

## The Nature of Active Sites on Zeolites

### X. The Acidity and Catalytic Activity of X Zeolites

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The infrared spectra of pyridine chemisorbed on several alkali, alkaline earth, transition metal, and rare earth cation forms of X zeolites have been studied. Pyridinium ion, characterized by an absorption band at  $1545\text{ cm}^{-1}$ , is a measure of the Bronsted acidity and coordinately bound pyridine, with an absorption band near  $1451\text{ cm}^{-1}$ , is a measure of Lewis acidity. All of the zeolites studied, apart from the alkali cation and copper forms, are Bronsted acids. After dehydration at  $480^\circ\text{C}$ , only the rare earth forms showed detectable Lewis acidity. The acidity of the X zeolites is much less than that of the Y zeolites. Reasons for this difference are suggested. For the alkaline earth forms, the Bronsted acid site concentration increases with decreasing cation radius and increasing electrostatic field. No simple relationship between the acidity of the transition metal forms and physical parameters was found. The catalytic activity for several reactions is, in general, related to the Bronsted acidity. However, although the relationship is good for the alkaline earth and rare earth forms, it is poor for the transition metal forms. Differences in the activation energy for the different groups of cations suggest that different mechanisms or sites might be involved.

#### INTRODUCTION

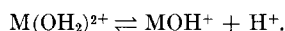
In recent years, synthetic faujasite-containing catalysts have become important commercial catalysts (1). The ability of faujasites to catalyze a number of different reactions has been demonstrated (2-8). Thus, for hexane cracking, it has been estimated that synthetic faujasites are 1000 times more active than conventional amorphous aluminosilicate catalysts (7). Friette, Weisz, and Golden (2) showed that although sodium and calcium X zeolites were active for *n*-decane cracking, the product distribution was typical of a radical mechanism for the sodium form and of a carbonium ion mechanism for the calcium form. At low temperatures, the sodium form was much less active than the calcium form. Other studies (3, 4) have also shown the influence of cations on the

catalytic activity. However, few attempts have been made to relate catalytic activity to the structural properties of the synthetic faujasites.

Richardson (8) has studied the electron spin resonance spectra of adsorbed polynuclear aromatic hydrocarbons on alkali, alkaline earth, cadmium, and silver Y zeolites together with measurements of their activities for cumene cracking. The activities for cumene cracking and the number of polynuclear aromatic radicals formed both increased with the polarizing power ( $e/r$ ) of the cation. A model was proposed in which the bond strength of acidic hydroxyl groups is perturbed by the polarizing effects of the neighboring cations. Hirschler (22) and Lunsford (42) have proposed similar schemes.

In previous papers in this series (9, 10),

it was shown that at 250°C, the sodium Y form of faujasite was inactive for cumene cracking and *o*-xylene isomerization whereas the multivalent cation and hydrogen forms were quite active. It was also shown that for the alkaline earth Y forms, the activity increased with decreasing cation radius and increasing electrostatic field, electrostatic potential, hydroxyl group content, and Bronsted acidity. It was suggested that the field associated with the cation polarized adsorbed water resulting in the formation of acidic hydroxyl groups:



The proton released attaches itself to the lattice so as to form an acidic hydroxyl group. These hydroxyl groups were considered to be similar to those observed on hydrogen Y zeolite and to be the primary active sites for carbonium ion reactions.

From studies of rare earth cation zeolites, Plank, Rosinski, and Hawthorne (3) and Venuto, Hamilton, and Landis (11) suggested that proton acid sites were responsible for catalytic activity. It was also shown that the catalytic activity of rare earth X zeolites was increased by the presence of proton donors.

Although it has been known for some time that there are marked differences in catalytic activities of X and Y zeolites, little attempt has been made to rationalize these differences in terms of the physical properties of the zeolite. Pickert, Rabo, Dempsey, and Schomaker (12) have shown that the calculated electrostatic field in Y zeolites is greater than in X zeolite and attributed the greater catalytic activity of Y zeolite to this property.

In this paper, the influence of exchangeable cations on the acidity and catalytic activity of X zeolites is considered with reference to the nature of the active sites. Alkali, alkaline earth, transition metal, and rare earth cation forms of X zeolites were studied. Attempts are made to relate the catalytic activity of the zeolites to their physical properties.

While this work was in progress, Nishizawa, Hattori, Uematsu, and Shiba (13)

reported a study of the acidity and catalytic activity of X zeolites for ethylene and propylene polymerization and butene isomerization. However, substantial differences are observed between the two studies.

## EXPERIMENTAL

### Materials

All forms of the X zeolite studied were prepared from a single sample of sodium X zeolite by ion-exchange in the conventional manner. The NaX zeolite had the following properties: SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio 2.6; Na, 14.4%; surface area, 840 m<sup>2</sup>g<sup>-1</sup>. X-ray diffraction studies showed it to be highly crystalline. Ion exchange was carried out

TABLE I  
ANALYSIS OF ZEOLITES

Cation	Na (%)	Analysis of samples	
		Percentage exchanged	Surface area m <sup>2</sup> g <sup>-1</sup>
Li	0.81	94	790
Na	14.4	—	840
K	0.12	100	749
Mg	3.07	79	797
Ca	0.18	99	750
Sr	<0.01	100	701
Ba	<0.01	100	659
Mn	1.17	92	758
Co	1.9	87	600
Cu	<0.01	100	85
Zn	0.89	94	679
Ag (1)	0.52	97	489
(2)	0.61	96	653
Cd	0.16	99	678
RE	0.25	98	721
NH <sub>4</sub>	0.41	97	211

at 90°C with 10% solutions of the appropriate salts. Two samples of AgX were prepared. AgX(1) was prepared via the nitrate salt and AgX(2) via the acetate. The analysis of the zeolites are given in Table I.

Pyridine was the heart-cut fraction obtained by distillation of Allied Chemical Research Grade material. It was further dried over activated Linde 4A zeolite.

*O*-xylene was Eastman Research Grade and was used without further purification.

