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The Nature of Active Sites on Zeolites

VIII. Rare Earth Y Zeolite

JOHN W. WARD

From the Union Oil Company of California, Union Research Center, Brea, California 92621

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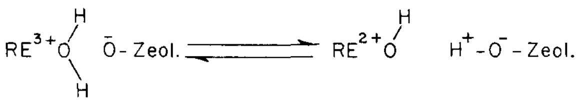
The catalytic activity for *o*-xylene isomerization and the acidity, as measured by infrared studies of chemisorbed pyridine, of rare earth Y zeolite have been investigated. The zeolite is shown to be a Brönsted acid after calcination at 480°C but Lewis acidity is also observed after 700°C calcination. The Brönsted acid sites are believed to be hydroxyl groups similar to those observed in hydrogen and alkaline earth Y zeolites. The hydroxyl groups believed to be associated with rare earth cations are nonacidic with respect to a base of the strength of pyridine. The Brönsted acid site concentration and catalytic activity are intermediate between those of magnesium and hydrogen Y zeolites. There is a good correlation between the Brönsted acidity and catalytic activity of the three zeolites. Hence, Brönsted acid sites seem to be important in zeolite catalysis, but other types of sites may also play an important role.

INTRODUCTION

Previously, the acidities of the hydrogen (decationated), alkali, and alkaline earth ion-exchanged forms of Y zeolites have been investigated and related to the catalytic activity of the zeolites (*1–5*). It was shown that the alkali cation forms were nonacidic and contained no structural hydroxyl groups. On the other hand, the alkaline earth cation and hydrogen forms contained hydroxyl groups and were Brönsted acids if calcined at a temperature insufficient to cause dehydroxylation. On calcination at higher temperatures, Brönsted acid sites were converted into Lewis acid sites. It was suggested that the Brönsted acid sites were certain of the structural hydroxyl groups and it was shown that there was a relationship between the concentration of hydroxyl groups and catalytic activity for cumene dealkylation.

The rare earth forms of Y zeolite have been shown to be active catalysts for many reactions by a number of workers (*6–10*). Several different concepts have been used to explain the activity of these zeolites. Rabo and co-workers (*6, 10, 11*) have suggested that the electrostatic fields associated with the multivalent cations were responsible for the catalytic activity. It was, however, also suggested that hydroxyl residues in trivalent cation zeolites might be proton donors. Lewis acid sites have been proposed as active sites in zeolites by Turkevich, Nozaki, and Stamires (*12*) and by Boreskova, Lygin, and Topchieva (*13*). On the other hand, Venuto, Hamilton, and Landis (*14*) have suggested that protonic acid sites are important in catalytic reactions. They propose that the acid sites are formed by the following mechanism:



$$\mathrm{RE}^{3+}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{O}}}\quad \bar{\mathrm{O}}\text{-Zeol.} \rightleftharpoons \mathrm{RE}^{2+}\overset{\mathrm{H}}{\mathrm{O}}\quad \mathrm{H}^{+}\text{-}\mathrm{O}^{-}\text{-Zeol.}$$

A similar hydrolysis has been also suggested by Plank for rare earth zeolites (*15*).

This paper discusses infrared spectral observations and catalytic activity measurements on a rare earth Y zeolite. The resulst of acidity and activity measurements are related to each other and compared with previously reported results for hydrogen, alkali, and alkaline earth Y zeolites.

EXPERIMENTAL

Materials. The composition of the sodium Y starting material was Na 10.3%, SiO_2/Al_2O_3 ratio 4.9. The nitrogen surface area ($P/P_0 = 0.02$) was 901 m^2g^{-1}. X-Ray diffraction examination showed the sample to be highly crystalline. The rare earth form was prepared by repeated ion-exchange with excess 10% aqueous solutions of mixed rare earth chlorides. The rare earth chloride mixture was supplied by American Potash and Chemical Company, Rare Earth Division. A typical analysis of the mixture for major components was CeO_2, 47.8; La_2O_3, 24.2; Nd_2O_3, 18.2; Sm_2O_3, 2.8; Gd_2O_3, 0.9. The rare earth-exchanged zeolite contained 0.81% residual sodium and had a surface area of 776 m^2g^{-1}.

Pyridine was Allied Chemical Research Grade. The heart cut was collected after distillation from sodium hydroxide and dried over 4A molecular sieve. It was further dried by the freeze–pump–thaw technique. Piperidine was obtained from Matheson, Coleman, and Bell and similarly purified. *o*-Xylene was Eastman Research Grade and used without further purification.

