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Ion Exchanged Ultrastable Y Zeolites

I. Formation and Structural Characterization of Lanthanum–Hydrogen Exchanged Zeolites

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The preparation, composition and structural characteristics of a variety of lanthanum–hydrogen exchanged ultrastable Y zeolites (La,H-USY) is described and discussed. A general discussion of reactions taking place between acidic metal salt solutions and USY zeolites is also presented.

La,H-USY zeolites were prepared by two methods: (a) acid treatment of ultrastable Y zeolites at controlled pH followed by lanthanum exchange; (b) treatment of ultrastable Y zeolites with acidic solutions of lanthanum salts at controlled pH. The resulting materials have high thermal and hydrothermal stability. They possess both Brønsted and Lewis type acidity.

The infrared spectra of La,H-USY zeolites in the OH stretching region and in the framework vibrational region are described. The spectra are similar to those of ultrastable Y zeolites. The effect of steaming on the zeolitic structure, as reflected in the infrared spectra, is discussed.

INTRODUCTION

Ultrastable Y zeolites (USY) are of considerable interest, especially to the petroleum refining industry, due to their catalytic properties and unusually high thermal, hydrothermal and chemical stability. The synthesis and properties of these zeolites have been described by McDaniel and Maher (*1*). A number of articles has been published concerning the crystal structure (*2*), infrared spectra (*3–6*), formation mechanism (*7*, *8*) and acidic properties (*9*, *10*) of USY zeolites. Patents have been issued describing the use of these and related materials as catalysts in different petroleum refining processes, e.g., cracking, hydrocracking or hydrotreating.

The literature gives no detailed account of metal exchanged forms of USY zeolites. Such compounds have the potential of combining the properties of metal exchanged Y zeolites with those of USY zeolites. We have therefore investigated the products resulting from reactions between metal salt solutions of different acidity and USY zeolites. A large number of metal–hydrogen exchanged USY zeolites (M,H-USY) has been prepared and characterized.

In the present paper we describe and discuss the preparation, composition and structural characteristics of different lanthanum–hydrogen exchanged USY zeolites (La,H-USY). A general discussion of the reactions taking place between acidic metal salt solutions and USY zeolites is also presented.

EXPERIMENTAL METHODS

A. Materials. The starting material used for the preparation of La,H-USY zeolites was a low-soda, ultrastable Y zeolite, type II, prepared by the method described in (*1*) or (*4*). The USY zeolite had the following composition: SiO_2/Al_2O_3 mole ratio, 4.85; Na_2O, 0.2 wt%; BET surface area, 763 m²/g; unit cell size, 24.52 Å. The lanthanum-hydrogen exchanged forms of this zeolite were prepared by the following two methods: (a) The zeolite was treated with hydrochloric acid solutions of different pH (3.5, 3.0, 2.5, 2.0, 1.5) for 30 min at about 90°C, under stirring. This was sufficient to reach exchange equilibrium. These acid-treated USY zeolites are designated H-USY. The resulting materials were filtered, washed, and subsequently exchanged with 6 wt% lanthanum chloride solutions at ambient pH between 4.0 and 4.3 For materials prepared by such consecutive treatment we use the notation La,H-USY_c. (b) The zeolite was treated with solutions of about 7 wt% lanthanum chloride acidified with hydrochloric acid close to the exchange pH. After the zeolite addition, the pH was adjusted to the desired pH. The exchange was then carried out for 30 min at 90°C. Materials prepared by simultaneous acid and lanthanum chloride treatment bear the notation La,H-USY_s.

Zeolites prepared by direct exchange of USY zeolites with lanthanum chloride solutions without any acid addition bear the notation La,H-$USY_{a.i.}$ (a.i. = as is). The pH of these exchange slurries was close to 4.0.

B. Instrumentation and infrared measurements. The details of the infrared measurements have been described previously (*4*). The spectra were recorded on a Beckman IR-12 spectrophotometer.

Spectra of the hydroxyl region (3000–4000 cm^{-1}) and of adsorbed pyridine (1300–1800 cm^{-1}) were obtained from self-supporting pellets ranging in "thickness" from 6 to 9 mg/cm². The pellets were heated in vacuum at the indicated temperatures for 1 hr, cooled and lowered into the infrared beam. When pyridine was adsorbed, the pellets were first heated in vacuum for 1 hr at 500°C, cooled and pyridine adsorbed at room temperature. Physically adsorbed pyridine was removed by heating at 200°C under vacuum overnight.