#### Apparatus and Technique

The infrared cell used in this study was the same as reported previously (9). A Cary-White 90 infrared spectrophotometer was used. The spectral resolution was  $4\text{ cm}^{-1}$  and the scan speed  $1\text{ cm}^{-1}\text{ sec}^{-1}$ .

The zeolite samples were studied in the form of thin wafers. About 0.05 g of powdered zeolite was compacted at 15,000 psi in a 1-inch diameter metallurgical die. The resulting wafers had an optical thickness of 6–10  $\text{mg cm}^{-1}$ . The samples were inserted in the cell and evacuated to  $10^{-3}$  Torr. The temperature was then slowly raised to  $480^\circ\text{C}$  and maintained for 16 hr. The sample was then cooled to room temperature and its spectrum recorded. The sample was then allowed to equilibrate with pyridine at 1-Torr pressure for 2 hr. The gas phase and physically adsorbed pyridine were then removed by evacuation for 2 hr at  $250^\circ\text{C}$  and, after cooling to room temperature, the spectrum of the chemisorbed pyridine was recorded.

The zeolite acidity was also studied after partial hydration. Water was allowed to equilibrate with the zeolite for 1 hr and then the excess water was removed by evacuation at  $250^\circ\text{C}$ . After cooling, the spectra were again recorded. Under these conditions, the zeolites contain about 2% water.

The surface areas of the zeolites were measured after dehydration for 4 hr at  $400^\circ\text{C}$ . Measurements were made at a nitrogen pressure of  $p/p_0$  of about 0.018 using a Perkin Elmer Sorptometer.

Thermogravimetric analyses were recorded in flowing helium with a temperature program of  $1^\circ\text{C min}^{-1}$ . An Aminco Thermograv Instrument was used.

Catalytic activity of the zeolites for *o*-xylene isomerization was measured in the microreactor and using the conditions described previously (10). The zeolite was used in the form of 20- to 40-mesh granules. Helium was used as the carrier gas. Activity data, for comparison, were also taken from the literature (3).

The electrostatic fields in the zeolite were calculated from the data of Rabo *et al.* (14) and Dempsey (15).

#### RESULTS

The use of pyridine to characterize the surface acidity of catalysts is now well established (9, 16, 17). Briefly, a band at  $1545\text{ cm}^{-1}$ , due to pyridinium ions, is indicative of Bronsted acidity while a band at  $1451\text{ cm}^{-1}$ , due to coordinately bound pyridine, is characteristic of Lewis acidity. A band due to coordinately bound pyridine between  $1448$  and  $1435\text{ cm}^{-1}$  is due to pyridine-cation interactions. A number of other bands are observed in the spectrum of chemisorbed pyridine but these are not as useful for diagnostic purposes.

Figure 1 shows the spectrum of pyridine chemisorbed on NaX zeolite. No bands are observed at  $1545$  or  $1451\text{ cm}^{-1}$ . It is therefore concluded that NaX zeolite has no detectable acidity. A band is observed at  $1442\text{ cm}^{-1}$  which can be assigned to pyridine-cation interaction. As reported

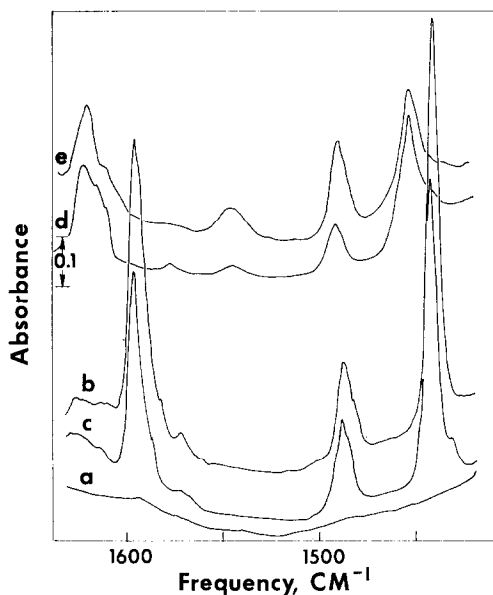


FIG. 1. Infrared spectra of pyridine chemisorbed on Na and  $\text{NH}_4\text{X}$  zeolites; (a) NaX dehydrated at  $480^\circ\text{C}$ ; (b) pyridine adsorbed on NaX and evacuated at  $250^\circ\text{C}$ , (c) (b) after hydration, (d) pyridine adsorbed on  $\text{NH}_4\text{X}$  and evacuated at  $250^\circ\text{C}$ , (e) (d) after hydration.

TABLE 2  
ACIDITY AND PHYSICAL PARAMETERS OF EXCHANGED X ZEOLITES

Cation	Ionic radius Å	Electrostatic field (V/Å)	Electrostatic potential (e/r)	Ionization potential (eV)	Pyridine-cation frequency (cm <sup>-1</sup> )
Li	0.6	1.4	1.7	5.36	1442
Na	0.95	0.8	1.1	5.12	1442
K	1.33	0.4	0.8	4.3	1438
Mg	0.65	4.8	3.1	14.96	1446
Ca	0.99	3.3	2.0	11.82	1443
Sr	1.13	2.6	1.8	10.98	1441
Ba	1.35	2.2	1.5	9.95	1439
Mn	0.80	4.3	2.5	15.70	1446
Co	0.78	4.3	2.6	17.3	1447
Cu	0.69	4.7	2.9	20.34	1448
Zn	0.74	4.6	2.7	17.89	1451
Ag	1.26	0.5	0.8	7.54	1443
Cd	0.97	3.3	2.1	16.84	1448
RE	≈1.65	—	1.9	≈12	1443

previously (18), addition of water has no effect on the acidity. Similar results were found with lithium and potassium X zeolites except that the frequency of the coordinately bound pyridine varied with cation radius in a similar manner to that observed for Y zeolite (9). The frequencies are listed in Table 2.

