na-X and K-X. The spectra of pyridine adsorbed on Na-X and K-X are shown in Fig. 1. The absorption bands of pyridine on K-X were present at 1585, 1490, 1445 cm^{-1} after the evacuation at 100°C for 1 hr, but disappeared with further evacuation at 200°C for 1 hr.

The absorption bands of pyridine on Na-X were present at 1590, 1490, 1445 cm^{-1} and did not disappear with evacuation at 250°C for 1 hr. The characteristic band of pyridinium ion near 1540 cm^{-1} which was produced by the adsorption of pyridine on Brönsted acid was present neither on Na-X nor on K-X. The band at 1445 cm^{-1} on Na-X did not change and the band at

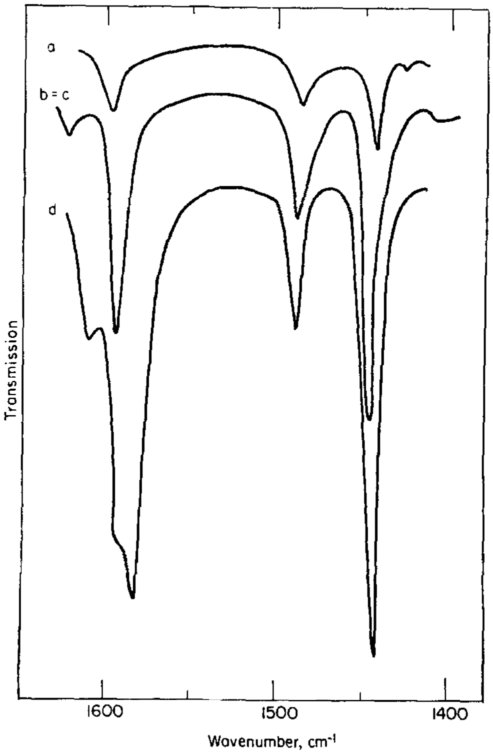

FIG. 1. Infrared spectra of pyridine adsorbed on Na-X and K-X. Na-X and K-X were pretreated at 450°C in vacuum. a, After evacuation of pyridine on Na-X at 250°C for 1 hr; b, after evacuation of pyridine on Na-X at 200°C for 1 hr; c, b + H_2O at 0.1 mm and evacuated at 200°C for 30 min; d, after evacuation of pyridine on K-X at 100°C for 1 hr.

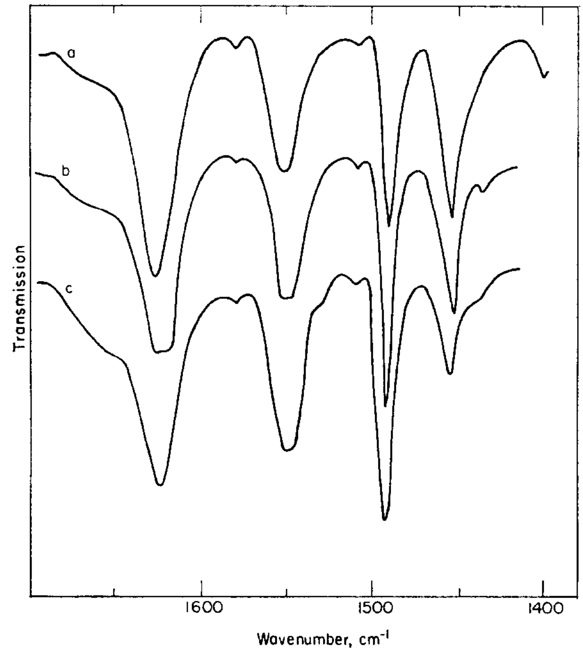

FIG. 2. Infrared spectra of pyridine adsorbed on NH_4-X. a, After evacuation of pyridine on NH_4-X_{300} at 200°C for 1 hr; b, after evacuation of pyridine on NH_4-X_{270} at 200°C for 1 hr; c, b + H_2O at 0.1 mm and evacuated at 200°C for 30 min.

1540 cm^{-1} did not appear by the addition of water.

