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Infrared Spectra of Ultrastable Zeolites Derived from Type Y Zeolites*

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An infrared spectroscopic study has been carried out on ultrastable zeolites derived from type Y zeolites and on their precursors. Both the hydroxyl stretching (3400 to 3800 cm^{-1}) and the silica-alumina vibrational (300 to 1300 cm^{-1}) regions of the spectra have been investigated. The effect of moisture content in the zeolite environment during calcination on the infrared spectrum of the zeolite has been established. An increase in moisture content at fixed calcination temperature results in additional absorption bands in the hydroxyl stretching region and in shifts to higher frequencies of absorption bands in the framework vibrational region, due primarily to dealumination of the zeolite framework. An increase in calcination temperature at fixed moisture content has a similar effect. Other effects observed are the suppression of dehydroxylation with increasing moisture content at temperatures up to 760°C, and an increase in the degree of ordering of the zeolite structure under 100% steam at high temperatures. The last phenomenon is interpreted as being due to a structural rearrangement, involving silica migration into the vacancies created by the dealumination process. Pyridine adsorption experiments were done to determine the type of acid sites on ultrastable zeolites.

INTRODUCTION

Ultrastable zeolites derived from type Y zeolites have recently raised considerable interest due to their extraordinary thermal and chemical stability. McDaniel and Maher (*1*) reported the preparation of these materials from synthetic ammonium exchanged Y sieves and named them Z-14 US zeolites. They described these zeolites as having very high thermal stability, low ion exchange capacity and catalytic activity in cracking reactions. Their thermal stability at temperatures in excess of 1000° contrasts with that of hydrogen or "decationated" type Y zeolites, which are less stable than cationic forms.

The crystal structures of ultrastable zeolites derived from type Y zeolites as well as those of their precursors have been established from X-ray powder data by Maher, Hunter and Scherzer (*2*). The authors have shown that in the ultrastable zeolite, the framework has lost 15 Al atoms, 25 O_3 and 13 O_4 framework oxygen atoms/unit cell. By repeated treatment of the ultrastable form with ammonium sulfate solution and high-temperature calcination, a structure resulted with a mean Si–O bond length of 1.610 Å, which indicates that little aluminum is left in the framework (high silica ultrastable zeolite).

The literature concerning ultrastable zeolites and related materials has been reviewed in (*2*).

Relatively little information is available about the infrared spectra of ultrastable zeolites. The hydroxyl region of the infrared spectra of these materials has been briefly investigated by Ward (*3*). Jacobs and Uytterhoeven (*4*) have recently investigated the hydroxyl stretching region in the infrared spectra of "deep-bed" calcined NH_4Y zeolite.

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The objective of the present work is to provide additional structural information for ultrastable zeolites derived from type Y zeolites, based on infrared spectroscopic data. The spectral characteristics are correlated to the thermal and hydrothermal treatment of ammonium Y sieves under different conditions, as well as to available structural X-ray data.

EXPERIMENTAL METHODS

A. Materials. Ultrastable zeolites type I and type II were prepared by the method recommended by McDaniel and Maher (*1*). A thoroughly washed commercial NaY sieve was used as starting material. The sieve contained 67.6% SiO_2, 24.0% Al_2O_3 and 10.6% Na_2O on a dry basis (silica–alumina ratio 4.75). The NaY (4.75) sieve was ammonium exchanged until the sodium level dropped to 2.6% Na_2O on a dry basis. To obtain the ultrastable form type I, the partially ammonium exchanged Y sieve was calcined in a muffle furnace at 540°C for 3 hr, then again ammonium exchanged until the sodium content dropped below 0.2% Na_2O and finally calcined in the muffle furnace at 820°C for 5 hr.

The ultrastable form type II was prepared by calcining the partially ammonium exchanged Y sieve at 760°C for 3 hr and then removing the remaining sodium ions to less than 0.2% Na_2O by additional ammonium exchange.

