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Acid Sites in Rare-Earth Exchanged Y-Zeolites

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The effect of drying of rare-earth (RE) exchanged Na–Y-zeolites on the formation of acid sites was studied using well-known analytical techniques as the Karl Fischer titration and the $LiAlH_4$ reaction.

It was found that during drying of RE–Y-zeolite from total water content of 30–14% d.b. hydrated RE ions move from the supercages into the sodalite cages, while the formation of acidic hydroxyl groups takes place during zeolite drying from total water contents of 14–10% d.b. Each RE ion in the zeolite produces one acidic hydroxyl group in the supercages. Prolonged drying of RE–Y-zeolite results in dehydroxylation.

For RE–Y-zeolite with a SiO_2/Al_2O_3 molar ratio of 5.0, and 75% of the sodium exchanged by RE, the density of acidic OH groups (Brönsted sites) was found to be 7×10^{20} sites/g, which is about 70 times higher than for amorphous silica–alumina catalyst.

INTRODUCTION

Catalytic activity of crystalline aluminosilicates is generally attributed to acid sites on the zeolite surface. Plank (*1*), Venuto *et al.* (*2*) and Benesi (*3*) have demonstrated that acidic hydroxyl groups (Brönsted sites) are the source of catalytic activity. Pickert (*4*) however suggested that electrostatic fields are the main reason for activity. The occurrence of Brönsted and Lewis acid centers in zeolites has been shown by Ward (*5*) who concluded that only acidic hydroxyl groups are active in cracking of hydrocarbons. This is in accordance with Rabo's (*6*) interpretation of his experiments. Rabo found that dehydroxylated La^{3+}–Y-zeolites have low activities in butane cracking. The origin of acid centers in zeolites has been proposed by Plank (*1*) who postulated a reaction of the type:

$$[RE(H_2O)]^{3+} \rightarrow [RE(OH)]^{2+} + H^+$$

with the rare earth aluminosilicate being inactive and the protonic site being active. Rabo *et al.* (*6*) assumed that this protonic site is probably formed during the dehydration of the zeolite rather than by ion exchange with already hydrolyzed rare-earth ions. From X-ray structural analysis Smith *et al.* (*7*) concluded that $[RE(OH)]^{2+}$ species exist after dehydration of RE–Y-zeolite.

Most of the foregoing conclusions and speculations are based on determination of hydroxyl groups by infrared spectroscopy, which provides semiquantitative information. Besides, (due to broad overlapping bands of water in the IR spectrum) only relatively dry zeolites can be studied by IR techniques.

The present study deals with the quantitative measurement of water and acidic hydroxyl groups in Y-zeolites using reagents which are expected to be unable to penetrate into the sodalite cages of the zeolite crystal. If so, the techniques used will discriminate between groups present in the larger supercages and groups present in the smaller sodalite cages and hexagonal prisms. The analytical methods used were: (i) determination of loss of weight on ignition (LOI); (ii) reaction with Karl Fischer reagent (KF); (iii) reaction with $LiAlH_4$. Table 1 shows the various methods and the groups expected to be determined by them.

TABLE 1
MEASUREMENT OF WATER AND HYDROXYL GROUPS IN Y-ZEOLITES

Group	Position	Measured with		
		LOI	KF	$LiAlH_4$
H_2O	Between crystallites	X	X	X
H_2O	In supercages	X	X	X
H_2O	In sodalite cages	X		
Acidic OH	In supercages	X		X
Nonacidic OH	In supercages	X		
Acidic and nonacidic OH	In sodalite cages	X		

The combination of the three measurements was used as follows:

$LOI–LiAlH_4$ = $H_2O + OH$ in sodalite cages and nonacidic OH in supercages.
LOI–KF = $H_2O + OH$ in sodalite cages and OH in supercages, or if no hydroxyl groups are present: H_2O in sodalite cages.
$LiAlH_4$–KF = acidic OH in supercages.