Apparatus and sample preparation. Spectroscopic studies were conducted as reported previously, except all measurements were made with a Cary-White 90 Spectrometer (*3*). The flow microreactor previously described was also used (*3*).

Technique. For infrared studies, the sample wafers were placed in the furnace end of the infrared cell and evacuated. The temperature was raised to 110°C and held until a vacuum of 10^{-4} torr was obtained. The temperature was then slowly raised to 480°C and maintained for 6 hr. The sample was cooled to room temperature and its spectrum recorded between 4000 and 2800 and 1700 and 1400 cm^{-1}. Excess pyridine was adsorbed on the sample (i.e., sufficient to leave a small residual pressure of pyridine in the gas phase) and allowed to equilibrate for 2 hr. The excess pyridine was then desorbed by evacuation for 2 hr at 250°C. Spectra of the structural hydroxyl groups were also observed as a function of calcination temperature.

For catalytic activity measurements, the sample, as 20-mesh granules, was dried in the reactor in a stream of flowing helium. The temperature of the reactor was slowly raised from ambient to 480°C and then maintained for 3 hr. The catalyst was then cooled to 200°C and the helium stream diverted through an *o*-xylene saturator. The isomerization of the *o*-xylene was measured for a series of temperature. The conversion (which was kept below 40%) was measured in terms of the concentration of *o*-xylene in the products. A plot of log conversion against $1/T$ was made. For comparison purposes, the activities of the MgY, NaY, and HY samples reported on previously (*2*, *3*) were also measured under the same conditions. No detectable loss of zeolite structure was observed after the activity tests.

RESULTS

The infrared spectra in the hydroxyl stretching region of the rare earth Y zeolite after calcination at several temperatures are shown in Fig. 1. Distinct hydroxyl groups are seen with frequencies at 3740, 3640, and 3522 cm^{-1}. These frequencies are similar to those reported by Rabo, Angell, Kasai, and Schomaker (*11*) for CeY. After calcination at 250°C, an absorption band is also observed at 3615 cm^{-1} while after calcination at 680°C, no distinct hydroxyl absorption bands are observed.

On chemisorption of pyridine, it is seen in Fig. 2 that the bands at 3740 and 3640 cm^{-1} interact with the pyridine, whereas the 3522-cm^{-1} band does not. A similar interaction is observed for piperidine chemisorption.

Figure 3 shows the absorption spectrum of chemisorbed pyridine in the 1700 to 1400 cm^{-1} region. The characteristic band due to pyridinium ions near 1545 cm^{-1} is observed. A band due to pyridine–cation interaction is also seen near 1443 cm^{-1}. A weak band near 1451 cm^{-1} due to coordinately bound pyridine (i.e., pyridine adsorbed on Lewis acid sites) is also seen for the sample calcined at 480°C. At higher

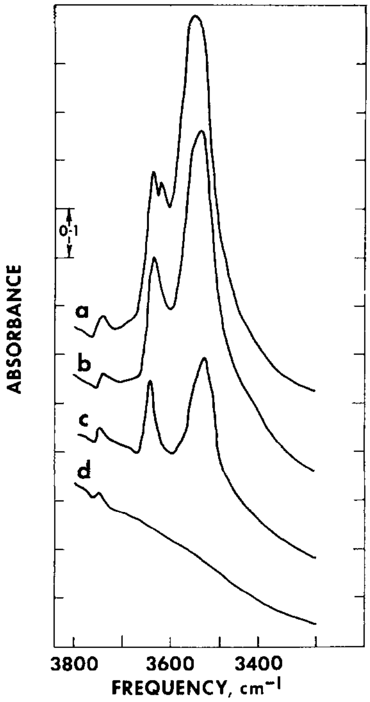


Fig. 1. Infrared spectra of hydroxyl groups on rare earth Y zeolites after calcination at various temperatures: (a) 250°C, (b) 340°C, (c) 450°C, (d) 680°C.

calcination temperatures, e.g., 680°C, the 1451-cm^{-1} band increases in intensity at the expense of the 1545-cm^{-1} band in a manner analogous to that reported for hydrogen Y zeolite (*2*).

Data for the isomerization of *o*-xylene over several catalysts are given in Table 1. The data were calculated from the log conversion versus $1/T$ plots. The Brönsted acidity (peak height 1545-cm^{-1} band/sample mass) is also given in Table 1 for the same samples. These catalysts were described previously (*2, 3*).