Pyridine on NH_4-X. The spectra of pyridine on NH_4-X are shown in Fig. 2. The presence of a band near 3200 cm^{-1} showed that NH_4^+ was still present after the pretreatment of NH_4-X at 300°C for 2 hr. With this zeolite, the bands at 1630–1620, 1540, 1490, and 1455 cm^{-1} of adsorbed pyridine were present. This fact shows that NH_4-X after evacuation at 270° (NH_4-X_{270}) or 300°C (NH_4-X_{300}) has both Brönsted and Lewis acid sites.

The ratio of absorbance at 1540 cm^{-1} to that at 1455 cm^{-1} was larger in NH_4-X_{270} than in NH_4-X_{300}. Therefore the ratio of Brönsted acidity to Lewis acidity was larger in NH_4-X_{270} than in NH_4-X_{300}. By the addition of water, the absorbance at 1455 cm^{-1} decreased and that at 1540 cm^{-1} increased correspondingly. These facts show that Lewis acidity decreases and Brönsted acidity increases by the addition of water or that Lewis acid is converted into Brönsted acid by the addition of water.

Pyridine on Ca-X and Sr-X. Both Ca-X and Sr-X showed strong absorption in the region of 1500–1300 cm^{-1} and the shapes of the absorption bands changed with the evacuating temperature. It was difficult to identify the absorption band of pyridine in this region because of the reason mentioned above. The spectra on Ca-X and on Sr-X are shown in Fig. 3.

Pyridine adsorbed on Ca-X did not show the absorption near 1540 cm^{-1} and also did not show the absorption near 3000–3200 cm^{-1} which was assigned to the N-H stretching vibration of pyridinium ion (*13*). There was no Brönsted acid on Ca-X after the evacuation at 450°C for 2 hr. On adding water the strong band near 1540 cm^{-1} appeared. Again, the change of the absorption near 1450 cm^{-1} could not be followed clearly for the reason described above.

Sr-X showed almost the same behavior as Ca-X. However, weak absorptions were present near 3000–3200 cm^{-1} and near 1540 cm^{-1} on Sr-X which had been previously evacuated at 450°C. This fact shows a small amount of Brönsted acid is present on Sr-X.

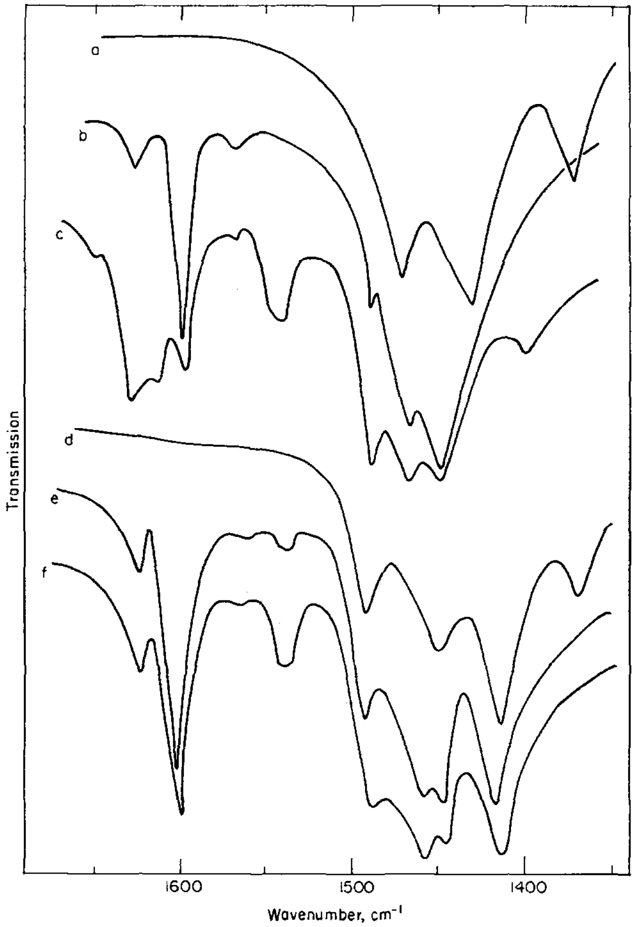

FIG. 3. Infrared spectra of pyridine adsorbed on Ca-X and Sr-X. Ca-X and Sr-X were pretreated at 450°C in vacuum. a, Background of Ca-X evacuated at 450°C; b, after evacuation of pyridine on Ca-X at 200°C for 1 hr; c, b + H_2O at 0.1 mm and evacuated at 200°C for 30 min; d, background of Sr-X evacuated at 450°C; e, after evacuation of pyridine on Sr-X at 200°C for 1 hr; f, e + H_2O at 0.1 mm and evacuated at 200°C for 30 min.