Besides the two types of ultrastable zeolites, a group of related materials was prepared from partially and totally ammonium exchanged Y sieves, by modifying the calcination environment and calcination temperature of these zeolites. The starting NaY sieve used in these experiments contained 60.6% SiO_2, 24.3% Al_2O_3 and 15.1% Na_2O on a dry basis, which corresponds to a unit cell composition of 31 Na_2O:31 Al_2O_3:130 SiO_2:$n$$H_2O$ (silica–alumina ratio 4.2).

The preparations involved basically the same steps and the same calcination temperatures as those outlined for the preparation of ultrastable zeolites. However, the calcinations were carried out in four different environments: (a) under vacuum (partial pressure less than 1 mm Hg); (b) in a flow of moist air containing 10% water; (c) under a static atmosphere in a muffle furnace, the sample having a bed depth of about 1.5 cm and the steam resulting from the 40 to 50 wt% water retained by the sieve ("self-steaming" conditions); and (d) under a flow of 100% steam. The preparation steps involved in obtaining different sieves from NaY (4.2) as well as the changes occurring during the thermal treatment are schematically shown in Fig. 1.

The crystallinity and unit cell size of the samples prepared was established from X-ray diffraction data. The collapse of certain samples during calcination was established from diffraction data and BET surface area measurements.

The pyridine used in the adsorption experiments was Baker analyzed reagent, dried over anhydrous KOH.

B. Instrumentation and infrared measurements. Infrared spectra were recorded using a Beckman IR-12 spectrophotometer at a scanning speed of 40 cm^{-1}/min and a spectral slit width of about 3 cm^{-1} at 3300 cm^{-1}. Self supporting pellets were used for the hydroxyl and pyridine region. A Wilks Model 38 attenuated total reflection (ATR) unit was used for the silica–alumina framework region.

The self supporting pellets were prepared by spreading about 0.03 g of zeolite powder over a polished hardened steel die, 1.9 cm in diameter, and pressing with a Carver laboratory press from 8000 to 10,000 psi. The pellets were supported in a stainless steel holder with a chromel–alumel thermocouple touching the edge of the pellet, placed in a special evacuable cell and heated by an element containing Watlow Firerod cartridges surrounding the pellet. The cell was positioned in the spectrometer and evacuated to about 10^{-5} mm Hg. Physically adsorbed water was removed by heating the pellet at the rate of 8°/min, under vacuum, to 500°C. This temperature was held for 1 hr. Then the pellet was cooled and lowered into the sample beam without breaking vacuum. Since the pellets usually transmitted less than 20% in the