In order to investigate the influence of

cation radius, charge, and electrostatic field, the alkaline earth cation forms were studied. In Fig. 2, spectra of pyridine chemisorbed on magnesium and strontium X zeolites are shown. The absorbance of the bands due to pyridinium ion divided by sample mass are listed in Table 3. Spectra after treatment with water are also shown. As observed previously for Y

TABLE 3  
ACIDITY, HYDROXYL CONTENT AND CATALYTIC ACTIVITY OF EXCHANGED X ZEOLITE

Cation	Bronsted acidity		Wt loss on heating (%)		Conversion of <i>o</i> -xylene		
	(Peak ht 1545 cm <sup>-1</sup> sample mass)		400-1000°C	500-1000°C	Temp., °C for 25%	Conversion at 400°C	Gas oil conversion <sup>3</sup> (%)
	Anhydrous	Hydrated					
Na	0	0	1.5	0.9	>500	0	
K	0	0	2.8	2.2	—	—	
Mg	2.9	8.5	3.6	2.5	454	11.8	
Ca	0.7	5.1	3.8	2.5	>500	3.8	24.9
Sr	0.2	3.0	2.8	2.1	>500	1.6	
Ba	0.1	0.6	2.3	1.8	—	—	
Mn	1.2	3.1	3.6	2.7	467	3.6	26.7
Co	1.1	2.1	3.3	2.3	429	12.0	
Cu	<0.1	<0.1	—	—	>500	0	
Zn	0.5	3.2	3.9	2.9	369	51.1	
Ag (1)	6.9	7.4	5.4	4.9	278	—	
(2)	4.1	4.7	—	—	303	—	
Cd	0.4	2.0	3.4	2.5	410	15.5	
RE	10.0	14.5	4.1	3.3	216	—	49.9
NH <sub>4</sub> (H)	0.6	1.2	6.7	3.9	437	14.8	

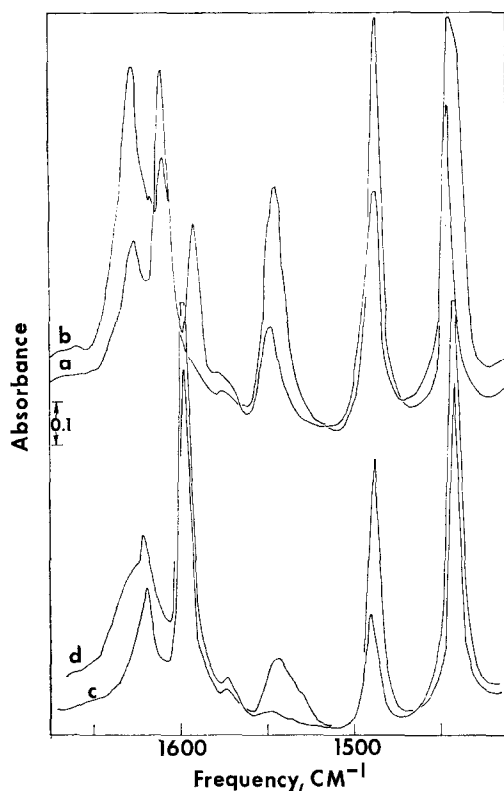


FIG. 2. Infrared spectra of pyridine chemisorbed on alkaline earth cation X zeolites; (a) MgX after pyridine chemisorption, (b) (a) after hydration, (c) SrX after pyridine chemisorption, (d) (c) after hydration.

zeolites (9), the absorption band due to coordinately bound pyridine increases in frequency with decreasing ionic radius and increasing electrostatic field of the exchanged cation. No band near  $1451\text{ cm}^{-1}$  was observed for any of the alkaline earth forms. All the alkaline earth zeolites had a band near  $1545\text{ cm}^{-1}$  due to pyridinium ions which could be attributed to Bronsted acidity.

Weight losses on dehydration between 400 and  $1000^\circ\text{C}$  and 500 and  $1000^\circ\text{C}$  are also given in Table 3.

Figure 3 shows the spectra of the rare earth forms of X zeolite. After adsorption of pyridine, absorption bands due to chemisorbed pyridine are observed at  $1545$ ,  $1451$ , and  $1443\text{ cm}^{-1}$  indicating the presence of Bronsted and Lewis acidity and

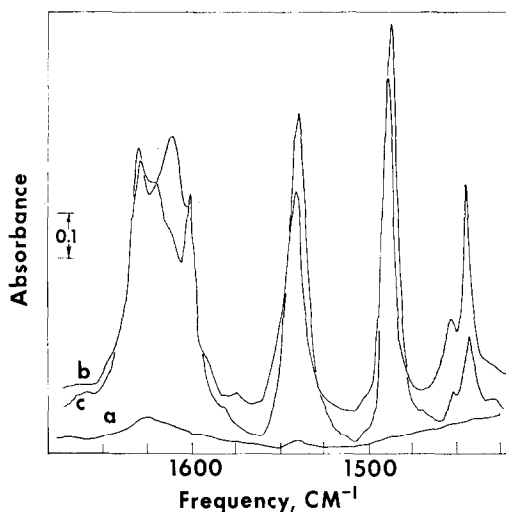


FIG. 3. Infrared spectra of pyridine chemisorbed on rare earth cation X zeolite; (a) evacuated at  $480^\circ\text{C}$ , (b) after addition of pyridine and evacuation at  $250^\circ\text{C}$ , (c) after hydration and evacuation at  $250^\circ\text{C}$ .

pyridine-cation interactions. The absorbance of the  $1545\text{ cm}^{-1}$  bands divided by sample mass are listed in Table 3.

Spectra of pyridine adsorbed on deaminated ammonium X are shown in Fig. 1 for the dehydrated and hydrated zeolite. Absorption bands at  $1545$  and  $1452\text{ cm}^{-1}$  indicate the presence of both Bronsted and Lewis acid sites.

Spectra of pyridine adsorbed on the transition metal zeolites, cobalt, manganese, zinc, cadmium, and silver are shown in Figs. 4 and 5. The ion exchanged zeolites exhibit Bronsted acidity and also an absorption band due to pyridine-cation interaction. No bands attributable to Lewis acidity are observed (see below).