Pyridine on La-X and Ce-X. Infrared spectra of pyridine adsorbed on La-X and Ce-X were very complicated compared with those of other zeolites. Spectra on La-X are shown in Fig. 4. The presence of the strong absorption band near 1540 cm^{-1} shows a large amount of Brönsted acid is present on La-X. Since there are several absorption bands near 1450 cm^{-1}, it is probable that several kinds of Lewis acid are present on La-X. As for the main two bands, (1455 and 1445 cm^{-1}), the 1445-cm^{-1} band decreased much more in its intensity than the 1455-cm^{-1} band by prolonging the evacuation time and by elevating the evacuation temperature after the adsorption of pyridine. These facts show that the species responsible for the band at 1455 cm^{-1} was more strongly held to the surface or was adsorbed on stronger Lewis acid than that of the 1445-cm^{-1} band. A small amount of water resulted in a decrease in the intensity of the 1455-cm^{-1} band first, and an additional amount of water decreased that of 1445-cm^{-1} band also. Corresponding to the decrease of the 1455- and the 1445-cm^{-1} bands, the increase of the band at 1540 cm^{-1} was observed. These facts show that Lewis acid is converted into Brönsted acid by the addition of water and that the stronger Lewis acid is much more easily converted.

With Ce-X, its nature on adsorbing pyri-

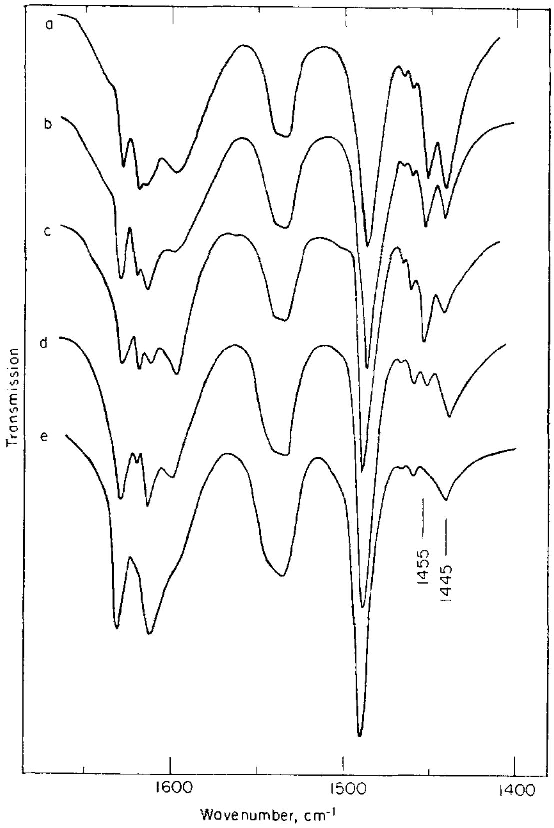

FIG. 4. Infrared spectra of pyridine adsorbed on La-X. La-X was pretreated at 450°C in vacuum. a, After evacuation of pyridine at 150°C for 1 hr; b, after evacuation of pyridine at 150°C for 17 hr; c, after evacuation of pyridine at 200°C for 1 hr; d, c + H_2O at 0.1 mm and evacuated at 200°C for 30 min; e, d + additional amount of water.

dine was almost the same as that of La-X. However, a new band at 1510 cm^{-1} developed gradually on contact with pyridine, and this band did not disappear by evacuation at 400°C in spite of the disappearance of the band of adsorbed pyridine. It seems that some kind of reaction of pyridine occurred and the reaction product was hard to desorb by evacuation at 400°C.

Pyridine on Zn-X, Mg-X, and Mn-X. Pyridine adsorbed on Zn-X, Mg-X, and Mn-X previously evacuated at 450°C showed no band or only a weak band at 1540 cm^{-1}. The spectra of pyridine on Zn-X are shown in Fig. 5. The absorption band near 1540 cm^{-1} grew upon addtion of water, but the increase in its intensity was not so large compared with La-X or Ca-X. The band near 1450 cm^{-1} did not disappear completely with the addition of larger amount of water (~0.1 mm of H_2O at 200°C).