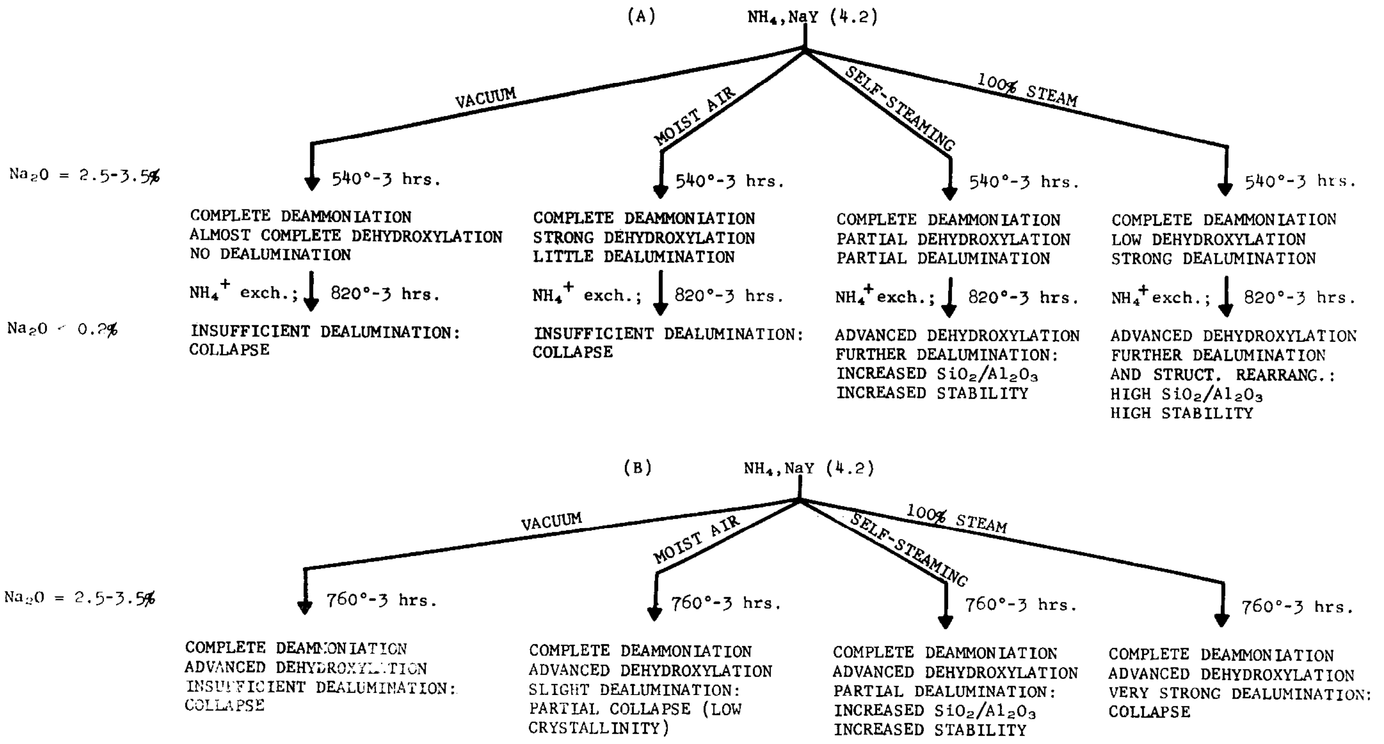


FIG. 1. Preparation steps and schematic representation of the processes taking place in ammonium exchanged Y sieves under different calcination conditions. (A) Calcination steps corresponding to the preparation of ultrastable zeolite, type I; (B) calcination steps corresponding to the preparation of ultrastable zeolite, type II

hydroxyl region because of light scattering, an attenuator was placed in the reference beam to obtain full scale deflection.

Water was readsorbed at 120°C and at 4 mm pressure for 2 hr. Deionized water was frozen using a dry ice–acetone bath, pumped to less than 10^{-3} mm Hg and thawed until the thermocouple gauge on a Granville-Phillips gauge controller read the desired pressure. The water container was then closed off from the system. After 2 hr the temperature was raised to either 200, 400 or 600°C, the chamber evacuated at this temperature for 2 hr, and then the sample was cooled to room temperature and lowered into the infrared beam for analysis.

Pyridine was adsorbed at room temperature using a similar freeze–pump–thaw procedure, except that the pyridine container was left open to the system for 2 hr to establish equilibrium with the zeolite pellet. Then the container was closed off from the system and the pellet was heated to 200°C for 2 hr under vacuum. This step is necessary because adsorbed pyridine at room temperature is totally absorbing at the infrared frequencies of interest. Then the sample was cooled, lowered into the beam and its spectrum was run.

A 10% (by wt) slurry of zeolite powder in ethanol was evaporated onto one side of a KRS-5 ATR plate (2 mm thick) and placed in the Wilks ATR unit. Because of the energy losses from the optical arrangement of this unit, an attenuator was placed in the reference beam to obtain full scale deflection. KRS-5 is transparent to infrared radiation throughout the region of most framework vibrations and is not affected by atmospheric moisture. The ATR spectra are similar to KBr spectra in the location of absorption maxima.

RESULTS

We will consider first the spectra of partially ammonium exchanged Y zeolites (NH_4,NaY) with a silica–alumina ratio of 4.2 and a sodium content of 3.5% Na_2O. Figure 2 shows the absorption bands in the hydroxyl stretching region of the spectra for NH_4,NaY samples after calcination at 540°C for 3 hr under vacuum, moist air, self-steaming conditions and under 100% steam.