TABLE 1

Catalytic Activity and Brönsted Acidity of Y Zeolites

Zeolite	Brönsted acidity Peak ht. 1545-cm^{-1} band	Temperature for 25% conv. of *o*-xylene
	Sample mass	
NaY	0	>500°
MgY	6.9	284°
REY	11.3	260°
HY	15.8	230°

Discussion

Structural Hydroxyl Groups

The nature of the hydroxyl groups on rare earth Y zeolite has been discussed previously (*16*). The 3740-cm^{-1} band can be attributed to Si–OH groups which terminate the aluminosilicate lattice. The absorption band at 3640 cm^{-1} probably represents hydroxyl groups attached to silicon atoms similar to those present in the alkaline earth (*3*) and hydrogen forms (*2, 4, 5*). Such hydroxyl groups could be generated if the rare earth forms undergo a hydrolytic fission similar to that suggested by Venuto, Hamilton, and Landis (*14*) or as suggested by several workers for alkaline earth cations (*3, 11, 17, 18*).

$$RE(OH_2)_2^{3+} \rightleftharpoons REOH(H_2O)^{2+} + H^+ \rightleftharpoons RE(OH)_2^+ + 2H^+$$

A similar hydrolysis of rare earth ions occurs in aqueous solutions (*7*). In the case of the trivalent ions in zeolites, it is possible for the hydrolysis to take place in two stages. The protons liberated are then thought to attack the lattice so as to form silanol groups. The hydroxyl groups attached to the rare earth cations are thought to give rise to the absorption band near 3522 cm^{-1} (*11, 16*). The absorption band near 3615 cm^{-1} is probably due to physically adsorbed water (*16*).

The spectra in Fig. 1 show that as the calcination temperature is increased, the population of hydroxyl groups declines progressively until after calcination at 680°C, very few hydroxyl groups remain. Similar observations at 500° and 700°C have been reported by Rabo *et al.* (*11*). The dehydroxylation is probably similar to that discussed previously for divalent cation zeolites (*3*) except that two or three ion-exchange sites may be involved depending on the chemistry of the rare earth hydrolytic reaction.

Addition of pyridine to the calcined rare earth zeolites yields interesting results. Addition of excess pyridine eliminates most of the absorption bands due to hydroxyl groups, indicating that extensive hydrogen bonding is occurring. However, as shown in Fig. 3, on evacuation at 250°C, the 3522-cm^{-1} band is restored. This observation indi-

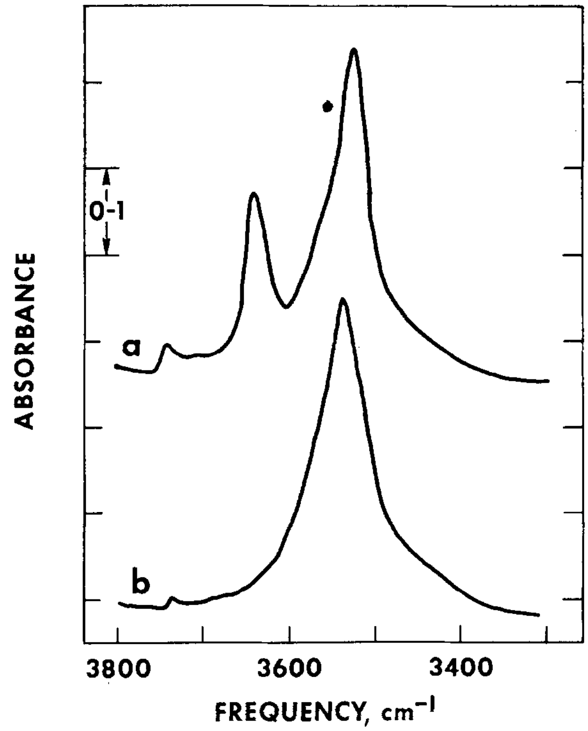


FIG. 2. Infrared spectra of hydroxyl groups on rare earth Y zeolite: (a) zeolite calcined at 480°C, (b) pyridine chemisorbed and evacuated for 2 hr at 250°C.