2. OH Stretching Vibration of Zeolites

Figures 6–8 show the spectra of NH_4-X, Ca-X, and La-X in the region of the OH stretching vibration as the evacuation temperature was varied and also show those when pyridine was adsorbed.

OH stretching of NH_4-X. Strong absorption bands were present at 3660 and at 3570 cm^{-1} and weak absorption at 3750 cm^{-1}. By the adsorption of pyridine, the 3660-cm^{-1} band decreased in its intensity and the 3570-cm^{-1} band increased, especially in its width. The 3660-cm^{-1} band was much less sensitive than the 3570-cm^{-1} band to the evacuation temperature.

OH stretching vibration of Ca-X. After the pretreatment at 450°C, water was added back and evacuated at several temperatures. More than three bands were present when the evacuation temperature was below 300°C, but these bands, except that at 3740 cm^{-1}, disappeared when evacuated at 450°C. When pyridine was adsorbed on Ca-X which had been pretreated at 450°C, had water added back, and evacuated at 200°C to reduce the water, the 3650-cm^{-1} band disappeared but the retention of bands at 3570 and 3740 cm^{-1} was observed.

By the addition of a small amount of water at 200°C on Ca-X previously evacuated at 450°C, the 3700-cm^{-1} band appeared. This band decreased and the 3650- and 3570-cm^{-1} bands increased in their intensities upon elevation of the temperature to 450°C without evacuation.

OH stretching vibration of Zn-X. When the evacuation temperature was below 300°C, the 3750- and 3570-cm^{-1} bands were present. The 3570-cm^{-1} band disappeared but the small band at 3750 cm^{-1} was still present after evacuation at 450°C.

OH stretching vibration of La-X. Figure 8 shows that bands are present at 3740, 3650, 3570, and 3530 cm^{-1}. After evacuating La-X at 450°C, pyridine was adsorbed, followed by the evacuation of pyridine at 200°C. The 3650-cm^{-1} band and the

FIG. 5. Infrared spectra of pyridine adsorbed on Zn-X. Zn-X was pretreated at 450°C in vacuum. a, After evacuation of pyridine at 200°C; b, a + H_2O at 0.1 mm and evacuated at 200°C for 30 min; c, b + additional amount of water; d, c + additional amount of water (pressure of water was 0.1 mm at 200°C).

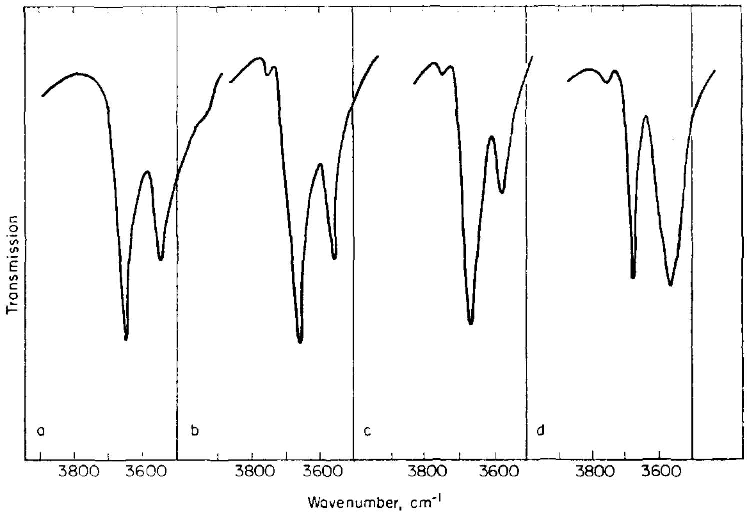

FIG. 6. Infrared spectra of NH_4-X in the OH stretching region. No treatment was done previously. a, After evacuation at 150°C for 2 hr; b, after evacuation at 270°C for 2 hr; c, after evacuation at 300°C for 2 hr; d, b + pyridine and evacuated at 200°C for 1 hr.