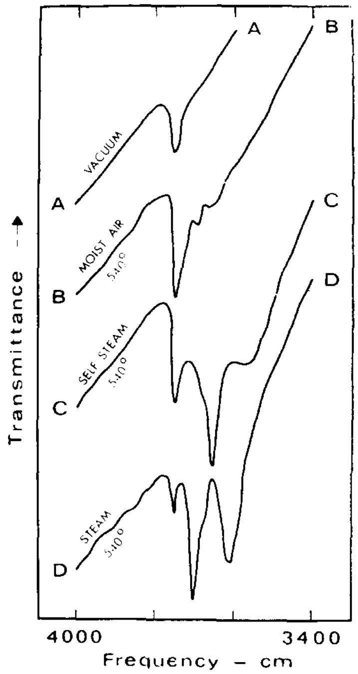


FIG. 2. Hydroxyl stretching region of H,NaY (540°C, 3 hr) zeolites: (A) vacuum, (B) moist air, (C) self steam, (D) steam.

The effect of pyridine adsorption on the hydroxyl stretching region in the spectra of NH_4,NaY zeolites calcined at 540°C under different conditions is shown in Fig. 3.

Figure 4 shows the infrared spectra of the same samples in the region between 300 and 1200 cm^{-1}. In a recent study by Flanigen, Khatami, and Szymanski (*5*), the bands in this region of the spectra were assigned to different types of vibration which occur in the zeolitic framework (see Table 1). We have selected several of these bands from our spectra in order to characterize the zeolites.

The spectra of the initial NaY and of noncalcined NH_4,NaY zeolite are practically identical in the 300 to 1200 cm^{-1} region. This indicates that in the absence of a high temperature thermal treatment, the exchange of sodium by ammonium ions

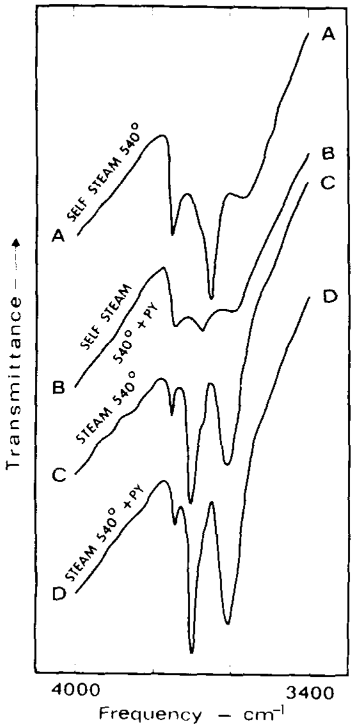


FIG. 3. Hydroxyl stretching region of H,NaY (540°C, 3 hr) zeolites: (A) self steam, (B) self steamed, then pyridine adsorption, (C) steam, (D) steamed, then pyridine adsorption.

has little or no effect on the vibrations in the zeolite framework.

The spectra of the completely exchanged ammonium Y zeolites ($Na_2O < 0.2\%$) in the 300 to 1200 cm^{-1} region are practically identical to those of the calcined NH_4, NaY zeolites used for their preparation.

TABLE 1

ZEOLITE FRAMEWORK INFRARED ASSIGNMENTS (5)

Internal tetrahedrons	External linkages
Asym. stretch 1250–950 cm^{-1}	Double ring 650–500 cm^{-1}
Sym. stretch 720–650	Pore opening 420–300
T–O bend[a] 500–420	Sym. stretch 820–750
	Asym. stretch 1150–1050 sh

[a] T represents Si or Al.