The framework region (400–1300 cm^{-1}) spectra were obtained by evaporating a 10 wt% slurry of zeolite powder in ethanol onto one side of a 2 mm thick KRS-5 ATR plate which was placed in a Wilks Model 38 attenuated total reflection (ATR) unit. The cell was evacuated and the spectra were then recorded.

Since both of these methods result in substantial energy losses, a reference beam attenuator was used to obtain full scale deflection on the recorder.

C. Other measurements. The unit cell size and crystallinity of different samples was established from X-ray diffraction data. BET surface area measurements and X-ray diffraction data were used to establish the degree of structural collapse of different materials. The surface areas were measured on an Aminco Adsorptomat. The X-ray diffractograms were obtained on a Norelco powder diffractometer.

RESULTS

Analytical data for H-USY and La,H-USY zeolites discussed in this article are shown in Table 1. The corresponding data for the USY zeolite used in these preparations are also shown.

Table 2 summarizes the unit cell sizes of La,H-USY and H-USY zeolites prepared at different pH values, before and after steaming at 540°C for 3 hr. Besides a general decline in unit cell size with decreasing exchange pH, the data also show a decrease in size as a result of steaming. The latter effect appears stronger in the case of H-USY zeolites.

Table 3 summarizes the different framework and nonframework aluminum species that can be encountered in ultrastable Y and in other hydrothermally stabilized zeolites.

TABLE 1

Characteristics of H-USY, La,H-USY$_c$ and La,H-USY$_s$ Zeolites

No.	Zeolite	Treat pH	SiO_2/Al_2O_3 mole ratio	% Al_2O_3 removed	La_2O_3 mmole/100 g	Relative peak height[a]	Unit cell size (Å)
1	USY	—	4.85	0	—	100	24.52
2	H-USY	3.5	5.0	3	—	96	24.51
3	H-USY	3.0	5.1	5	—	93	24.50
4	H-USY	2.5	5.9	18	—	86	24.48
5	H-USY	2.0	8.0	39	—	76	24.43
6	H-USY	1.7	9.6	49	—	70	24.41
7	H-USY	1.5	11.9	59	—	57	24.37
8	La,H-USY$_{a.i.}$[b]	4.0	4.85	0	19.1	100	24.54
9	La,H-USY$_c$	3.5	5.0	3	17.6	94	24.52
10	La,H-USY$_c$	2.5	5.9	18	17.0	86	24.49
11	La,H-USY$_c$	2.0	8.0	39	15.8	75	24.46
12	La,H-USY$_c$	1.5	11.9	59	13.7	58	24.40
13	La,H-USY$_{a.i.}$[b]	4.0	4.85	0	19.3	100	24.54
14	La,H-USY$_s$	3.5	4.85	0	17.1	96	24.53
15	La,H-USY$_s$	2.5	5.5	12	14.4	91	24.52
16	La,H-USY$_s$	2.0	6.5	25	11.2	82	24.50
17	La,H-USY$_s$	1.5	9.6	49	7.1	62	24.40

[a] Expressed as percentage of peak height at $2\theta = 23.8°$ in X-ray diffractogram of corresponding nonacid treated compound.

[b] No free acid was added during the preparation of these zeolites.

Figure 1 illustrates the change in silica/alumina ratio and surface area of a USY zeolite after treatment with hydrochloric acid at different pH values and subsequent exchange with lanthanum ions. Little change in the silica/alumina ratio was observed above pH 3.0. Below pH 3.0, the ratio increases rapidly due to progressive aluminum removal from the zeolite. The surface area measured after calcination at 900°C for 2 hr begins to drop for zeolites prepared at pH less than 2.0.