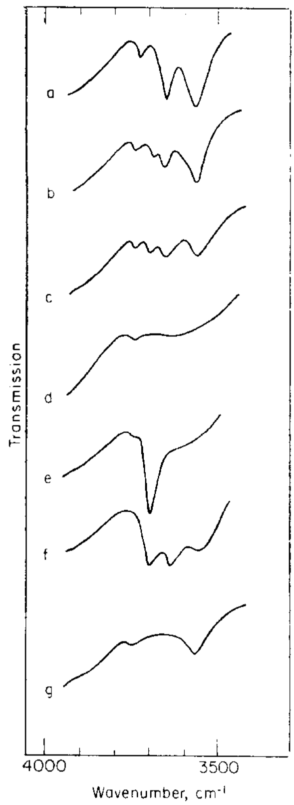

FIG. 7. Infrared spectra of Ca-X in the OH stretching region. Ca-X was pretreated at 450°C in vacuum and water was added back, except for d. a, After evacuation of added back water at 150°C for 1 hr; b, after evacuation of added back water at 200°C for 1 hr; c, after evacuation of added back water at 300°C for 1 hr; d, after evacuation at 450°C for 2 hr; e, d + H_2O at 0.1 mm at 200°C with no evacuation; f, after heating e to 450°C with no evacuation; g, b + pyridine and evacuated at 200°C for 1 hr.

3570-cm^{-1} band disappeared but the 3530-cm^{-1} band changed little in its intensity. The intensity of the 3530-cm^{-1} band was almost constant with evacuation temperature between 200° and 400°C. The 3570-cm^{-1} band disappeared by evacuating at 470°C.

The OH stretching frequencies observed on these zeolites are listed in Table 2.

DISCUSSION

OH Stretching Vibration Bands

Two different explanations of the 3750-cm^{-1} band have been presented. One of them is that the 3750-cm^{-1} band is caused by OH, the oxygen of which is part of the silica portion of zeolites (*9*). Another explanation, though concerned with Y-type zeolites, is that the band is caused by OH inside the sodalite baskets or site I cation position (*11*).

In the present experiment, the 3750-cm^{-1} band did not change on the adsorption of pyridine and also showed little change on the elevation of the evacuation temperature. The intensity of this band was nearly the same for all zeolites, and small compared with that of silica-alumina. Therefore it is more probable that this band is caused by the silica portion of zeolites contained as impurity.

The 3570-cm^{-1} band was present on all of the zeolites used here. Though the 3570-cm^{-1} band of NH_4-X increased in its peak width, this band of other zeolites decreased in its peak height by the adsorption of pyridine. White *et al.* (*12*) observed that the OH stretching band shifted to the lower frequency and increased in its absorbance by the perturbation by the adsorbed molecules. Galkin, Kiselev, and Lygin (*14*) also reported the change in the intensity and the position of the absorption band due to OH groups on silica as a result of the interaction with adsorbed molecules. So the apparent increase in the intensity of the 3507-cm^{-1} band by the adsorption of pyridine could be explained as follows: A part of the OH groups of NH_4-X responsible for the 3660-cm^{-1} band might be hydrogen-bonded

TABLE 2
OH STRETCHING FREQUENCIES (CM^{-1}) OF ZEOLITES

Zeolite					
NH_4-X	3570(w)		3660(s)		3570(s)
Ca-X	3750(w)	3700(m)	3650(w)		3570(s)
Zn-X	3750(w)		3650(w)		3570(s)
La-X	3750(w)		3650(s)	3570(m)	3530(s)

