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The Nature of Rare-Earth Exchanged Y Zeolites

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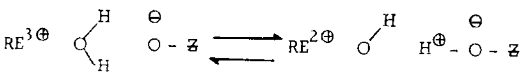
Thermogravimetric analyses of a series of rare-earth exchanged Y zeolites show that, stochiometrically, one molecule of water is associated with each rare-earth cation. Two bands in the hydroxyl stretching region of the infrared spectra of the rare-earth exchange zeolites, at 3640 and 3520 cm^{-1}, have previously been attributed to hydroxyl groups derived from the hydrolysis of the rare-earth cations. However, the relative intensities of these bands are shown to change with the degree of rare-earth exchange. Since an hydrolysis reaction would produce the hydroxyl groups in equal amounts, it is concluded that the band at 3640 cm^{-1} is not entirely a result of hydrolysis but also of hydrogen-ion exchange during the treatment of the zeolite with the acidic rare-earth salt solution.

INTRODUCTION

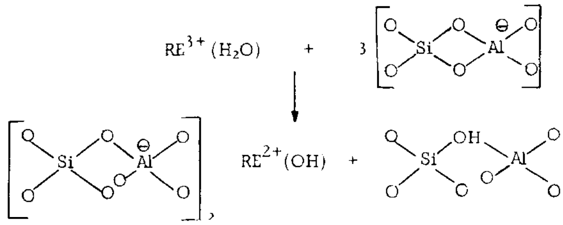
The rare-earth exchanged form of Type Y zeolite has been shown to be an active catalyst for many reactions (*1–3*). The nature of the activity of this cation-exchanged form has been the subject of recent studies (*4*, *5*). It has been proposed that the catalytic activity may be explained in terms of the hydrolysis of the rare-earth cation, yielding protons (*2–5*). The existence of protonic acid sites allows a correlation to be drawn between the catalytic activities of rare-earth exchanged Y and the deaminated derivative of ammonium exchanged Y.

Venuto, Hamilton, and Landis proposed that the hydrolysis of the rare-earth cations takes place by the following mechanism (*2*):



$$RE^{3\oplus}\ O\langle^{H}_{H}\quad \overset{\ominus}{O}-Z \rightleftharpoons RE^{2\oplus}\ O^{\diagup H}\quad H^{\oplus}-O-Z$$

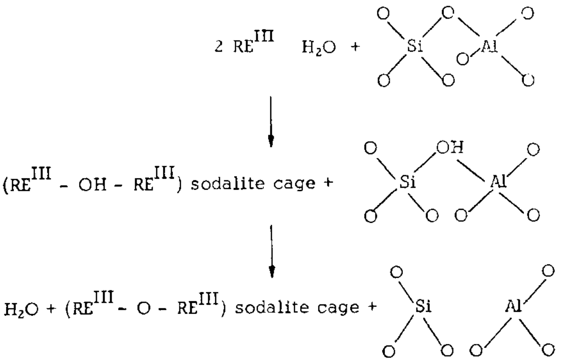
Evidence for the existence of two distinct types of hydroxyl groups is provided by infrared studies. Ward (*6*) and Rabo *et al.* (*7*) have reported the presence of two bands with frequencies at approximately 3640 and 3520 cm^{-1} in the hydroxyl stretching region of rare-earth exchanged Y after calcination. Thus the following scheme may be written:



SCHEME I

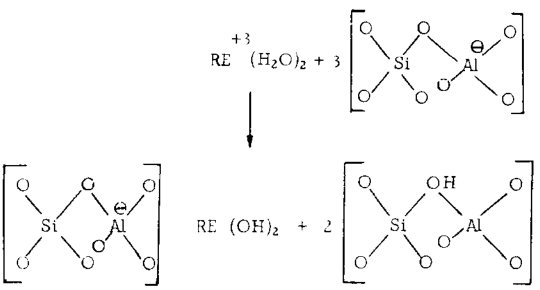
Rabo *et al.* proposed that only one water molecule is present in each sodalite cage and that the hydroxyl group associated with the rare-earth cation is shared by two rare-earth cations (*4*). Upon subsequent dehydroxylation, the resulting structure is, in effect, stabilized by an oxide ion removed from the framework. Such a scheme would require a H_2O to RE^{3+} ratio of 0.5.

An estimation of Bronsted acidity by pyridine adsorption carried out by Ward (*6*), indicated that the rare-earth exchanged



SCHEME II

form exhibits 2/3 of the acidity of deaminated Y. Thus, the following scheme was proposed, requiring a H_2O to RE^{3+} ratio of two.