The infrared spectra in the OH region of USY zeolites treated with solutions of hydrochloric acid at different pH values are shown in Fig. 2. The initial USY

TABLE 2

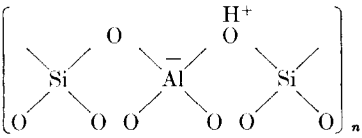
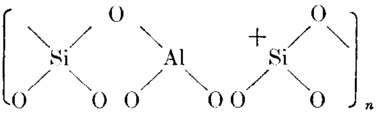
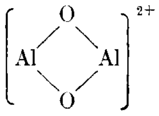
Unit Cell Sizes of La,H-USY$_s$, La,H-USY$_c$ and H-USY Zeolites Before and After Steaming[a]

Treat pH	La,H-USY$_s$ (Å)		La,H-USY$_c$ (Å)		H-USY (Å)	
	Fresh	Steamed	Fresh	Steamed	Fresh	Steamed
4.0	24.54	24.41	24.54	24.41	24.52	24.30
3.5	24.53	24.40	24.52	24.41	24.51	24.30
2.5	24.52	24.38	24.49	24.39	24.48	24.29
2.0	24.50	24.37	24.46	24.38	24.43	24.28
1.5	24.40	24.32	24.40	24.36	24.37	24.25

[a] Steaming conditions: 540°C for 3 hr, 100% steam, atmospheric pressure.

TABLE 3

Aluminum Species Encountered in Ultrastable Y Zeolites

Framework species (Al_F)	Extra framework species	
	Cationic (Al_C)	Neutral (Al_N)
 (*1*, *14*)	Al^{3+} (*2*, *12*) AlO^+ (*2*, *11*) $Al(OH)^{2+}$ (*2*, *7*, *12*) $Al(OH)_2^+$ (*2*, *7*)	AlO(OH) (*2*, *12*) $Al(OH)_3$ (*7*)
 (*1*, *14*)	 (*13*) $[Al\text{-}O\text{-}Al]^{4+}$ (*13*)	

zeolite shows the following OH bands: near 3750, 3700, 3640, and 3570 cm^{-1}. After partial dehydroxylation a band in the 3600 cm^{-1} region could also be detected. The spectra of H-USY, which were recorded after vacuum-calcination at 300°C, show striking similarities. The acid treatment does not appear to affect significantly the OH groups in the zeolite even at pH as low as 2.0.

The spectra in the OH region for La,H-USY$_c$ and La,H-USY$_s$ zeolites are shown in Fig. 3. The spectra show bands very similar to those encountered in the original USY zeolite. There are few differences among the spectra of La,H-USY$_c$ zeolites prepared above pH 2.0. However, the spectrum of the zeolite treated at pH 1.5 shows a very strong band at 3750 cm^{-1}, whereas the intensity of the other bands is considerably diminished. A similar, but less pronounced effect is observed in the spectrum of La,H-USY$_s$ treated at pH 1.5.

The thermal stability of different OH

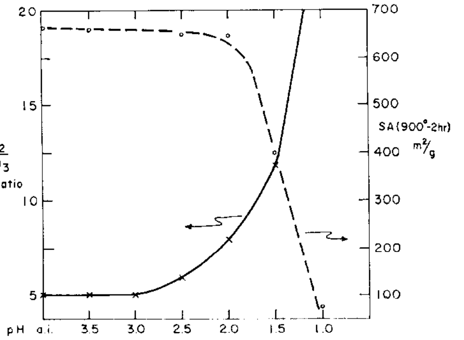


Fig. 1. Variation in SiO_2/Al_2O_3 mole ratio, and surface area of La,H-USY$_c$ prepared at different pH.

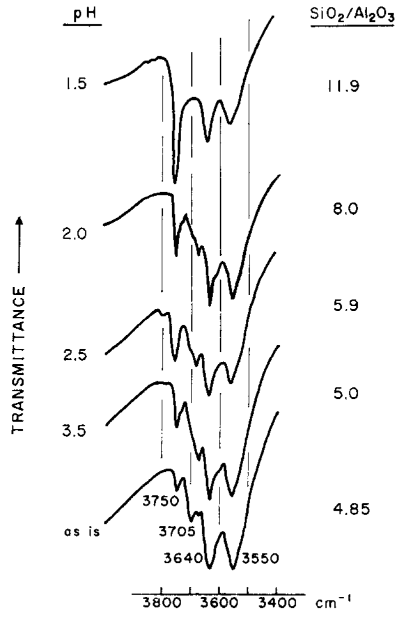


Fig. 2. Hydroxyl stretching region of H-USY zeolites treated at differed pH.