cates that the hydroxyl groups represented by the 3522-cm^{-1} band are nonacidic with respect to a base of the strength of pyridine. The nonacidity or very weak acidity of these hydroxyl groups is confirmed by the lack of interaction with the stronger base, piperidine, Hydroxyl groups considered to be attached to magnesium and calcium cations have similarly been shown to be nonacidic (*16*, *19*). Hence, unless very weak acid sites are responsible for catalytic activity, hydroxyl groups attached to multivalent cations are not important centers in acid-catalyzed reactions. At this stage of understanding, it seems that the 3640-cm^{-1} band type of hydroxyl groups are similar to those present on hydrogen and alkaline earth zeolites. Since the 3522-cm^{-1} band hydroxyl groups do not protonate piperidine, they must have weaker acidic properties than the 3540-cm^{-1} type hydroxyl groups of hydrogen Y zeolite (*4*). However, since the 3522-cm^{-1} band hydroxyl groups do hydrogen-bond to pyridine and piperidine, they must be located in accessible positions or be mobile.

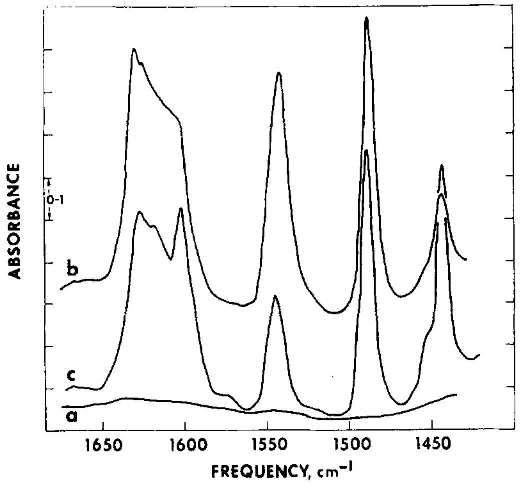


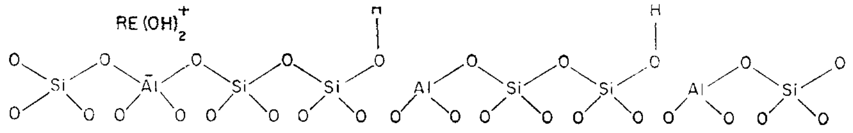
FIG. 3. Infrared spectra of rare earth Y zeolite: (a) calcined zeolite, (b) pyridine chemisorbed on 480°C calcined zeolite followed by evacuation at 250°C, (c) pyridine chemisorbed on 680°C calcined zeolite followed by evacuation at 250°C.

The Nature of Acid Sites

The use of the spectrum of chemisorbed pyridine to characterize the surface of catalytic solids has been reported several times (*1–5*, *20*, *21*) and the assignment of the absorption bands well established. In brief, a band near 1545 cm^{-1} is indicative of Brönsted acidity while a band near 1450 cm^{-1} is indicative of Lewis acidity. An absorption band near 1450 to 1440 cm^{-1} can also occur due to interaction of pyridine with cations in the solid. Previously, it was shown that alkali cation zeolites are nonacidic while alkaline earth zeolites are Brönsted or Brönsted and Lewis acids depending on the calcination temperature (*1*, *3*). The spectra shown in Fig. 3 show that after calcination at 480°C, rare earth Y zeolite is mainly a Brönsted acid. Only a very weak absorption band near 1450 cm^{-1} is observed, indicating that few Lewis acid sites are present. The band near 1443 cm^{-1} is probably due to pyridine interaction with the rare earth cations. On calcination at higher temperature, the absorption band of pyridine at 1451 cm^{-1} is observed, indicating the presence of Lewis acid sites, while the 1545-cm^{-1} band, indicative of Brönsted acid sites, has decreased substantially in intensity compared to the 480°C calcined sample band intensity (from 11.3 to 5.9). These observations are probably indicative of dehydroxylation of the zeolite structure similar to that proposed for hydrogen Y zeolite (*2*, *5*, *6*, *22*) whereby Brönsted acid sites are converted to Lewis acid sites.

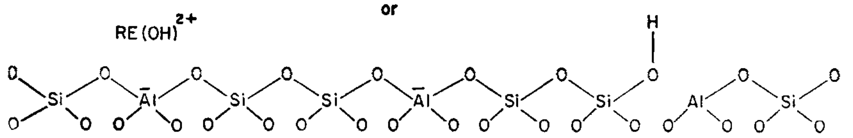
In Table 1, the Brönsted acidity of rare earth Y zeolite is compared with that of sodium, magnesium, and hydrogen Y zeolites. It is seen to be intermediate between hydrogen and magnesium, which was previously shown to be the most acidic alkaline earth zeolite (*1*, *3*).