EXPERIMENTAL METHODS

Zeolite Preparation

Na–Y-zeolite, obtained from Union Carbide, Linde Division, was purified by repeated washing until the molar ratio of the zeolite was:

$$Na_2O/Al_2O_3/SiO_2 = 1.03:1.00:4.90.$$

The crystallinity of the zeolite was 95%, as measured by X-ray diffraction.

The RE–Y-zeolite was obtained from the purified Na-Y-zeolite by exchanging about 75% of the sodium ions with rare-earth ions. This exchange was carried out in one treatment with excess rare-earth chloride solution at $pH = 5.5$. After exchange the zeolite was washed with water. The distribution of rare earths in the rare-earth chloride solution used was approximately: 50% CeO_2; 29% La_2O_3; 15% Nd_2O_3; 4% Pr_6O_{11}; and 2% other rare-earth oxides. The composition of the final RE–Y-zeolite was: 20.4% Al_2O_3; 59.2% SiO_2; 3.5% Na_2O and 16.8% RE_2O_3 or expressed in molar ratio: $Na_2O/RE_2O_3/Al_2O_3/SiO_2 = 0.28:0.26:1.00:4.90$.

Loss on Ignition

Loss on ignition was determined as the weight loss after 1 hr calcination at 1000°C. It is calculated on dry basis. It is assumed that the LOI gives the sum of all water and 18/34 part of the hydroxyl groups present in the sample (since $2\,OH \rightarrow\, \rangle O + H_2O$).

Karl Fischer Titration

This titration method is based on the well-known reaction of water with iodine and SO_2, in combination with pyridine in methanol solution. The reaction is very fast and quantitative. In order to exclude a possible reaction of hydroxyl groups in the zeolite with the reagent, a titration method was followed as used by Noll *et al.* (*8*) for amorphous silica, i.e., titration with a constant excess of reagent and extrapolation of the titration curve to time zero.

Lithium Aluminum Hydride Reaction

The use of $LiAlH_4$ as an analytical reagent in the study of surface groups on solids has been introduced by Rivin (*9*) for the analysis of carbon black surfaces. The analysis of zeolites is based on the reaction of water and acidic hydroxyl groups (ZO^-H^+) both under evolution of hydrogen gas:

$$2H_2O + LiAlH_4 \rightarrow LiAlO_2 + 4H_2,$$
$$4ZOH + LiAlH_4 \rightarrow LiAl(OZ)_4 + 4H_2.$$

Nonacidic hydroxyl groups $(OH)^-$ do not contain active hydrogen and hence will not react with $LiAlH_4$.

TABLE 2

ANALYSIS OF Na–Y-ZEOLITES, DRIED AT 120°C DURING DIFFERENT TIMES

	(% H_2O d.b.)			(% H_2O d.b.)		
Sample	LOI	KF	$LiAlH_4$	LOI–$LiAlH_4$	LOI–KF	$LiAlH_4$–KF acidic OH in supercages
1	107.8	100.5			7.3	
2	70.9	63.9			7.0	
3	47.1	42.5			4.6	
4	33.9	30.0			3.9	
5	24.1	20.8			3.3	
6	14.7	11.7	11.7	3.0	3.0	0.0
7	9.0	6.2	6.2	2.8	2.8	0.0

The reaction is carried out by adding $LiAlH_4$–diethyleneglycoldiethylether solution to a glass bottle, filled with dried hydrogen gas and the zeolite and connected to a gas buret. The amount of hydrogen gas evolved is read from the buret after 3–6 hrs reaction time. A blank is run in the same way. The combined H_2O and acidic hydroxyl content of the zeolite is expressed in % H_2O:

$$\% \; H_2O = \left[\left(a \cdot \frac{p_1}{76} \cdot \frac{273}{T_1}\right) - \left(b \cdot \frac{p_2}{76} \cdot \frac{273}{T_2}\right)\right] \frac{18}{2} \cdot \frac{100}{1000} \cdot \frac{1}{g} \cdot \frac{1}{22.4},$$

where:

a = ml of H_2 gas evolved (sample);
b = ml of H_2 gas evolved (blank);
p_1, p_2 = barometer reading (cm Hg);
T_1, T_2 = temperature of gasburet (°K);
g = weight of sample (g).