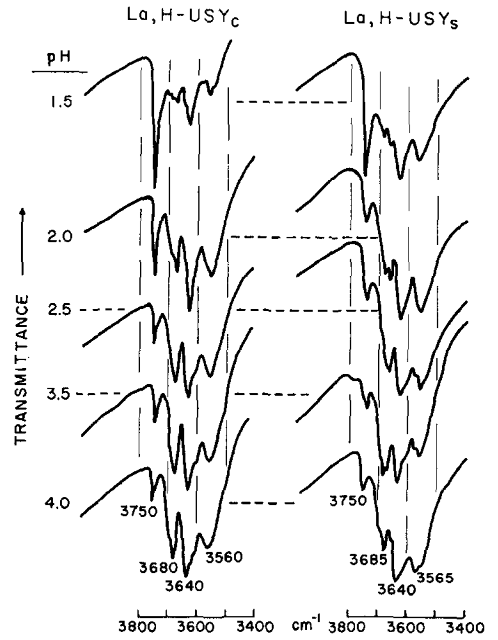


FIG. 3. Hydroxyl stretching region of La,H-USY$_c$ and La,H-USY$_s$ prepared at different pH.

groups in La,H-USY is compared in Fig. 4. The band at 3680 cm^{-1} shows the highest thermal stability.

The affect of pyridine adsorption on the OH region of H-USY, La,H-USY and La,H-Y zeolites is shown in Fig. 5. The spectra in the OH region of H-USY and La,H-USY$_c$ reveal the presence of a band near 3620 cm^{-1}, which is otherwise masked by a fairly strong 3650 cm^{-1} band before pyridine adsorption. In addition, the spectrum of La,H-USY$_c$ shows the presence of a band at 3550 cm^{-1}.

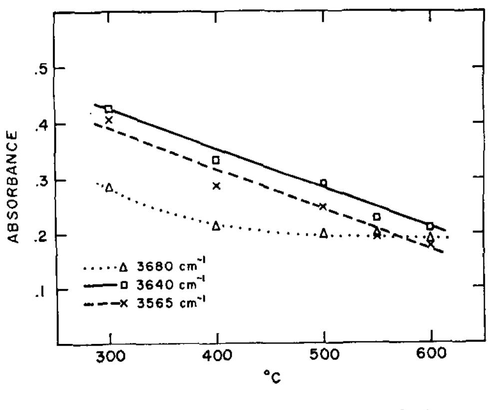


FIG. 4. Thermal stability of different OH groups in La,H-USY$_c$ obtained at pH 3.5.

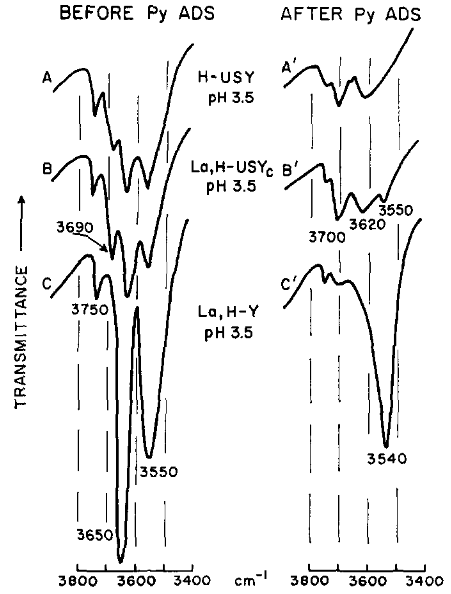


FIG. 5. Effect of pyridine on OH stretching region of H-USY, La,H-USY$_c$, and La,H-Y zeolites.

Figure 6 compares the affect of steaming at 540°C for 3 hr on the OH region of H-USY, La,H-USY$_c$, and La,H-Y, all exchanged at pH 3.5. In La,H-Y, steaming

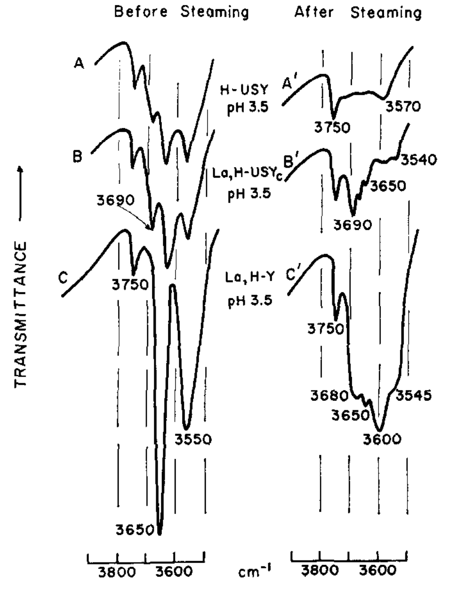


FIG. 6. Effect of steaming on OH stretching region of H-USY, La,H-USY$_c$, and La,H-Y.