It remains now to interpret these observations in terms of the zeolite structure. As mentioned above, it is possible for the rare earth cation to ion-exchange into the zeolite in two ways:



(1)

or



(2)

Scheme (2) is similar to that suggested by Rabo *et al.* (*11*) and Venuto *et al.* (*14*). It resembles the structure proposed for alkaline earth cation forms (*3*, *17*). If this mechanism occurred, a similar hydroxyl group content and Brönsted acidity to magnesium Y would be observed. However, the hydroxyl content of the 3640-cm^{-1} band type hydroxyl groups, the hydroxyl groups attached to the cation, and the Brönsted acidity are both greater than that of magnesium Y zeolite but less than that of hydrogen Y. This would be expected if scheme (1) occurred. Moreover, if complete hydrolysis of the rare earth cation is assumed, scheme (1) would give an acidity of about two-thirds of that of hydrogen Y whereas scheme (2) would give only one-half. The former is more closely observed.

It can be concluded, then, that for every six exchange sites, a maximum of six Brönsted acid sites are formed in hydrogen Y, four in rare earth Y, and three in magnesium Y.

Relationship between Acidity and Catalytic Activity

The catalytic activities for *o*-xylene isomerization of the magnesium, rare earth, and hydrogen Y zeolites are listed in Table 1. The activities are compared in terms of temperature required to give 25% conversion of the *o*-xylene. Again, it is seen that the rare earth form is intermediate between the magnesium and hydrogen forms. In Fig. 4, the temperature for 25% conversion is plotted against the Brönsted acid site concentration. A good correlation between acidity and activity is observed, confirming the relationship found previously for alkaline

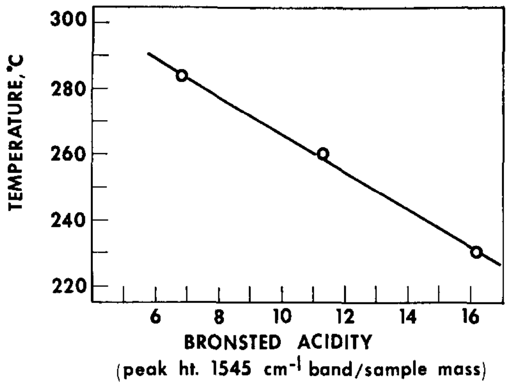


FIG. 4. Temperature for 25% conversion of *o*-xylene as a function of zeolite acidity.

earth forms (*3*). Although these results indicate a relationship between Brönsted acidity and catalytic activity, they do not rule out the possibility of a second type of site playing an important role. Such a phenomenon is suggested by recent results which show maximum catalytic activity at temperatures of 600–650°C (*7*, *8*, *23*). At these temperatures, the Brönsted acidity has declined considerably from its maximum. Studies of the acidity of hydrogen Y (*2*) and magnesium hydrogen Y zeolite (*24*) have shown that there are approximately equal concentrations of Brönsted and Lewis acid sites in the 600–650°C temperature range. Hence, the possibility of a mechanism involving Brönsted and Lewis acid sites simultaneously or sequentially cannot be ruled out.

In conclusion, the rare earth Y zeolite contains several types of structural hydroxyl groups and is a Brönsted acid. The Brönsted acid sites are hydroxyl groups similar to those in hydrogen Y zeolite but the hydroxyl groups attached to the rare earth cations are nonacidic. The acidity and catalytic activity are intermediate between those of magnesium and hydrogen Y zeolites. The Brönsted acid sites seem to be important in catalysis but other types of sites may also be important.

Note added in proof. Although these results suggest that hydrogen zeolite should be the ultimate zeolite catalyst, measurements of catalytic acidity and activity of MgHY, REHY, and HY [Hansford and Ward, *J. Catalysis* **13**, 316 (1969); **10**, 34 (1968)] indicate that the cation could have a promoting effect or influence the acid strength [Richardson, *J. Catalysis* **9**, 182 (1967); **10**, 275 (1968); Hirschler, *J. Catalysis* **2**, 428 (1963); **11**, 275 (1968)]. Thus, although these three zeolites have the same concentration of acid sites measured by pyridine adsorption, the rate constants for xylene isomerization at 260°C are 49, 122, and 45, respectively.

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