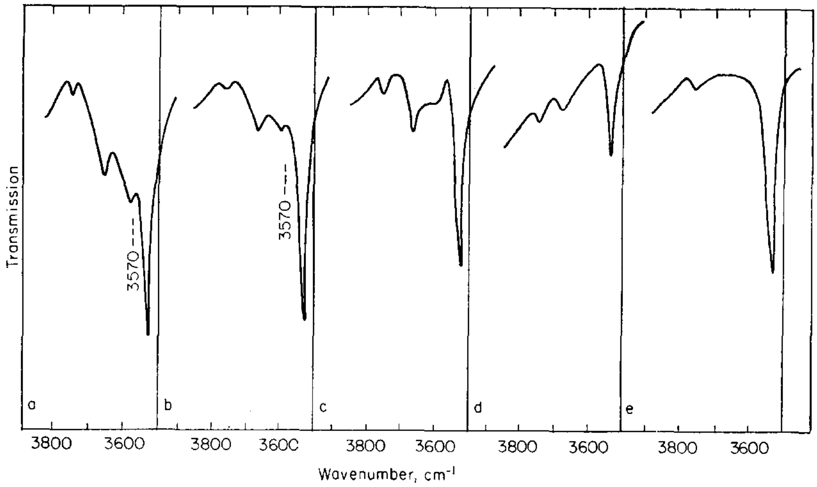

FIG. 8. Infrared spectra of La-X in the OH stretching region. La-X was pretreated at 450°C and water was added back (a, b). a, After evacuation of added back water at 200°C for 1 hr; b, after evacuation of added back water at 300°C for 1 hr; c, after evacuation at 450°C for 2 hr; d, after evacuation at 475°C for 2 hr; e, c + pyridine and evacuated at 200°C for 1 hr.

to pyridine and shifted nearer to 3570 cm^{-1}. At the same time, the remainder of the 3660-band slightly shifted to higher frequency. Although the shift was too small to indicate clearly the reason for it, it could be explained as follows:

Two kinds of OH groups absorbed near 3660 cm^{-1} and only the OH group responsible for the lower frequency band preferentially shifted to near 3570 cm^{-1} by the addition of pyridine. This resulted in the apparent shift of the peak position of the remainder of the 3660-cm^{-1} band to higher frequency.

The 3570-cm^{-1} band on Ca-X has the lowest frequency of OH bands. This band did not appear by contact with 0.1 mm H_2O vapor at 200°C, but appeared by heating the Ca-X under the same pressure of H_2O vapor at 450°C. It is suggested that an OH group of this kind is so placed that the water molecule can not easily reach the position. Such a site may be so-called site I. Less possible is the OH group caused by hydrolysis of the surface at high temperature.

The 3570-cm^{-1} band on La-X is quite different from the same frequency band on Ca-X or NH_4-X. That band readily disappeared by exposure to pyridine vapor. This band could be assigned to an OH group of the Brönsted acid type.

The 3530-cm^{-1} band on La-X scarcely changed in its intensity by the adsorption of pyridine and was the lowest in frequency. It seems that the OH group at 3530 cm^{-1} on La-X has the same character as that of the 3570-cm^{-1} band on Ca-X or NH_4-X.

The 3660–3650 cm^{-1} bands decreased or disappeared in all zeolites when exposed to pyridine vapor. It may be safe to assume that these OH groups are of the Brönsted acid type. Since these bands decreased or increased in intensity corresponding to the decrease or increase in the amount of absorbed water, it would be considered that Brönsted acid sites on zeolites are formed by the adsorbed water.

Pyridine on zeolite. According to Parry (*1*), Basila *et al.* (*2*), and Hughes and White (*5*), the band near 1450 cm^{-1} may be attributed to pyridine adsorbed on an aprotic Lewis acid. On the other hand, Farmer and Mortland (*15*) and Hirschler (*16*) have suggested that the pyridine molecule adsorbed on an acidic OH group by hydrogen bondingabsorbs near 1450 cm^{-1}. Farmer and Mortland, and Hirschler regarded a kind of acidic OH group as a Lewis acid. Such a protonic Lewis acid may be present on the surface of silica-alumina. The OH group of a protonic Lewis acid is expected to absorb at a different position from that of the OH which is responsible for the 1540-cm^{-1} band of adsorbed pyridine. The absorption intensity near 1450 cm^{-1} of pyridine increased in all of the zeolites used here by elevating the pretreatment temperature. So, if a protonic Lewis acid is present on the surface of zeolites, there should be an OH group whose absorption band decreases by the adsorption of pyridine and also decreases by the addition of water or increases by elevating the pretreatment temperature. None of the zeolites except La-X, Ce-X (not shown in Fig. 4), and NH_4-X showed an OH stretching band other than that at 3750 cm^{-1} after pretreatment at 450°C. This shows that the bands near 1450 cm^{-1} can be attributed to pyridine adsorbed on aprotic Lewis acid in all of zeolites except La-X, Ce-X, and NH_4-X. OH groups whose absorption bands were decreased by the addition of pyridine were present in La-X and NH_4-X at 3650 and 3660 cm^{-1}, respectively. These bands, however, were constant, rather than increased in intensity by elevating the pretreatment temperature. These facts do not support, though they do not entirely rule out, the view of Farmer and Mortland (*15*) or Hirschler (*16*) in the case of La-X, Ce-X, and NH_4-X.