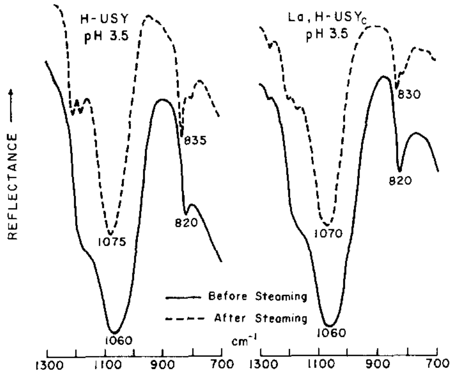


FIG. 7. Framework bands of H-USY: and La,H-USY$_c$ before and after steaming (540°C, 3 hr).

generates additional bands near 3680 and 3600 cm^{-1}. These spectra have been described elsewhere (*17*). The spectra of steamed H-USY and La,H-USY$_c$ show significant differences. In H-USY, steaming eliminates the bands at 3680 and 3640 cm^{-1}, leaving only a weak band near 3570 cm^{-1}. In La,H-USY$_c$, the band at 3690 cm^{-1} is fairly strong and bands at 3650 and 3540 cm^{-1} can also be detected.

The affect of steaming on some of the framework vibrational bands of La,H-USY$_c$ and H-USY zeolites is shown in Fig. 7. Before steaming, the (Si,Al)–O asymmetric stretching band in the spectra of these compounds is located at 1060 cm^{-1}. The symmetric stretching band is located at 820 cm^{-1}. Steaming at 540°C for 3 hr shifts these bands to higher frequencies: 1075 cm^{-1} for the (Si,Al)–O asymmetric stretching band in H-USY and 1070 cm^{-1} in La,H-USY$_c$. The symmetric stretching bands shift to 835 and 830 cm^{-1}, respectively.

Similar effects to those described in Figs. 5, 6 and 7 have been observed for La,H-USY$_s$ zeolites.

DISCUSSION

Structural studies have shown that ultrastable Y zeolites can contain a variety of aluminum species that occupy both framework and nonframework positions. In framework positions the aluminum is usually tetrahedrally coordinated to 4 oxygen atoms. Upon dehydroxylation, some of the aluminum atoms in the framework become tricoordinated and form Lewis acid sites (*1*, *14*). The aluminum species found in nonframework positions are occupied by cationic and/or neutral aluminum species. The different aluminum species that can be encountered in ultrastable zeolites or related compounds are listed in Table 3.

By treating ultrastable Y zeolites with acidic solutions of metal salts, the following reactions can take place: (a) The metal ions exchange with some of the protons in the zeolite, without affecting the nonframework aluminum species; (b) the metal ions exchange with both protons and cationic aluminum species; (c) the cationic aluminum species are exchanged by the protons in solution; (b) the neutral nonframework alumina species are extracted by the acidic solution; (e) some framework aluminum is leached out by the acidic solution; (f) if the solution is too acidic, structural breakdown will occur due to extensive alumina leaching from the framework. These reactions are represented schematically as follows:

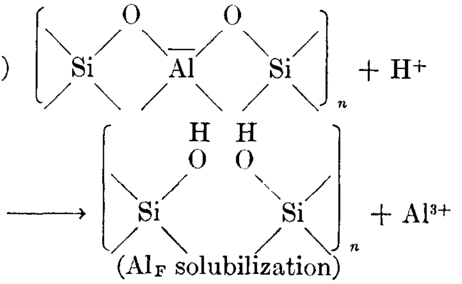
(a) $H^+[Z] + M^{n+} \rightarrow M^{n+}[Z] + H^+$ (ion exchange),

(b) $H^+, Al_C[Z] + M^{n+} \rightarrow M^{n+}[Z] + Al^{3+} + H^+$ (ion exchange),

(c) $Al_C[Z] + H^+ \rightarrow H^+[Z] + Al^{3+}$ (ion exchange),

(d) $AlO(OH) + H^+ \rightarrow Al^{3+} + H_2O$ (Al_N solubilization),

(e)



(Al_F solubilization)

Al_C, Al_N, and Al_F represent cationic, neutral and framework aluminum species, respectively. Depending upon the salt concentration and acidity of the solution, some or all of these processes can take place during the metal exchange of USY zeolites. An increase in metal ion concentration at constant acidity results in a shift from reaction (a) to (b). An increase in acidity will enhance reactions (c), (d), and (e). From these considerations it becomes obvious that a variety of M,H-USY zeolites can be prepared from the same ionic species.