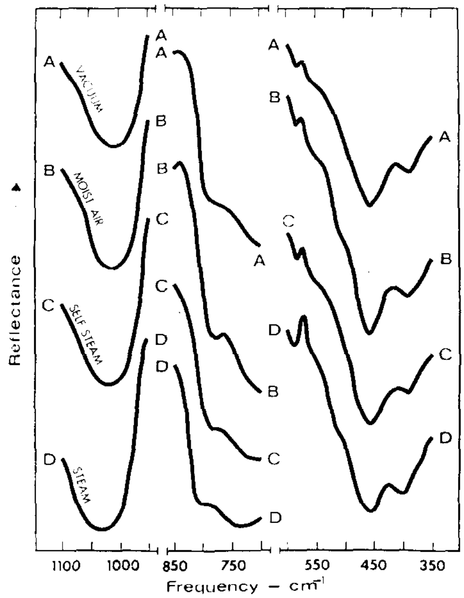


FIG. 4. Framework bands of H,NaY (540°C, 3 hr) zeolites: (A) vacuum, (B) moist air, (C) self steam, (D) steam.

However, when these ammonium exchanged Y zeolites were submitted to a final calcination at 820°C for 3 hr under the same conditions as the initial calcination at 540°C, only the samples calcined under self-steaming conditions or under 100% steam did not collapse. Structural X-ray data obtained for these two materials indicate that they are ultrastable zeolite, type I, and high silica ultrastable zeolite, respectively.

The hydroxyl stretching region of the spectra of these two stabilized zeolites indicates almost complete dehydroxylation. Besides a band at 3750 cm^{-1}, only weak shoulders can be detected in the 3680 and 3600 cm^{-1} region.

In Fig. 5 the spectra are shown for the same two materials in the 300 to 1200 cm^{-1} region (curves D and E). For comparison, the spectra in the same region are shown for the starting NaY zeolite (curve A) and for the two intermediate materials calcined at 540°C under self-steaming conditions and under 100% steam (curves B and C). The main T–O asymmetric stretching band in the spectra of the materials calcined at

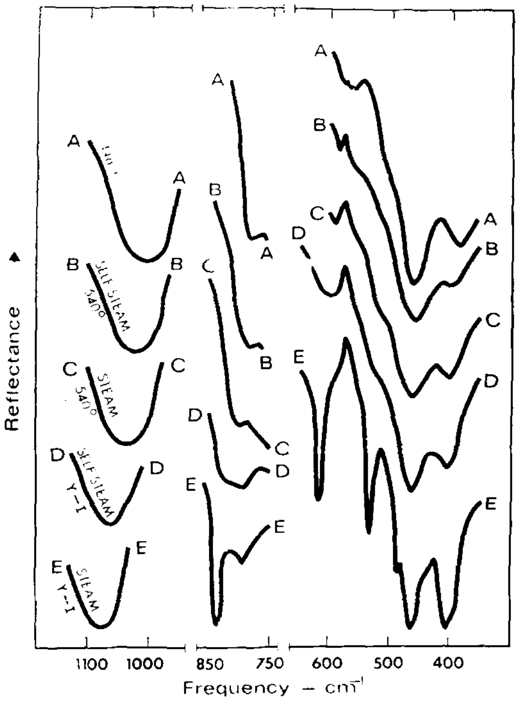


FIG. 5. Framework bands of YI zeolites: (A) NaY; (B) self-steam, 540°C; (C) steam, 540°C; (D) self steam, YI; (E) steam, YI.

820°C is drastically shifted toward higher frequencies: 1082 cm^{-1} for the steamed sample and 1067 cm^{-1} for the self-steamed sample, compared to 995 cm^{-1} for the initial NaY zeolite. The corresponding absorption bands of the two intermediate materials occupy an intermediate position. Similar shifts are found also in other parts of the spectra. The shift of absorption bands toward higher frequencies is accompanied by a shrinking of the unit cell size of these materials: 24.24 Å for the final, steamed sample vs 24.70 Å for the initial NaY zeolite.

The spectrum of the sample calcined at 820°C under 100% steam shows some additional features. Besides the strong shift toward higher frequencies, many absorption bands are stronger, sharper and some additional peaks can be detected. If the self-steamed material is slurried in water, filtered and then calcined at 820°C under self-steaming conditions, and the whole process is repeated three or four times, the spectrum of the resulting product is almost identical to that of the material calcined under 100% steam.