The catalytic activities of the various zeolites for the *o*-xylene isomerization are listed in Table 3. Deactivation due to reduction of the metal ions to metal as reported by Yates (40) was minimized by using helium as the carrier gas. Silver, cadmium, and zinc were found to deactivate rapidly at high temperatures. All activity measurements were, therefore, made at temperatures below which deactivation was observed. However, in the AgX studies, Ag metal was detected in the used samples.

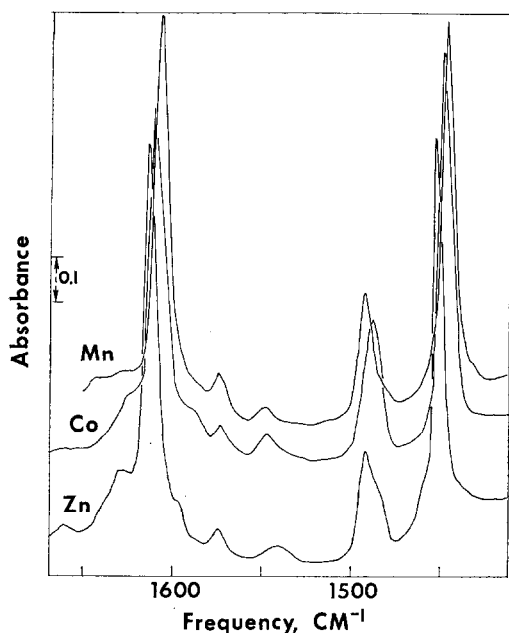


FIG. 4. Infrared spectra of pyridine chemisorbed on transition metal X zeolites; (a) CoX, (b) MnX, (c) ZnX.

Temperatures required for 25% conversion of the feed and the percentage conversion of the feed at 400°C are given. Activity data reported by others are also listed (3).

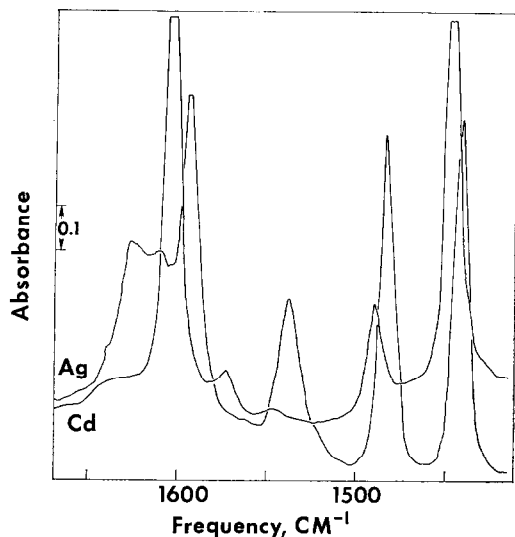


FIG. 5. Infrared spectra of pyridine chemisorbed on; (a) CdX and (b) AgX.

## DISCUSSION

### Variation of Acidity with Cation

**Alkali and alkaline earth cation forms.** Analogous to results for NaY (9, 19, 20), NaX zeolites after calcination at 480°C show no absorption bands in the spectra of chemisorbed pyridine due to adsorption on Bronsted or Lewis acid sites. Similarly, no structural hydroxyl groups, which could give rise to acid sites, were observed in the samples studied (9, 20). The absorption band near 1442 cm<sup>-1</sup>, due to interaction of pyridine with sodium ions, is observed as found for NaY. Like NaY, no Bronsted acid sites were generated on addition of water. These results would be expected from a consideration of the structure of NaX which, when pure, contains neither hydroxyl groups which are potential Bronsted acid sites nor tricoordinated aluminum atoms, which could act as Lewis acid sites. In their studies of NaX, Watanabe and Habgood (21) found Bronsted acid sites under conditions of partial dehydration but not under condition of partial hydration. However, it seems that their samples were cation deficient. The bands due to Lewis acidity reported by Nishizawa *et al.* (13) are probably due to cation-pyridine interaction rather than true Lewis acid sites.

Results for lithium and potassium X zeolites were similar to those for NaX zeolite except the frequencies of the band due to pyridine-cation interaction varied in frequency with the cation radius and electrostatic field similar to the results previously reported for Y zeolites (9). As the radius of the cation decreased, the absorption band frequency increased indicating stronger interactions with increasing electrostatic field and potential.

The decrease in intensity of the cation-pyridine band near 1442 cm<sup>-1</sup> on hydration is possibly due to movement of the sodium ions into inaccessible positions or to replacement of coordinated pyridine by water.

Analogous to the Y zeolites, alkaline earth X zeolites exhibit Bronsted acidity as shown by the absorption band near 1545

$\text{cm}^{-1}$  (Fig. 2) in the spectrum of chemisorbed pyridine. The variation of the concentrations of Bronsted acid sites on the alkaline earth X zeolites with cation (Table 3) is similar to that found for the Y zeolites (9). As the ionic radius increases and the electrostatic field and potential decrease, the concentration of Bronsted acid sites decreases in a linear manner for the anhydrous zeolites as shown in Fig. 6. The data of Table 3 shows

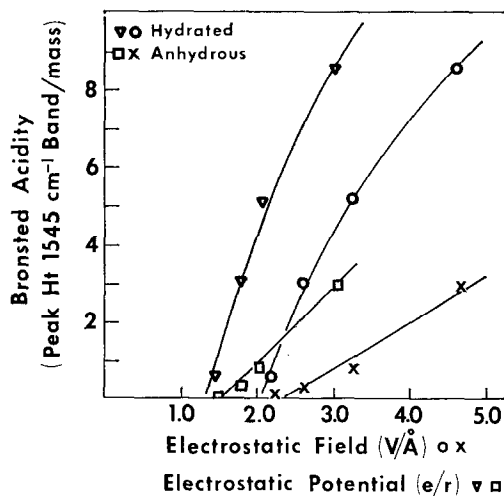


FIG. 6. Bronsted acidity of alkaline earth cation X zeolites as a function of the electrostatic field and electrostatic potential.