Formation of La,H-USY. For illustration, we shall discuss the case of La,H-USY zeolites prepared by either of the two methods described earlier. The data for La,H-USY$_s$ shown in Table 1 indicate that for an exchange pH of 4.0, reaction (a) is practically the only one taking place, since the SiO_2/Al_2O_3 ratio remains unchanged. At pH 3.5, only a slight increase in SiO_2/Al_2O_3 is observed, suggesting that besides reaction (a), reactions (b), (c), and (d) begin also to take place. The lower lanthanum content in the zeolite prepared at pH 3.5 is due to the increased competitiveness of protons for exchange sites in the zeolite. Both zeolites show high X-ray crystallinity.

By decreasing the pH, the SiO_2/Al_2O_3 ratio begins to increase rapidly, due to increased aluminum removal from the zeolite. The lanthanum content of the zeolite will drop, due to both increased competitiveness from hydrogen ions and incipient destruction of exchange sites by leaching of framework aluminum. The progressive removal of aluminum and decrease in lanthanum input is accompanied by lower X-ray crystallinity and decreased unit cell size.

The infrared spectra indicate that at pH values higher than 2.0, the damage to the framework is minimal. This is reflected by the strong similarity of spectra in the OH region of corresponding La,H-USY$_s$ zeolites. However, at pH 1.5 the spectrum shows a strong silanol band at 3750 cm^{-1} and a considerable weakening of the OH bands characteristic for the faujasite structure, indicating partial destruction of the zeolitic framework (reaction e). This is also reflected by the sharp drop in X-ray crystallinity, surface area and unit cell size.

A similar pattern emerges for La,H-USY$_c$ zeolites. Acid treatment of the USY zeolite and subsequent lanthanum exchange results in very little change in the SiO_2/Al_2O_3 ratio above pH 3.0 (Fig. 1 and Table 1). As the pH decreases to 2.0 the SiO_2/Al_2O_3 ratio increases to 8, due to progressive removal primarily of nonframework aluminum. The ion-exchange capacity of the zeolite is only slightly affected when the pH decreases from 3.5 to 2.5, but drops at lower pH. This is shown by the lower lanthanum content of the material treated at pH 2.0. The incipient structural damage at pH 2.0 is also indicated by the strong silanol band in the infrared spectrum (Fig. 3). At pH 1.5 the framework destruction is significant, as reflected by the strong silanol band in the spectrum, the low ion-exchange capacity for lanthanum, low X-ray crystallinity and the decline in surface area.

For a given pH, the SiO_2/Al_2O_3 ratio is higher in La,H-USY$_c$ than in La,H-USY$_s$. This is related to the more advanced aluminum removal in the former compound, due to the absence of competing lanthanum ions during the acid treatment of the zeolite. This is also shown by the infrared spectra: the silanol band at 3750 cm^{-1} is stronger in the spectra of La,H-USY$_c$ treated at pH 2.0 and 1.5 than in the spectra of corresponding La,H-USY$_s$. At these pH values, framework destruction is more advanced in the absence of lanthanum ions during acid treatment.

Thermal stability of La,H-USY. Figure 1 shows that the thermal stability of La,H-USY$_c$ zeolites, as reflected by their surface area after calcination at 900°C, is maintained up to a SiO_2/Al_2O_3 ratio of about 10. This corresponds to a pH of about 1.75. At lower pH, the thermal stability of the zeolite drops sharply due to framework destabilization by extensive aluminum leaching.

The thermal stability of La,H-USY (pH 4.0) relative to that of USY and low-soda, 80% lanthanum exchanged Y zeolite is shown by the corresponding BET surface areas after calcination at 925°C for 2 hr: 342, 530, and 156 m^2/g, respectively. These data lead to the following thermal stability series: USY > La,H-USY (pH 4.0) > La,H-Y.