SCHEME III

Accordingly, a study of the H_2O to RE^{3+} stoichiometry was undertaken using a series of rare-earth exchanged Y zeolites in order to determine the extent and nature of the hydrolysis of the rare-earth cation.

EXPERIMENTAL

Materials

The rare-earth exchanged zeolites used in this study were prepared from pure Type Y Molecular Sieves synthesized in our laboratories. Prior to ion exchange, these materials were extensively washed with a 20% aqueous solution of sodium chloride at reflux temperatures. The rare-earth ion exchanged forms were prepared by repeatedly contacting the zeolite powders with a 10% aqueous solution of lanthanum chloride (American Potash and Chemical Company); other samples were prepared using a mixture of the rare-earth chlorides, containing 47% cerium (American Potash and Chemical Company). The chemical analyses of these samples are given in Table 1.

Thermogravimetric Analyses

A DuPont Model 950 Thermogravimetric analyzer was used under the following conditions: The sample was purged with air at 3 liters/hr; the heating rate was 18°C/min; and sample weight was 22.80–24.00 mg.

TABLE 1
CHEMICAL ANALYSES

Atom ratios			
Si/Al	Na/Al	La/Al	Cation deficiency/Al
2.5	0.42	0.55	0.03
2.5	0.29	0.64	0.07
2.5	0.23	0.74	0.03
2.4	0.16	0.83	0.01
2.4	0.01	0.98	0.01
2.4	0.01	0.97 (RE/Al)	0.02

Infrared Analyses

The samples were run as self-supporting wafers and scanned on a Perkin-Elmer Model 621 Spectrophotometer from 4,000 to 12,000 cm^{-1}. The wafers had a weight of ~6 mg/cm^2. Each sample was heated for two hours in a cell essentially the same as that described by Angell and Shaffer (*8*). Heating was carried out at various temperatures while the cell was purged with dry air after which the spectrum was obtained at room temperature.

RESULTS

The quantitative estimation of the amount of water associated with each rare-earth cation was carried out using thermogravimetric analysis. The data obtained from a series of lanthanum and mixed rare-earth exchanged Y zeolites having SiO_2–Al_2O_3 molar ratios of approximately 5.0, are shown in Tables 2 and 3. Table 2 shows that the weight loss between 350–970°C gives a H_2O to La^{3+} ratio of approximately unity. The weight loss over the temperature range 350–970°C was chosen as representatives of that occurring during the dehydroxylation of the water molecules or hydroxyl groups associated with the rare-earth cations, based upon the following observations. A variation in the intensities of the adsorption bands in the hydroxyl stretching region of the infrared spectrum at 3640 and 3520 cm^{-1}, shown in Fig. 1, indicates that under isothermal conditions, dehydroxylation commences at approximately 350°C, occurs to a major extent between 400–600°C, and is essentially complete by 700°C. That complete dehydroxylation has taken place during the 350 to 970°C portion of the thermogram was confirmed by the absence of any further weight loss during a subsequent isothermal treatment of the samples in the thermal analyzer at 970°C for 1 hr. The infrared

TABLE 2
TGA DATA—DEHYDROXYLATION BETWEEN 350–970°C

% Rare-earth exchange	% Wt loss (350–970°C)	Mole % H_2O	At. % rare earth	Ratio H_2O/RE
0	0.05	—	—	—
55 La	1.25	0.0695	0.0690	1.01
64 La	1.50	0.0834	0.0808	1.03
74 La	1.50	0.0835	0.0930	0.90
83 La	2.00	0.1250	0.1076	1.03
98 La	1.50	0.1034	0.0994	1.04
97 RE	1.85	0.1028	0.0994	1.03

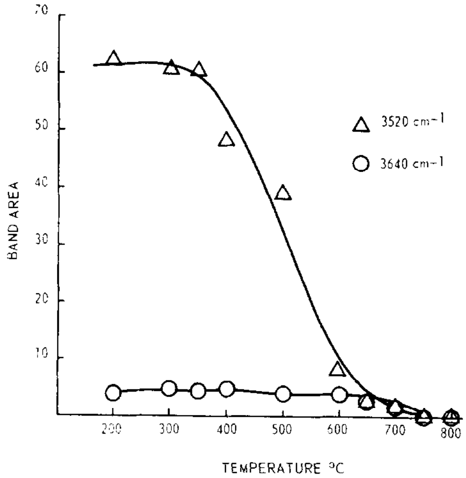


FIG. 1. Variation in band intensities of 98% lanthanum–exchanged Y with temperature.