When NH_4,NaY samples are calcined at 760°C under different conditions, the effect of the environment upon the zeolite is different from that observed at 540°C. The X-ray diffraction data of the samples calcined at 760°C show that those calcined under vacuum or under 100% steam have collapsed, and the sample calcined in moist air has low crystallinity.

Figure 6 shows the absorption bands in the hydroxyl stretching region for the two zeolites which did not collapse at 760°C: the material calcined in moist air (curve C) and the material calcined under self-steaming conditions (curve D). For comparison, the absorption bands in the same region of the spectra are shown for the NH_4, NaY zeolites calcined at 540°C under similar conditions. Besides the band at 3750 cm^{-1}, the spectra of the two samples

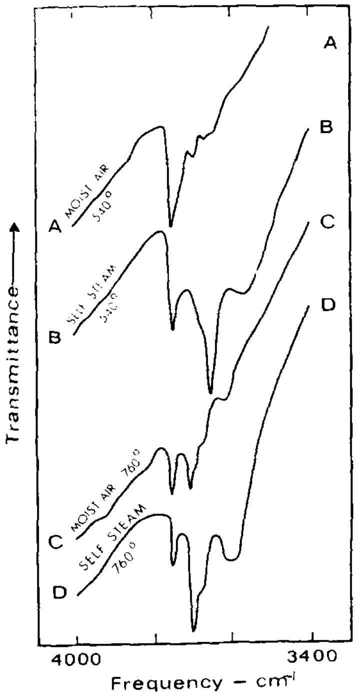


FIG. 6. Hydroxyl stretching region of H,NaY (540°C, 3 hr and 760°C, 3 hr) zeolites: (A) moist air, 540°C; (B) self steam, 540°C; (C) moist air, 760°C; (D) self steam, 760°C.

calcined at 760°C show bands in the 3700 and 3600 cm^{-1} region, with shoulders at about 3680 cm^{-1}. The bands are stronger and sharper in the spectrum of the self-steamed sample. Pyridine adsorption does not affect these bands.

In Fig. 7 some of the absorption bands in the 300 to 1200 cm^{-1} region are shown for the NH_4,NaY samples calcined in moist air (curve C) and under self-steaming conditions (curve D) at 760°C. For comparison, the corresponding bands of the NH_4,NaY zeolite calcined under the same conditions at 540°C are also shown (curves A and B). For the samples calcined at 760°C, the main asymmetric stretching band of the self-steamed material has a higher frequency than the one of the sample calcined in moist air: 1037 vs 1024 cm^{-1}. Both bands are located at significantly higher frequencies than the asymmetric stretching band of the NH_4,NaY zeolite prior to its thermal treatment (995 cm^{-1}). Similar shifts are observed for other bands in the spectra, as compared to the corresponding bands of the uncalcined sample. Figure 7 also shows that in the same environment, an increase in calcination temperature from 540 to 760°C causes a stronger shift to higher frequencies, especially for the asymmetric stretching band (compare curves A and C, B and D). The stronger shift to higher frequencies is accompanied by a corresponding decrease in unit cell size.

When the two samples calcined at 760°C were ammonium exchanged and then submitted to a final calcination at 820°C for 3 hr under conditions identical to those of their first thermal treatment, X-ray diffraction data showed that only the self-steamed material did not collapse.

Figure 8 shows the effect of rehydration of ultrastable zeolite type I, on Bronsted and Lewis acid sites, as indicated by the spectrum of adsorbed pyridine in the 1400–1600 cm^{-1} region. The band at 1545 cm^{-1} is considered characteristic for the presence