RESULTS

Na–Y-Zeolite

Before analysis the zeolite was predried at 120°C to different water contents. As shown by samples 6 and 7 in Table 2, no acidic hydroxyl groups are present in the supercages of the Na–Y-zeolite.

RE–Y-Zeolite

The first sets of measurements of RE–Y-zeolites were carried out with LOI

TABLE 3

ANALYSIS OF RE–Y-ZEOLITES, DRIED AT 200, 400, AND 600°C

		(% H_2O d.b.)			(% H_2O d.b.)	
Sample	Pretreatment (°C)	LOI	KF	$LiAlH_4$	LOI–$LiAlH_4$ H_2O + OH in sodalite cages	$LiAlH_4$–KF acidic OH in supercages
8	200	18.5	13.9	14.0	4.5	0.1
9	200	14.9	8.9	8.9	6.0	0.0
10	200	13.2	7.0	7.8	5.4	0.8
11	200	10.0	4.2	5.3	4.7	1.1
12	200	6.2	1.9	2.7	3.5	0.8
13	400	2.9	0.6	0.7	2.2	0.1
14	600	2.1	0.5	0.5	1.6	0.0
15	120	13.7	8.4	9.5	4.2	1.1
16	120	13.3	8.3	9.4	3.9	1.1
17	120	13.8	8.3	9.4	4.4	1.1
18	120	12.0	7.0	7.9	4.1	0.9
19	180	8.8	3.4	4.4	4.4	1.0

TABLE 4

ANALYSIS OF RE–Y-ZEOLITES, DRIED AT VARIOUS TEMPERATURES

Sample	Pretreatment (°C)	(% H_2O d.b.) LOI	KF	LOI–KF	pH after rewetting	% Na_2O after second RE exchange
20	120	103.0	95.1	7.9	8.1	3.3
21	120	46.5	40.6	5.9	8.1	3.3
22	120	25.6	22.3	3.3	8.0	3.0
23	120	19.2	14.4	4.8		1.6
24	120	14.7	9.4	5.3	8.2	1.3
25	120	12.7	7.3	5.4		0.8
26	120	11.1	5.9	5.2	6.2	1.0
27	120[a]	103.0	95.1	7.9	8.1	3.3
28	120[a]	42.4	37.0	5.4	8.2	3.3
29	120[a]	25.7	22.2	3.5	8.2	3.2
30	120[a]	17.1	12.0	5.1	8.3	1.9
31	120[a]	13.3	8.1	5.2	8.2	1.1
32	120[a]	12.1	6.8	5.3	7.8	1.1
33	120[a]	9.7	4.5	5.2	6.0	1.3
34	200	103.0	95.1	7.9	8.1	3.3
35	200	26.4	22.9	3.5	7.8	3.2
36	200	25.4	21.9	3.5	8.1	2.6
37	200	18.0	13.2	4.8	8.0	1.8
38	200	10.8	5.7	5.1	5.7	1.2
39	200	7.8	3.3	4.5	5.3	1.4

[a] Dried in a vacuum.

measurements and both $LiAlH_4$ and KF reagent. It was found that at LOI > 14% d.b. of the zeolite no difference between KF and $LiAlH_4$ data were found, which indicates that no acidic hydroxyl groups are present in the supercages (Table 3, samples 8 and 9). At lower water content the zeolite contains acidic hydroxyl groups in the supercages.

Another set of experiments with RE–Y-zeolites was carried out at various pretreatment temperatures (Table 4). Also the pH is given after rewetting 20 g of the zeolite with 100 g of deionized water.

Figure 1 shows the relationship between LOI and water content of sodalite cages for RE–Y-zeolite and Na–Y-zeolite, pretreated at various conditions. At LOI > 15% the water content in sodalite cages of RE–Y-zeolite is calculated by taking the difference of LOI and KF titration. At LOI < 15% this difference will not exactly express the sodalite water content, due to the formation of acidic hydroxyl groups. In Fig. 2 the effect of RE–Y-zeolite drying is given on the pH after rewetting and on the content of acidic hydroxyl groups in supercages.