TABLE 3
TGA DATA—DEHYDROXYLATION BETWEEN 350–970°C 64% LANTHANUM–EXCHANGED Y

Pretreatment	% Wt loss (350–970°C)	Mole % H_2O	At. % Lanthanum	Ratio H_2O/La
None	1.50	0.0834	0.0808	1.03
100°C – 16 hr	1.57	0.0875	0.0808	1.07
250°C – 16 hr	1.50	0.0834	0.0808	1.03
350°C – 16 hr	1.65	0.0916	0.0808	1.13
900°C – 1 hr	1.55	0.0860	0.0808	1.07

spectra of samples removed from the thermogravimetric analyzer at 350°C did not exhibit adsorption at 1645 cm^{-1}; this band has been attributed to the presence of physically adsorbed water (*6*). In order to confirm that the weight loss is due to water associated with the rare-earth cations and not to traces of physically adsorbed water, not detected by infrared analysis, the weight loss over 350 to 970°C of 64% lanthanum exchanged sample was determined after various pretreatments. These data, together with a sample heated to 900°C and subsequently rehydrated under ambient conditions, are given in Table 3 and show that the H_2O to RE ratio remains approximately unity.

The infrared spectra of a series of rare-earth exchanged Y zeolites after calcination at 400°C are shown in Fig. 2. Three bands in the hydroxyl stretching region at 3740, 3640, and 3520 cm^{-1} are observed in agreement with other studies (*6*, *7*, *9*). The relative intensities of the 3640 and 3520 cm^{-1} bands vary with degree of rare-earth exchange. At high levels of rare-earth exchange, the 3640 cm^{-1} band decreases significantly. The infrared spectra in the hydroxyl stretching region of a 64 and a 98% lanthanum exchanged Y after calcination at different temperatures are shown in Figs. 3 and 4. Both the 3640 and the 3520 cm^{-1} bands are substantially removed by 700°C. Complete reconstitution of the 3520 cm^{-1} may be achieved by the rehydration of these samples for 16 hr at room temperature under ambient conditions followed by calcination at 400°C. Under these conditions, the 3640 cm^{-1} band in the spectra of both the 64 and 98% lanthanum exchanged materials is only partially reconstituted as shown in Fig. 5. The thermal and infrared studies did not detect any difference between the lanthanum materials and the mixed rare-earth exchanged materials.

FIG. 2. Infrared spectra of hydroxyl groups on rare-earth exchanged Y zeolite with varying rare-earth contents and after calcination at 400°C.

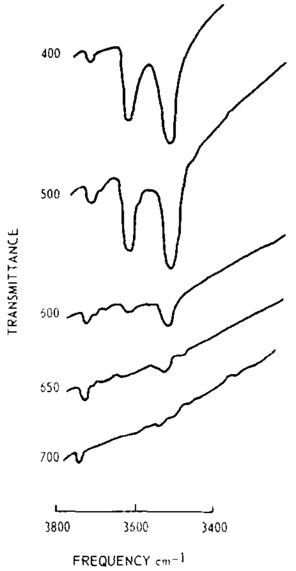


FIG. 3. Infrared spectra of hydroxyl groups on a 64% lanthanum-exchanged Y after calcination at various temperatures.

DISCUSSION

It has been pointed out that the hydroxyl groups present in rare-earth ex-

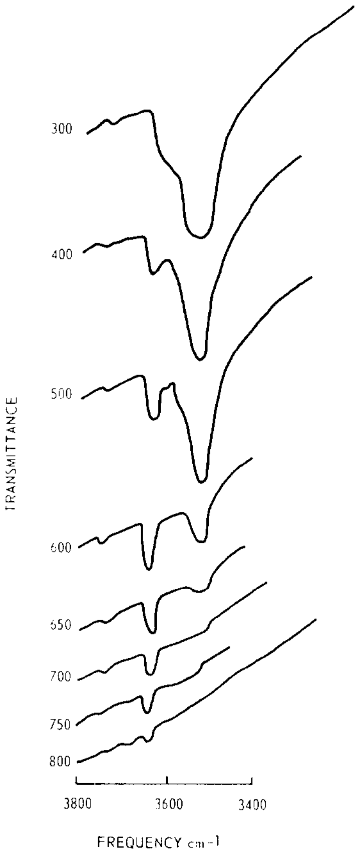


FIG. 4. Infrared spectra of hydroxyl groups on a 98% lanthanum-exchanged Y after calcination at various temperatures.