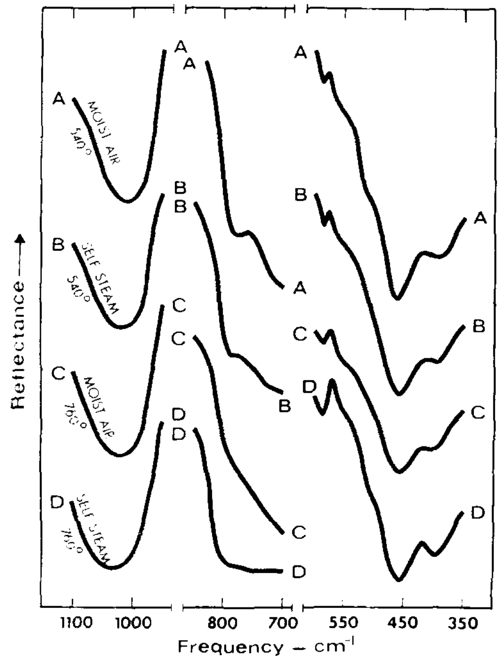


FIG. 7. Framework bands of H,NaY (540°C, 3 hr and 760°C, 3 hr) zeolites: (A) moist air, 540°C; (B) self steam, 540°C; (C) moist air, 760°C; (D) self steam, 760°C.

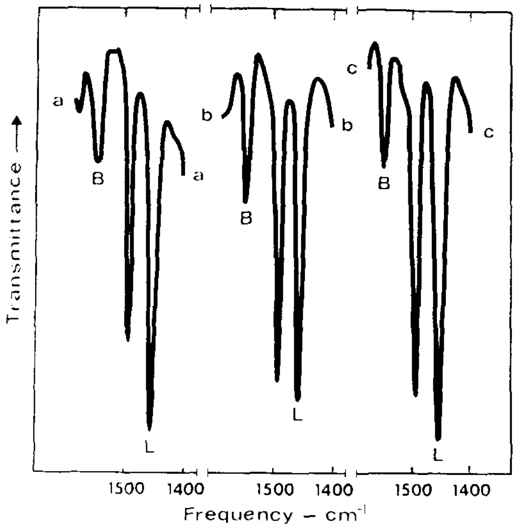


FIG. 8. Effect of rehydration of ultrastable zeolite, type I on Bronsted and Lewis acid sites using adsorbed pyridine spectrum: (B) Bronsted band, (L) Lewis band; spectrum (a) type I, not rehydrated, followed by pyridine adsorption; (b) type I after H_2O is adsorbed under 4 mm pressure at 120°C, then calcined at 400°C, followed by pyridine adsorption; and (c) type I after H_2O is adsorbed under 4 mm pressure at 120°C, then calcined at 600°C followed by pyridine adsorption.

TABLE 2
HYDROXYL STRETCHING FREQUENCIES[a]

Zeolite type[b]	cm^{-1}	cm^{-1}	cm^{-1}
H, NaY (540°C, vacuum)	3650 (sh)		
H, NaY (540°C, moist air)	3650 (w)	3690 (w)	
H, NaY (540°C, self steamed)	3575 (m)	3650 (s)	3680 (sh)
H, NaY (540°C, 100% steam)	3615 (s)	3670 (sh)	3705 (s)
US-YI (self steamed)	3600 (sh)	3670 (w)	
H, NaY (760°C, moist air)	3620 (sh)	3685 (sh)	3705 (m)
H, NaY (760°C, self steamed)	3600 (m)	3680 (sh)	3707 (s)

[a] w = weak; m = medium; s = strong; sh = shoulder.

[b] The formulas used for the different samples do not reflect the true composition and are only used to distinguish the compounds according to their preparation.

of Bronsted acid type sites, and the band at 1455 cm^{-1} is characteristic for Lewis acid type sites.

The hydroxyl stretching and selected framework vibrational frequencies of the previously described zeolites are summarized in Tables 2 and 3.

DISCUSSION

There are a number of references in the literature describing the correlation between the calcination temperature of a partially or totally ammonium exchanged type Y zeolite, and its characteristic infrared absorption bands, especially in the hydroxyl stretching region [see, for example, Refs. (4, 6–9)].