The RE–Y-zeolites investigated had a Na_2O content of 3.5%. It is well known that a second rare-earth exchange without intermediate zeolite drying does not decrease the Na_2O content appreciably. As parameter for sieve drying in the present studies the exchangeability of the sodium ions is used, as this exchangeability is correlated with the position of the sodium ions in the zeolite structure. Hence in Table 4 the percentages of Na_2O left in the zeolite after a second RE exchange are given.

DISCUSSION

It is known that two types of cavities are present in Y-type zeolite (*10*). Supercages or α-cages with internal diameters of 12–13 Å and apertures of 8–9 Å. They are formed by a tetrahedral arrangement of

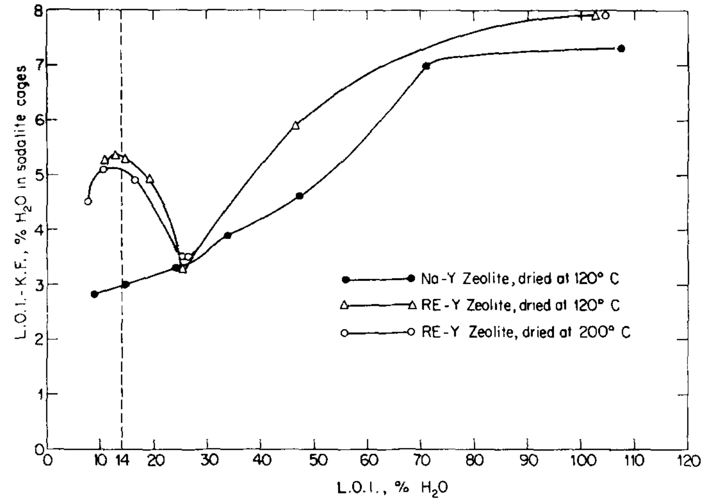

FIG. 1. Relation between total water content (LOI) and water content in sodalite cages of RE-Y-zeolite and Na-Y-zeolite.

truncated octahedra. The octahedra or sodalite units themselves enclose a second set of smaller cavities: sodalite or β-cages with internal diameters of 6–7 Å. They are connected to the supercages by means of apertures of 2.2 Å free diameter. A third type of cavity is present as hexagonal prisms by which the sodalite cages are coupled. Its internal diameter is ~2.5 Å. Breck (*10*) suggests that a variation of 0.3–0.4 Å in aperture diameter could result from the thermal vibration of oxygen atoms surrounding the apertures. From the critical diameter of the molecules it is clear that I_2 (4.3 Å) and $LiAlH_4$ (5–6 Å) will not be able to enter into sodalite cages and hexagonal prisms. At least at elevated temperatures water molecules (2.65 Å) will be able to pass the apertures of 2.2 Å.

Na-Y-Zeolite

The results in Table 2 show that no acidic hydroxyl groups are present in supercages as the same results are found with KF and $LiAlH_4$. They also indicate that part of the total water content (LOI)

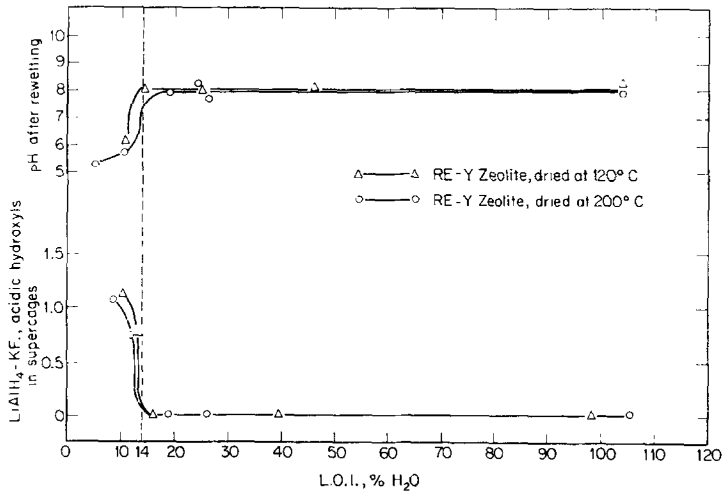

FIG. 2. Relation between total water content (LOI) and pH of zeolite after rewetting, and content of acidic hydroxyl groups in supercages.

cannot be titrated with KF or with $LiAlH_4$ and must be due to water in sodalite cages. In Fig. 1, the relation between LOI and water content in sodalite cages is given over a wide range of total water contents. The maximum water content in sodalite cages found for the Na–Y-zeolite is 7.3% (or 0.073 ml/g) which is continuously decreased by drying.