that the Bronsted acid site concentration also decreases with decreasing hydroxyl group content. However, the magnitude of the Bronsted acid site concentration is much less than that in the Y zeolite series [compare CaX, 0.71 units and CaY, 4.3 (9)]. In the Y zeolites, the Bronsted acidity was attributed to acidic hydroxyl groups formed by a reaction of the type  $M(\text{OH})_2^{2+} \rightleftharpoons \text{MOH}^+ + \text{H}^+$  (9). The proton formed was considered to attach itself to the lattice and form the acidic hydroxyl groups with an infrared band near  $3640 \text{ cm}^{-1}$ . Evidence for this reaction has been presented in several studies (5, 9, 19, 20, 22-24). The reaction is probable since the negative charge centers in the Y zeolite lattice associated with the aluminum atoms are too far apart to be satisfied by a simple

$M^{2+}$  ion. In contrast, in X zeolites, the negative charges associated with the aluminum tetrahedra lie much closer together and can possibly be satisfied to a large extent by a simple  $M^{2+}$  ion (4). Since the silica to alumina ratio of the X zeolite used was somewhat greater than the theoretical value of 2, it is probable that all the negatively charged aluminum tetrahedra are not satisfied by symmetrically located divalent cations. Hence, it seems that the acidity of alkaline earth X zeolites is similar in origin to that of Y zeolites, but due to the lesser charge separation, the concentration of acid sites is less. The acidity results from the hydrolysis of water, associated with the cation, by the electrostatic field existing in the zeolite. Thus, acidic hydroxyl groups are produced. Analogous to Y zeolites (9), hydroxyl bands near  $3640 \text{ cm}^{-1}$  and at lower frequencies are observed for the alkaline earth X zeolites attributable to acidic Si-OH groups and to hydroxyl groups associated with the cations (25). The differences in the acidity of X and Y zeolites will be discussed in more detail elsewhere (25).

For the calcination conditions used, none of the alkaline earth X zeolites showed an absorption band near  $1451 \text{ cm}^{-1}$  due to pyridine chemisorbed on Lewis acid sites. Absorption bands due to pyridine-cation interactions are observed near  $1440 \text{ cm}^{-1}$  (pseudo-Lewis acid sites). The frequency of this band increased with decreasing cation radius and increasing electrostatic field as previously observed for Y zeolites (9). That is, as the field around the cation increased, so did the strength of the pyridine interaction.

These results differ from those of Nishizawa *et al.* (13) who report Lewis acidity on alkali and alkaline earth X zeolites but no Bronsted acidity on the alkaline earth zeolites. It would appear that they attributed the band due to pyridine-cation interaction to be due to adsorption on Lewis acid sites. The fact that they report little change in band intensity on hydration confirms that true Lewis acid sites (tricoordinated aluminum atoms) were not being detected. Furthermore, the

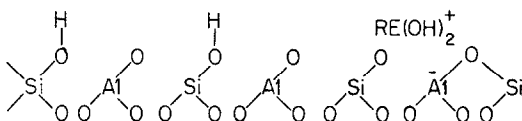
absorption band due to the chemisorption of pyridine on Lewis acid sites usually occurs near  $1450\text{ cm}^{-1}$ . The reason why they observed no Bronsted acidity is not apparent.

In all cases studied, partial rehydration of the alkaline earth X zeolites resulted in an increase in the Bronsted acidity. Because no Lewis acid sites are observed in the zeolites calcined at  $480^\circ\text{C}$ , the increase in the concentration of Bronsted acid sites cannot be due to the conversion of Lewis to Bronsted acid sites. Possible origins of these Bronsted acid sites will be considered in the discussion of transition metal cation zeolites. It should also be noted that for the partially hydrated zeolites, the Bronsted acidity is not a linear function of the electrostatic field or potential (Fig. 6). The results suggest that the cationic fields are not able to dissociate one molecule of water per cation and that some of the negative charge of the zeolite lattice can be satisfied by simple divalent cations. Such a phenomenon would be most expected for the larger cations. Thus, the increase in acidity of the larger cation zeolites is observed to be less than expected.

**Rare earth cation forms.** Of the zeolites studied, only the rare earth X zeolites showed an absorption band in the spectrum of adsorbed pyridine near  $1451\text{ cm}^{-1}$  due to Lewis acidity. Figure 3 shows the spectra of pyridine adsorbed on the rare earth form. In the hydroxyl stretch region, the calcined zeolite has strong absorption bands at  $3642$  and  $3512\text{ cm}^{-1}$  due to hydroxyl groups (14, 24). The  $3642\text{ cm}^{-1}$  band type of hydroxyl groups are acidic to pyridine like those observed in the hydrogen and multivalent Y zeolites. The  $3512\text{ cm}^{-1}$  band does not interact with pyridine indicating that this type of hydroxyl group is nonacidic or not accessible to a base of the strength of pyridine. It has been suggested that this type of hydroxyl group is attached directly to the rare earth cations (14) and hence the nonacidity supports the results previously obtained for hydroxyl groups attached to magnesium and calcium in Y zeolites (24). In all cases so far studied, hydroxyl groups associated

directly with the cations appear to be nonacidic.

The rare earth X zeolite has a much larger concentration of Bronsted acid sites (Table 3) than the alkaline earth and divalent transition metal X zeolites. It also contains a greater concentration of hydroxyl groups (Table 3). Although no clear cut data are available, it is probable that the dissociation of adsorbed water occurs in a similar manner to that occurring on the divalent zeolites, but extending over three aluminum atoms, thus  $\text{RE}(\text{OH}_2)_2^{+3} \rightleftharpoons \text{RE}(\text{OH})_2^+ + 2\text{H}^+$ .



In the case of the trivalent ion, it is unlikely that the negative charge centers could be satisfied by a symmetrically placed cation as is possible with the divalent cations. A similar hydrolytic scheme encompassing two negative centers has been proposed previously by Venuto *et al.* (5).