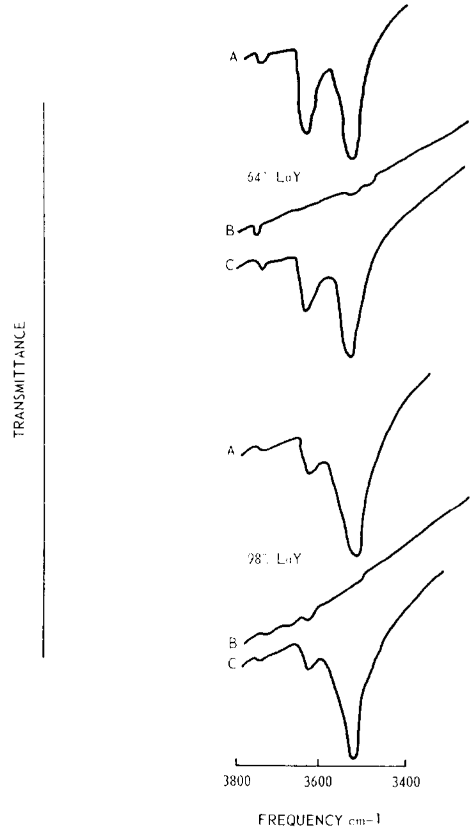


FIG. 5. Infrared spectra of hydroxyl groups on lanthanum-exchanged Y zeolite: (A) Calcined at 400°C; (B) calcined at 800°C; (C) treated with water vapor at room temperature and subsequently calcined at 400°C.

changed Y must originate after rare-earth cation exchange has taken place and probably during the dehydration of the zeolite (*4*). If this were not the case, and cation hydrolysis takes place during ion exchange, the ratio of equivalents of zeolite cations to aluminum atoms would be greater than unity. The thermogravimetric data in Tables 2 and 3 show that overall, one molecule of water is associated with each rare-earth cation. Thus Scheme II, requiring but one water molecule for two rare-earth cations must be discounted. These data would also cast doubt on the validity of Scheme III. Although the water–rare-earth cation stoichiometry could be satisfied by only 50% of the cations being associated with two molecules of water, the principal reason for proposing this scheme was to account for the Brönsted acidity of the rare-earth exchanged Y being ⅔ that of deaminated Y (*5*).

That one molecule of water has been shown to be associated with each rare-earth cation is not proof that hydrolysis takes place, and an examination of the infrared data is not consistent with a simple hydrolysis reaction. The hydrolysis by a water molecule of a rare-earth cation, according to the proposed schemes, should yield two types of hydroxyl groups. The infrared spectra in Fig. 2 show three bands to be present in the hydroxyl stretching region. The band at 3740 cm^{-1} is present to varying degrees in all cationic forms of Y and may be attributed to the presence of amorphous material. The band at 3520 cm^{-1} has been assigned to the hydroxyl group attached to the rare-earth cation

(*6*, *7*). The protons, liberated during the hydrolysis, are thought to react with a lattice oxygen and give rise to the band at 3640 cm^{-1} (*7*).

It has been proposed that this hydroxyl group is similar to that existing in deaminated Y and occurs at the same frequency (*4*, *5*). The hydrolysis of the rare-earth cations, even if the extent of hydrolysis is incomplete, should yield both hydroxyl groups at 3640 and 3520 cm^{-1} in equal amounts. Even though the extinction coefficients of these two bands may be significantly different, their relative intensities should be constant. The published spectra show that this is not the case (*4*, *6*, *9*). The spectra in Fig. 2 of different rare-earth exchange levels show the 3640 cm^{-1} band to decrease with increasing rare-earth exchange. The variation in the ratio of the intensities of the 3640 cm^{-1} and 3520 cm^{-1} bands as a function of the degree of rare-earth exchange is given in Fig. 6. These data show that samples with rare-earth exchange levels over 90% exhibit negligible adsorption at 3640 cm^{-1} compared to that at 3520 cm^{-1}. The relatively low adsorption at 3640 cm^{-1} in the spectra of highly exchanged samples would suggest that the 3640 cm^{-1} band present at lower levels of exchange is not entirely due to cation hydrolysis. An alternative explanation of the variation of the ratio of these two hydroxyl groups with rare-earth exchange level could be that both the species RE^{3+} (H_2O) and RE^{2+} (OH) have similar and thus unresolved hydroxyl stretching frequencies and that only partial hydrolysis takes place. However, if this were so, a band due to physically adsorbed water should be present at 1645 cm^{-1}; this was not observed at temperatures above 350°C.