It is difficult to distinguish the band at 1445 cm^{-1} from the band of hydrogen-bonded pyridine (1438 cm^{-1}) (*2*) by the absorption frequency (*1*). Since all pyridine desorbed from K-X by evacuation at 200°C for 1 hr and K-X had no acidity stronger than $H_0 = 3.3$, the 1445-cm^{-1} band present on K-X after evacuation at 100°C is caused by physically adsorbed pyridine. On the contrary, the 1445-cm^{-1} band on Na-X was present after evacuation at 250°C and Na-X had weak acid between 1.5 and 3.3 in H_0 units. It is then suggested that this band is caused by pyridine adsorbed on Lewis acid. Since the absorption bands of pyridine on Na-X did not change by the addition of water, it is suggested that the acid present on Na-X is weak Lewis acid and it is not converted into Brönsted acid by the addition of water.

On La-X, there were two bands of pyridine in the region of coordinately bonded pyridine. From the results of the experiments varying the evacuating temperature and time, it is concluded that the band at 1455 cm^{-1} is caused by pyridine adsorbed on the stronger Lewis acid. Since the 1455-cm^{-1} band reduced first by the addition of water, it is suggested that the stronger Lewis acid can be easily converted into Brönsted acid by water. The total acidities measured by ammonia adsorption using benzeneazodiphenylamine ($pK_a = 1.5$) as an indicator (*17*) were 1.0 meq/g for La-X evacuated at 450°C for 2 hr and 0.90 meq/g for La-X which was previously evacuated at 450°C for 2 hr, then had water added back, followed by evacuation at 200°C for 1 hr. Therefore, it could not be confirmed that one Lewis site was converted into one Brönsted site by the addition of water. In the case of Ca-X, Brönsted acid was produced only after the addition of water. The total acidities of Ca-X which was previously evacuated at 450°C for 2 hr, then had water added back, followed by evacuation at 200°C for 1 hr; and of Ca-X which was previously evacuated at 450°C for 2 hr, then had water added back, followed by evacuation at 100°C for 1 hr were 0.020 meq/g and 0.015 meq/g, respectively.* (Whether one Lewis site was converted into one Brönsted site could not be solved.) The decrease in acidity in these zeolites by the addition of water suggests that a part of the Lewis acid disappeared or could not be converted into Brönsted acid stronger than $H_0 = 1.5$.

Only a trace of the absorption band of pyridine near 1540 cm^{-1} was found with Zn-X, Mg-X, and Mn-X pretreated at 450°C and the band did not increase markedly by the addition of a relatively large amount of water (0.1 mm Hg at 200°C). It is suggested that only a small amount of Lewis acid which can be converted into Brönsted acid by water is present on these zeolites and that most of the Lewis acid is weak acid.

CONCLUSION

Two kinds of Lewis acid were found on cationized zeolites. The stronger Lewis acid

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* Since benzeneazodiphenylamine adsorbed on Ca-X pretreated at 450°C for 2 hr did not show the absorption at 540 mμ (purple), it was difficult to determine the acidity exactly (*17*).

can easily be converted into Brönsted acid by the addition of water. The weaker Lewis acid can not easily be converted into Brönsted acid by water. These zeolites can be classified into several groups according to the nature of the acids they have as follows:

First group: NH_4-X, La-X, and Ce-X have both Brönsted acid and strong Lewis acid which can be converted into Brönsted acid by the addition of water.

Second group: Almost all of the acid on Ca-X and Sr-X is strong Lewis acid which can be converted into Brönsted acid by the addition of water.

Third group: Zn-X, Mn-X, and Mg-X have Lewis acid which is too weak to easily be converted into Brönsted acid by the addition of water. They have relatively small amounts of Brönsted acid.

Other group: Na-X has only weak Lewis acid which can not be converted into Brönsted acid by water.

Among the OH groups, those of the highest and the lowest stretching frequency did not interact with pyridine and the OH groups of the bands near 3660 cm^{-1} are of Brönsted acid type.

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