However, if such was the case, it would be difficult to understand the origin of the greater acidity and hydroxyl content of rare earth X compared to MgX and even MgY (9). Furthermore, dissociation to  $\text{RE}(\text{OH})^{2+}$  would produce a cation species similar to that existing in the divalent cation zeolites before dissociation of adsorbed water. Hence, further dissociation of adsorbed water would be expected. Evidence for the involvement of three sites on Y zeolites has been reported previously (10). At the present time, it is not possible to distinguish between  $\text{RE}(\text{OH})_2^+$  and  $\text{RE-OH-RE}$  proposed by Rabo, Angell, and Schomaker (38).

The increase in Bronsted acidity and the decrease in Lewis acidity on hydration is probably due to rehydration of Lewis acid sites similar to that observed for dehydroxylated hydrogen and multivalent cation zeolites.



**Transition metal cations.** Four cations of the first transition series were studied, namely, manganese, cobalt, copper, and zinc. With the exception of copper, these cation forms exhibited Bronsted acidity. In the dehydrated state, manganese and cobalt are equally acidic, while zinc has about half the acidity of manganese although it has about the same ionic radius and electrostatic field. Copper X showed little if any Bronsted acidity. However, under the conditions used, its structure collapsed. In the partially hydrated state, zinc and manganese are about equally acidic and cobalt somewhat less acidic. When hydrated, the zeolites are two to four times as acidic as in the dehydrated state. None of the transition metal zeolites had any detectable Lewis acidity either in the anhydrous or hydrous states. They all showed an absorption band due to cation-pyridine interaction; the frequency of this band varied with the cation as observed for other types of cations. Because the bands near  $1440\text{--}1450\text{ cm}^{-1}$  vary in frequency with cation and are relatively little effected by water, it is probable that they do not represent Lewis acidity although in the case of Zn, Co, and Cd, the frequency is close to that observed for adsorption on true Lewis acid sites. It would appear, then, that the increase in Bronsted acid sites on hydration is not due to the conversion of Lewis acid sites into Bronsted acid sites as occurs on silica-alumina, decationized Y and dehydroxylated multivalent cation Y zeolites. However, since a decrease in the absorption bands due to cation-pyridine interaction is observed in all cases, the change in acidity is probably associated with the cations. Although it is not possible to be specific at this time, it is possible that on partial hydration, a movement of cations occurs from sites accessible to pyridine to sites not accessible to pyridine. Such a movement would allow the formation of additional Bronsted acid sites by making accessible exchanges sites available. Watanabe and Habgood (21) observed similar effects. The movement of cations in zeolite structures on hydration or dehydration has been reported by sev-

eral authors (26-28). Alternatively coordinated pyridine could be replaced by water or hydroxyl groups.

Unlike the acidity of alkaline earth X and Y zeolites, there seems to be no relationship between acidity and ionic radius, electrostatic field, electrostatic potential, or ionization potential. This is shown by consideration of the data of Tables 2 and 3. Although there is some scatter, the frequency of the pyridine-cation band generally increased with increasing field and potential.

Because the characteristic absorption band at  $3640\text{ cm}^{-1}$  occurs in the spectra of all the transition metal zeolites examined (25, 35, 39), it appears that the acid sites must be formed by a fission of the adsorbed water under the influence of the electrostatic field in a manner analogous to that proposed for alkaline earth zeolites above. By such a reaction and subsequent attachment of the proton to the zeolite lattice, acidic Si-OH groups could be formed. Barry and Lay (26) have reported evidence for this hydrolysis in the case of manganese.

Silver and cadmium of the second transition series were examined. In the dehydrated state, cadmium had about the same concentration of Bronsted acid sites as zinc although it has about a 20% greater radius. In the partially hydrated state, cadmium has substantially less Bronsted acid sites. However, silver X was much more acidic (about 15 times) than cadmium X. In fact, it was found to be the most acidic X zeolite with the exception of the rare earth form. Unlike cadmium and the other X zeolites, the acidity of silver X zeolite was hardly changed by rehydration. The two different silver samples behaved similarly, the acetate prepared sample being the least acidic.

The reasons for the lack of a relationship between the Bronsted acidity and the electrostatic field or potential of the transition metal zeolites are not apparent at this time. It is possible that the *d*-electrons of these cations could influence the ease of dissociation of adsorbed water and the stability of MOH<sup>+</sup> type groups. It is possible that a detailed study of the structural

hydroxyl groups may reveal the phenomena involved.

**Ammonium (hydrogen) X.** The ammonium form was examined after deamination at 480°C. As expected, the structure of the zeolite collapsed as indicated by surface area and x-ray diffraction measurements. The infrared spectra in the hydroxyl stretch region (25) also indicated a change from the zeolite structure to an amorphous aluminosilicate. The deaminated sample had both Bronsted and Lewis acid sites. The concentration of acid sites was low and like silica-alumina, the Lewis acid sites were converted to Bronsted acid sites by rehydration. These observations are similar to those reported by Nishizawa *et al.* (13).

#### *Variation of Catalytic Activity with Cation*

For the alkali and alkaline earth forms of X zeolites, the catalytic activity follows a similar pattern to that previously reported for Y zeolites (8, 9, 12). The results of catalytic cracking studies have shown that sodium X zeolite is a rather poor cracking catalyst at 500°C and that the products are typical of a radical rather than an ionic mechanism (2). At lower temperature, sodium X is inactive for cumene cracking. Pickert *et al.* (12) found that platinum on sodium zeolites to be inactive for *n*-hexane isomerization at 450°C. Similarly, results of the present study show the alkali metal X zeolites to be inactive for *o*-xylene isomerization.

In marked contrast, the alkaline earth forms of X zeolite are active catalysts for *o*-xylene isomerization at moderate temperatures. As observed for Y zeolites, Table 3 and Fig. 8 show that the catalytic activity decrease from magnesium to strontium X as the Bronsted acidity and hydroxyl group content decrease. The activity of barium X was not measured since it would be expected to be extremely small. The catalytic activity of alkaline earth X zeolites has been shown by several authors previously (2, 3, 7, 29-31) for various reactions but only three studies of the activity of several of the alkaline earth cations seem to have been reported. Most

studies seem to have been restricted to comparisons of sodium and calcium X zeolites.