We calculated the free internal volume of sodalite and prismatic cages in 1 g of Na–Y-zeolite under assumption of a spherical shape of the cages with diameters of 6.6 Å and 2.5 Å (ml/g): sodalite cages, 0.055; prismatic cages, 0.006; total calculated internal volume of sodalite and prismatic cages, 0.061. This calculated volume of 0.061 ml/g agrees qualitatively with the experimental value of 0.073 ml/g.

RE–Y-Zeolite

The experiments carried out with the RE–Y-zeolites show curves which deviate strongly from the Na–Y-zeolite curve (Fig. 1). RE–Y-zeolite drying from 100 to 30% LOI results in a decrease of the water content in sodalite cages, similar to the Na–Y behavior. However, further drying causes a sharp increase of water in the sodalite cages. This paradoxial behavior can be explained by migration of hydrated rare-earth ions from supercages to sodalite cages.

Generally it is known that heat treatment of RE–Y-zeolite causes stronger binding of RE cations to the zeolite structure and that at the same time the residual sodium cations become more easily exchangeable during a subsequent exchange with $RECl_3$ solution. Table 4 shows that decrease of Na_2O content and increase in H_2O content of sodalite cages take place at identical LOI ranges. This fact supports our migration hypothesis for the hydrated rare-earth ions.

So far, we discussed phenomena occurring during drying wet RE–Y-zeolites at LOI > 14%. Table 3 indicates that further drying results in the formation of acidic hydroxyl groups in the region between 14

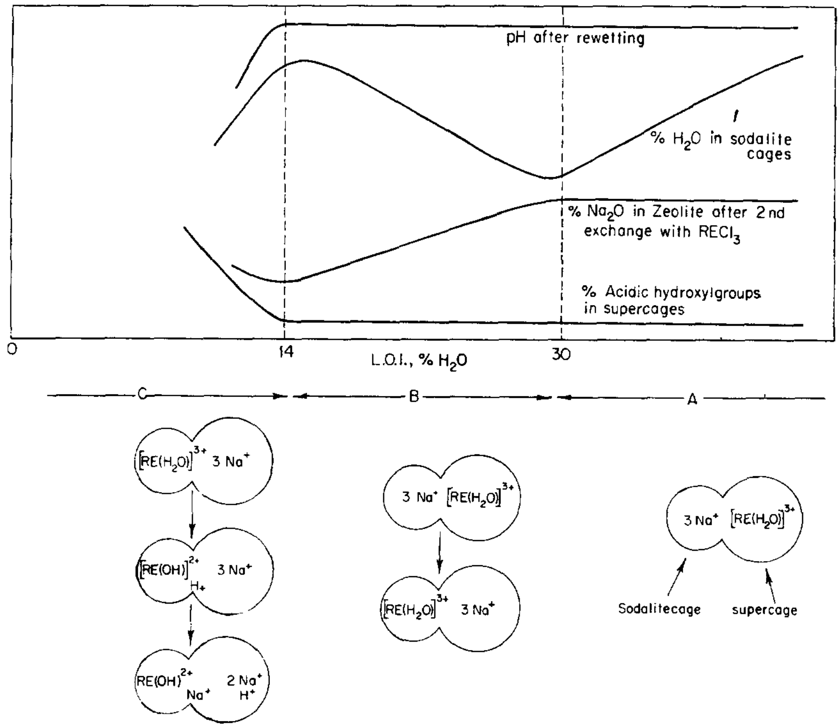

FIG. 3. Schematic summary of observed changes during RE–Y-zeolite drying with proposed mechanism of migrations.

and 10% LOI. These acidic OH groups are present in the supercages, since they react with $LiAlH_4$. The presence of acidic OH groups in the smaller cavities cannot be measured by this titration method. It is obvious to correlate the observed pH decrease with the formation of acid sites in the zeolite (Fig. 2).