The effect of calcination temperature on the spectra of the hydroxyl stretching region is shown in Fig. 3. Both the 3520 and 3640 cm^{-1} are almost completely removed by 700°C in agreement with previous studies (*6*, *7*). Rehydration at room temperature with a water saturated nitrogen purge followed by calcination to 400°C completely reconstituted the 3520 cm^{-1} bands, but only partially restored the 3640 cm^{-1} bands, Fig. 5.

Cation-exchange studies cast doubts about the 3640 cm^{-1} bands being derived from the hydrolysis of the rare-earth cation. The protons liberated by the hydrolysis of the rare-earth cation should be capable of ion exchange if they are similar to those known to be present in deaminated Y or mineral acid exchange Y (*10*). If hydrolysis of the rare-earth cations with one molecule of water per cation according to Scheme I is envisaged, then 33% of the structural aluminum atoms should be associated with exchangeable hydrogen ions. Reionexchange of a 98% lanthanum Y at room temperature with NH_4Cl solution introduced three ammonium cations for each rare-earth cation removed from the zeolite; the equivalent rare-earth plus ammonium cation to aluminum atom ratio never exceeded unity. Under the same conditions, at least 70% of the cation sites of deaminated Y may be exchanged with ammonium cations. These data would in-

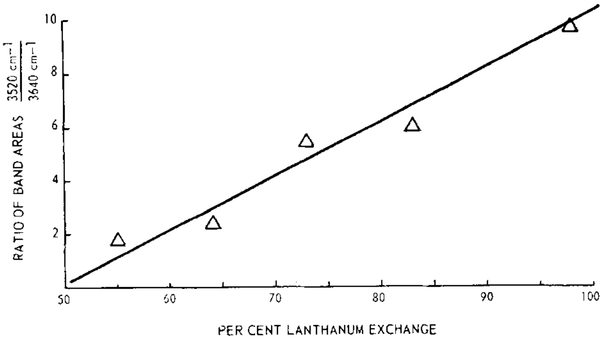


FIG. 6. Variation in the ratio of band intensities after calcination at 400°C.

dicate that if an hydrogen ion is liberated during rare-earth cation hydrolysis, it is not the same as that existing in deaminated Y. An alternative explanation is that hydrolysis is reversible during the dehydration and subsequent rehydration of the zeolite,

$$\underset{\text{hydrated form}}{RE^{3+}(OH_2)} \rightleftharpoons \underset{\text{dehydrated form}}{RE^{2+}(OH) + H^+},$$

and that both hydrolysis and some hydrogen ion exchange contribute to the intensity of the band at 3640 cm^{-1}. This explanation would be compatible with both the infrared and ion exchange studies. The hydrogen ion-exchange must originate during the rare-earth ion exchange step. According to the literature, the rare-earth forms of Type Y zeolite are usually prepared, as in this study, by repeatedly contacting sodium Y with an excess of a 10% aqueous solution of the rare-earth chlorides or lanthanum chloride. The pH of such solutions is approximately 4.5. A mineral acid solution of this pH can effectively remove sodium cations from NaY; indeed, at least 20% of the sodium cations may be removed from NaY by washing extensively with distilled water. However, a determination of cation deficiency from wet chemical analysis of rare-earth exchanged zeolites is an insufficiently accurate estimation of hydrogen ion exchange. The pH of a zeolite slurry in water is typically between 9.0–9.5 if the zeolite is well-washed. A less thoroughly washed sample containing residual sodium hydroxide and sodium silicate from its synthesis may have a pH as high as 12.0. Rare-earth exchange of the latter material causes precipitation of the rare-earth hydroxide and possibly the formation of insoluble rare-earth silicates. Thus even though the ratio of the zeolite cations to aluminum approaches unity, it is still highly possible that proton exchange is counterbalanced by rare-earth hydroxide precipitation.

It is suggested that the sodium removal from the zeolite during the cation–exchange step, is effected by both rare-earth cations and hydrogen ions. After 75% of the sodium cations have been displaced, the remaining 25% are progressively more difficult to displace. Above this exchange level, the more selective rare-earth cation displaces both the sodium and the hydrogen ion until nearly complete occupancy of the zeolite exchange sites by rare-earth cation is achieved. At this point, the cation deficiency is at a minimum and the intensity of the 3640 cm^{-1} band is principally that due to rare-earth hydrolysis alone.

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