Miale, Chen, and Weisz (7) have studied a variety of cation forms of zeolites. Nishizawa *et al.* (13) found Mg, Ca, and SrX to be inactive for ethylene and propylene polymerization and Mg and Ca to be equally active for butene isomerization. However, Matsumoto and Morita (32) showed the four alkaline earth X zeolites to be active for toluene disproportionation. Magnesium X was the most active and barium the least active.

With the exception of copper X, the transition metal zeolites investigated in this study were all active catalysts. The activities spanned a wide range from the high activity of silver X to the low activity of manganese X. Previous workers have studied cadmium, cobalt, manganese, and zinc X zeolites. Matsumoto and Morita (32) have shown cadmium X to be a more active catalyst than calcium X for toluene disproportionation. This order of activity is confirmed by the present study. Nishizawa *et al.* (13) obtained the following order of activities for butene isomerization: Zn, Mn > Ca, Mg > Cd > Na. The results of the present study indicate the order: Ag > Zn, Cd > Ca, Mg > Ca, Mn > Sr > Cu, Na. It is seen that there is little agreement between the two studies. For toluene disproportionation, Matsumoto and Morita (32) found the order: Cd > Ca > Zn, Mg > Sr > Ba.

The transition metal zeolites differ in a marked manner from the alkaline earth zeolites in that the activation energy for the *o*-xylene isomerization is found to be about 33 kcal mole<sup>-1</sup> whereas for the alkaline earth, forms, values of about 20 kcal mole<sup>-1</sup> were obtained. Hence, possibly a different active site or mechanism is involved. Schwab and Kral (43) found comparable differences for cumene cracking.

The rare earth form of X zeolite was found to be the most active of all the cation exchanged zeolites examined for *o*-xylene isomerization. This is in agreement with other authors who have reported rare earth zeolites to be very active catalysts for a

wide range of reactions (3, 5, 7). It also agrees with the results obtained for Y zeolites (1, 5, 7, 14).

The hydrogen form was more active for *o*-xylene isomerization than magnesium and calcium X zeolites but less active than the rare earth and several of the transition metal X zeolites. The observed sequence of activities is: RE, Ag, Zn, Cd > H > Co, Mg, Ca. In their study, Nishizawa *et al.* (13) found the sequence of activity for butene isomerization to be: Ce, La, H > Zn, Mn. The hydrogen form is less active than a silica-alumina cracking catalyst previously studied (44). This lower activity could be a reflection of the lower surface area (211 vs. 350 m<sup>2</sup>g<sup>-1</sup>). Rabo *et al.* found that silica-alumina was more active than hydrogen and calcium X for hexane isomerization (4) and Friette *et al.* (2) found silica-alumina more active than calcium X for cumene cracking.

#### *Relationship between Catalyst Acidity and Activity*

The catalytic activity of zeolite has been attributed to the electrostatic field, Lewis acid sites, and Bronsted acid sites (4-6, 8, 9, 19, 20, 33). Like the Y zeolites, the X zeolites provide a convenient system in which activity, acidity, and electrostatic field can be varied by changes of the exchangeable cation. Thus comparison of the catalytic activity with the physical parameters as the cation is varied should reveal information on the nature of the active sites.

The studies of pyridine adsorption show that the alkali cation X zeolites are non-acidic while the alkaline earth forms are Bronsted acids but not Lewis acids similar to previous results for Y zeolites (9). The cobalt, manganese, zinc, silver, and cadmium X zeolites also exhibit Bronsted acidity but no detectable Lewis acidity. Since multivalent cation forms of X zeolite are active cracking catalysts for gas oil (3), Lewis acid sites can be excluded from consideration as primary active sites. The data of Table 3 also shows that cumene does not dealkylate over NaX at 500°C and *o*-xylene does not isomerize at 480°C

whereas both of these reactions take place over the divalent cation zeolites. Hence, as in the case of the Y zeolites, the Bronsted acidity or electrostatic field introduced by the multivalent cations must play an important role in catalysis over zeolites.

Figure 7 shows the data of Plank, Rosinski, and Hawthorne (3) for gas oil cracking plotted against the Bronsted acidity for calcium, manganese, and rare earth X zeolites. The increase of activity with increasing Bronsted acidity is clear from the limited number of zeolites studied. Changes in activity for pairs of cation zeolites, for example, calcium and sodium, and

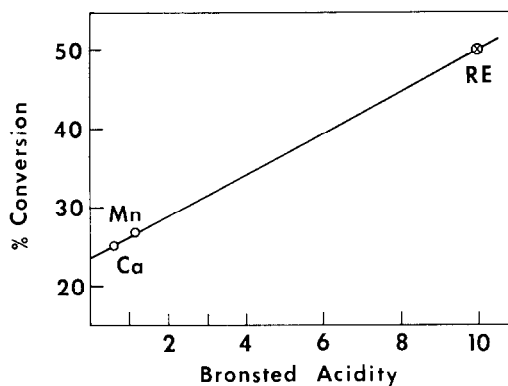


FIG. 7. Bronsted acidity of Ca, Mn, and REX zeolites versus activity for gas oil conversion (conversion data from Ref. 3).

calcium and magnesium, have been shown by several authors (2, 3, 12, 29-31). Increase in activity corresponded in all cases to an increase in Bronsted acidity and hydroxyl content of the zeolite similar to that shown for Y zeolites (8, 9).