Acidic properties of La,H-USY zeolites. By comparing the affect of pyridine adsorption on the OH region of infrared spectra, as well as the spectra of adsorbed pyridine itself, both Brønsted and Lewis type acid sites can be detected in La,H-USY zeolites. The presence of Brønsted acidity is reflected by the absorption band at 3650 cm^{-1} in the spectra La,H-USY and H-USY, and its disappearance after interaction with pyridine (Fig. 5). The band at 3570 cm^{-1} partially interacts with pyridine, suggesting that some of these hydroxyls are acidic.

The spectra of H-USY and La,H-USY prepared at the same pH are very similar, but show differences after pyridine adsorption. Interaction with pyridine results not only in the disappearance of bands at 3650 and 3570 cm^{-1}, but reveals the existence of a band at 3620 cm^{-1}. This latter band is characteristic for ultrastable Y zeolites (*3–5*). In the case of La,H-USY, an additional band is detected at 3550 cm^{-1}. Based on previous data obtained for lanthanum exchanged zeolites (*15, 17*) and in view of the absence of this band in the spectrum of H-USY, it is reasonable to assume that the band at 3550 cm^{-1} is due to OH groups attached to lanthanum ions.

Acidity measurements by the butylamine titration method gave the following results: La,H-Y, 1.8 meq/g; USY, 1.6 meq/g; La,H-USY (pH 4.0), 1.4 meq/g; and La,H-USY_c (pH 1.5), 0.88 meq/g.

We arrive to the following acidity series: La,H-Y > USY > La,H-USY (pH 4.0) > La,H-USY_c (pH 1.5).

The lower acidity of La,H-USY (pH 4.0) vs USY is due to partial exchange of hydrogen ions for lanthanum ions. The even lower acidity of La,H-USY_c (pH 1.5) is due to both lanthanum exchange and partial destruction of exchange sites.

Effect of steaming. The effect of steaming on La,H-USY zeolites has been investigated by infrared spectroscopy in the OH and framework region. The spectra in Fig. 6 show interesting differences in the effect of steaming upon H-USY, La,H-USY and La,H-Y zeolites. In La,H-Y steaming generates bands at about 3680 and 3600 cm^{-1}. The spectra and structural characteristics of steamed La,H-Y have been discussed in detail elsewhere (*16, 17*). The spectrum of steamed H-USY shows that the initial bands at 3690 and 3650 cm^{-1} have practically disappeared, and that a very weak band is left at 3570 cm^{-1} By contrast, steamed La,H-USY shows a fairly strong band at 3690 cm^{-1} and a distinct band at 3650 cm^{-1}.

The differences in the spectra of steamed H-USY and La,H-USY can be explained if we assume a structural rearrangement in steamed H-USY that results in a highly dehydroxylated structure. Such a framework rearrangement could involve silica migration (*4, 5, 18*) or some other form of bond rearrangement (*7, 11, 12*), leading to elimination of water from the partially dealuminated framework. Steaming is also likely to cause additional dealumination. Such a rearrangement results in a more silicious framework, shorter (Si, Al)–O bonds and smaller unit cell sizes. The spectra in the framework region for steamed H-USY and La,H-USY as well as unit cell size measurements before and after steaming tend to support this assumption.

The framework vibrational spectra of H-USY and La,H-USY before and after steaming (Fig. 7) show that steaming results in a shift to higher frequencies of the (Si, Al)–O asymmetric and symmetric stretching bands in the spectra of both compounds. However, the shift is stronger in the spectrum of H-USY, suggesting a higher SiO_2/Al_2O_3 ratio in the framework.

The unit cell sizes of H-USY and La, H-USY are fairly close prior to steaming (Table 2). Following steaming, a considerably stronger shrinking is observed in the case of H-USY, in line with a more silicious framework and shorter (Si, Al)–O bond distances.

The fact that under steam the framework modification and related unit cell shrinking is less advanced in La,H-USY is most likely related to the presence of lanthanum ions in the zeolitic cages. The presence of these relatively large ions ($r = 1.15$ Å) will tend to counteract structural changes that would result in framework shrinking. It will also counteract the formation of new cationic, aluminum-containing species. As the lanthanum content of the zeolite increases, the degree of framework rearrangement and unit cell shrinking will diminish. This has also been observed in the case of steamed LaY zeolites (*16*).

Pyridine adsorption experiments have shown that steamed La,H-USY zeolites contain both Brønsted and Lewis type acidity.

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