Figure 3 indicates that in region A (drying up to 30% LOI) no migrations take place. In region B (drying from 30 to 14% LOI) hydrated rare-earth ions migrate from supercages to sodalite cages and Na^+ ions move in the opposite direction which cause improved exchangeability with $RECl_3$ solution. Until now no acid species are formed, the pH after zeolite rewetting is unchanged, and no acidic hydroxyl groups are present. Further drying (Fig. 3, region C) causes a reaction as postulated earlier by Plank (*1*)

$$[RE(H_2O)]^{3+} \rightarrow [RE(OH)]^{2+} + H^+$$

Protons and zeolite lattice oxygen form acidic hydroxyl groups.

Obviously these groups are situated in the supercages, as they can be titrated with $LiAlH_4$. The formation of these acidic groups is also indicated by the decrease of pH on rewetting the zeolite. The observed decrease in Na_2O exchangeability with $RECl_3$ solution in region C might be due to back migration of Na^+ ions by exchange with the protons formed.

Our proposed model of RE–Y-zeolite drying is consistent with X-ray structural studies of Olson *et al.* (*11*) which indicate that upon dehydration of RE–Y-zeolites all RE ions move into sodalite cages.

The decrease of acidic hydroxyl groups in supercages at temperature >200°C (Table 3) is in good agreement with the trends in catalytic activities of RE–Y-zeolites with pretreatment temperature as reported by Hopkins (*12*) for the cracking of heptane.

Number of Acid Sites

An interesting point in this context is the number of acid sites of RE–Y-zeolite compared to amorphous silica–alumina surfaces (fluid cracking catalyst). Densities of acid sites on amorphous FCC surfaces are expressed as the number of sites per unit area. This is estimated (*13*) to be 10^{13} sites/cm^2. For equilibrium FCC with a surface area of 100 m^2/g, the number of sites is: $10^6 \times 10^{13} = 10^{19}$ sites/g. The maximum acidic hydroxyl content found in the RE–Y-zeolite investigated is 1.1% H_2O (Table 3, samples 15–17), this is equivalent to 7.3×10^{20} OH groups/g of zeolite. The number of acidic hydroxyl groups in RE–Y-zeolite can also be calculated from the rare-earth content of the sieve (16.8% RE_2O_3), based on the assumption that each rare-earth ion produces one acidic hydroxyl group (*1*) and on an assumed molecular weight of 150 for $\frac{1}{2}RE_2O_3$: $(16.8/100) \cdot (1/150) \cdot 6 \cdot 10^{23} = 6.7 \times 10^{20}$ OH groups/g of zeolite. The agreement of this value with the number calculated from the titration data provides an independent check on the reliability of the analytical methods developed in the present work.

CONCLUSION

The results of quantitative $LiAlH_4$ and KF titrations of Y-type zeolites show that only the supercages of the zeolite are accessible for both reagents. In combination with the LOI measurement these techniques discriminate between acidic hydroxyl groups in the supercages, water in the supercages and the combination of water and hydroxyl groups in the sodalite cages. The measurements show that during the drying of RE–Y-zeolites from 30 to 14% LOI hydrated rare earth ions migrate from supercages to sodalite cages. At the same time sodium ions move in the opposite direction. During the further drying of zeolite from 14 to 10% LOI dissociation of hydrate water occurs, resulting in the formation of protons which, together with lattice oxygen, act as Brönsted acid sites. The number of acidic hydroxyl groups in the supercages of the RE–Y-zeolite under investigation is 7×10^{20} groups/g, which is about 70 times higher than for amorphous silica–alumina catalyst.

The $LiAlH_4$ reaction discriminates between OH groups in supercages and those in sodalite cages. This is advantageous when OH densities of zeolites are compared with catalytic activities as neither $LiAlH_4$ nor feedstock molecules can enter the sodalite cages of the zeolite.

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