A similar trend is also found in this work for the relationship between *o*-xylene isomerization and acidity of alkaline earth X zeolites. A linear relationship is shown in Fig. 8 for reaction at 750 and 900°C. The conversion is also an almost linear function of the ionization potential. In terms of electrostatic field, there is a considerable deviation from a linear relationship suggesting that the calculated electrostatic fields (14, 15) are not a good representation of the zeolite under reaction conditions. The calculations assume bare divalent cations: such cations are unlikely

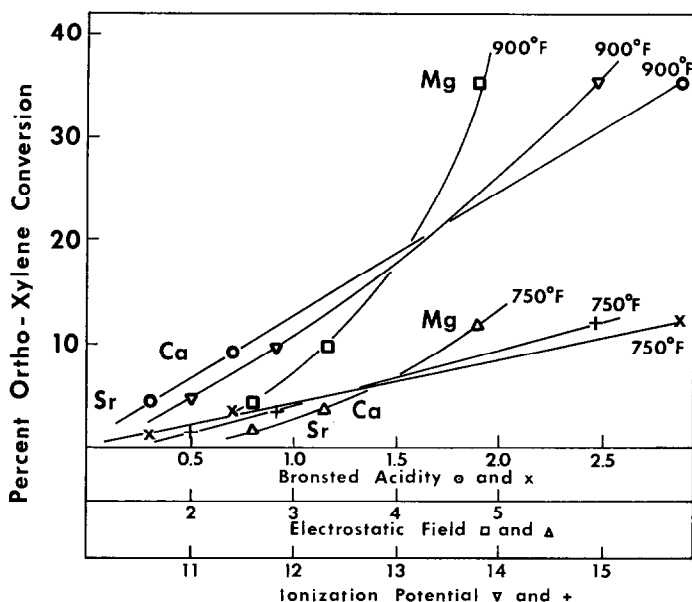


Fig. 8. *O*-xylene conversion versus Bronsted acidity, electrostatic field, and ionization potential of alkaline earth cation X zeolites.

to exist under reaction conditions and a form such as  $\text{MOH}^+$  is more probable. Recently, Huang, Benson, and Boudart (34) have shown that the field in a zeolite with  $\text{MOH}^+$  ions is very low, the original field having served to dissociate water, thus,  $\text{MOH}_2^{2+} \rightleftharpoons \text{MOH}^+ + \text{H}^+$ . Hence, it is unlikely that the residual electrostatic field due to the cations is sufficient to promote reactions and that acidic hydroxyl groups, formed by attachment of the proton liberated above to the lattice, are primary active sites as suggested previously for Y zeolites (5, 9, 10).

The transition metal X zeolites studied do not conform to the simple relationship between acidity and activity. There appears to be no good relationship between the concentration of Bronsted acid sites and catalytic activity although in general, the activity increases with increasing acidity. The catalytic activity is also not related in a simple manner to the electrostatic field or potential. With the exceptions of cadmium and zinc, the catalytic activity increases with increasing electrostatic potential.

The measurements of the activation

energy for the catalytic reaction, however, give an indication that other phenomena may be important. The different activation energy for the transition metal zeolites compared to the alkaline earth zeolites suggests that there is a variation in acid site strength of the hydroxyl groups and/or there is a marked difference in the accessibility of the hydroxyl groups, assuming that hydroxyl groups are still the primary active centers, or other active sites. Differences in acid site strengths have been suggested previously by Richardson (8) with regard to the acidity of alkaline earth Y zeolites. Little has been reported concerning the properties of transition metal zeolites in particular with reference to the cation locations. Angell and Schaffer (35) report that cobalt and nickel have no overwhelming preference for the sites in the hexagonal prisms. Carter *et al.* (41) have studied ethylene adsorption on lithium, sodium, potassium, calcium, barium, cadmium, and silver X zeolites. The heat of adsorption on cadmium and silver was considerably greater than on the other cation forms of the zeolite. Interaction between the  $\pi$ -electrons of the ethylene and the

5s,p orbitals of the cations were invoked together with interaction with the 4d orbitals of silver. Similar interactions may occur with other molecules thus influencing the catalytic activity. Further studies of these zeolites with reference in particular to the cation locations, structural hydroxyl groups, and strengths of acid sites are needed before the current results can be further evaluated.

Difficulties are also found in the understanding of silver X zeolite. Analysis of the sample indicates that the silver exchanges into the zeolite as a monovalent ion. Hence, it is difficult to interpret the catalytic activity and Bronsted acidity in the same manner as used to explain the acidity and activity of alkali and alkaline earth zeolites. As shown by Angell and Schaffer (36) for silver Y zeolite, silver X zeolite has structural hydroxyl groups and, in particular, a hydroxyl frequency near 3640  $\text{cm}^{-1}$  (25). Hence, the presence of the 3640  $\text{cm}^{-1}$  hydroxyl band, Bronsted acidity, and catalytic activity agrees with previous predictions. However, why a monovalent cation zeolite should have a substantial structural hydroxyl group content is difficult to understand. The introduction of hydroxyl groups by dissociation of adsorbed water would not be expected. Furthermore, the study of Eulenberger, Schoemaker, and Keil (37) has shown that the silver ions occupy similar positions to sodium and potassium in the dehydrated Y zeolite. Hence, they possibly occupy similar positions in the X zeolites. Thus similar properties to sodium and potassium might be expected. However, since the Ag(2) sample is less acidic and less catalytically active, it is possible that some hydrolysis is occurring during ion exchange, the amount increasing with decreasing pH. Another possibility is that small amounts of silver metal and hydrogen zeolite are formed by reduction of silver ions (40). Silver metal was detected in the used catalyst.

The results with silver are to be contrasted with those of the other Group 1B cation, copper, studied. No Bronsted acidity and no catalytic activity was observed despite

copper most likely being present as a divalent ion. However, structural collapse of the zeolite is probably the most significant factor with copper zeolite.

In conclusion a study of various cation exchanged X zeolites has shown that the catalytically active forms are Bronsted acids and contain structural hydroxyl groups. Bronsted acid sites are probably the primary acid sites. The alkali cation forms are nonacidic and not catalytically active. The acidity and activity of the alkaline earth forms decreases with increasing cation size. With the exception of copper, the transition metal zeolites studied are Bronsted acids and active catalysts. However, there is no apparent relationship between the concentration of Bronsted acid sites and catalytic activity. It is possible that the acid site strength is important. The monovalent silver X is also a Bronsted acid and catalytically active. Further studies are needed to understand the transition metal X zeolites. The rare earth X zeolite is the most acidic and most active X zeolite catalyst of those studied.

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