The HY zeolite, obtained by deamination of NH_4Y, has three absorption bands in the hydroxyl stretching region of its infrared spectrum: at 3750, 3650 and 3550 cm^{-1}. It is assumed that the band at 3750 cm^{-1} is due to terminal silanol groups or silica gel like impurities (*10*) and is not characteristic of the type Y zeolite structure. The other two bands—a high-frequency (HF) band at 3650 cm^{-1} and a low frequency (LF) band at 3550 cm^{-1}—are both due to type Y structural hydroxyls. It was suggested (*6, 11*) that the HF band is generated by OH groups containing "bridge oxygen" (O_1-type atoms forming the hexagonal prism between cubo-octahedrons), while the LF band is generated by OH groups involving "ring oxygens," probably O_3-type atoms. Hydroxyl groups generating the 3650 cm^{-1} band are generally considered responsible for the Bronsted type acidity in the zeolite. These OH groups interact with adsorbed pyridine. Both the 3650 and 3550 cm^{-1} bands interact with NH_3 (*7*).

TABLE 3
FRAMEWORK VIBRATIONAL FREQUENCIES

Zeolite type[a]	T–O asym. stretch (cm^{-1})	T–O sym. Stretch (cm^{-1})	Double 6 Ring (cm^{-1})	T–O bend (cm^{-1})	12-Ring pore opening (cm^{-1})	Unit cell (Å)
NaY	995	775	580	463	387	24.70
H, NaY (540°C vacuum)	1005	780	583	456	388	24.64
H, NaY (540°C, moist air)	1008	780	583	457	393	24.63
H, NaY (540°C, self steamed)	1023	780	583	456	393	24.61
H, NaY (540°C, 100% steam)	1035	805	590	460	398	24.57
US-YI (self steamed)	1067	810	600	460	403	24.37
HS US-YI (100% steam)	1082	837	614	465	408	24.24
H, NaY (760°C, moist air)	1024	795	584	455	402	24.61
H, NaY (760°C, self steamed)	1037	800	586	460	404	24.56

[a] See footnote *b* for Table 2.

The experimental data presented in the previous section show that calcination of ammonium exchanged type Y zeolites in the presence of variable amounts of moisture results in more complex spectra. This suggests that the presence of moisture during calcination affects the structure of the zeolite.

A. Spectra of NH_4, NaY Zeolites Calcined at 540°C: OH Stretching Region

Figure 2 shows that when partially ammonium exchanged sodium Y zeolite is calcined at 540°C for 3 hr, the hydroxyl stretching region of the resulting material is strongly affected by the moisture content of the zeolite's environment during calcination. The spectra also show that all the calcined samples completely lose NH_3.

Besides the band at 3750 cm^{-1}, the spectrum of the sample calcined under vacuum has only a shoulder in the region of 3650 cm^{-1}, which indicates a significant loss of hydroxyl groups responsible for this band. However, when the calcination under vacuum is done on a pelleted sample, the 3650 cm^{-1} band is still fairly strong after calcination at 540°C (see Fig. 9). This reflects the effect of geometrical configuration of the sample during calcination upon the dehydroxylation process. At lower calcination temperature, the 3550 cm^{-1} band is also clearly visible. No band can be identified in the 3550 cm^{-1} region after calcination at 540°C, due to the lower thermal stability of the hydroxyl groups responsible for this band (*6*).

By increasing the amount of moisture in the calcination environment, the number of hydroxyl groups absorbing in the 3650 cm^{-1} region increases, and in the spectrum of the sample calcined under self-steaming conditions there is a strong band in this region. Since the dehydroxylation of the zeolite occurs through elimination of water from its structure, it is reasonable to assume that a higher moisture content in its environment will retard this process. However, under severe steaming conditions (100% steam), this band has disappeared from the spectrum, due to more profound structural changes (vide infra). At the same time, new absorption bands appear in the 3600 and 3700 cm^{-1} regions; their intensity increases with increasing moisture content, reaching a maximum in the spectrum of the material calcined under steam. The presence of bands in the 3600 and 3700 cm^{-1} region, which was also observed by Jacobs and Uytterhoeven (*4*), obviously reflects structural changes that occur in the zeolite during calcination. These structural changes can be easier interpreted after analyzing the lower frequency region of the spectra of these materials.

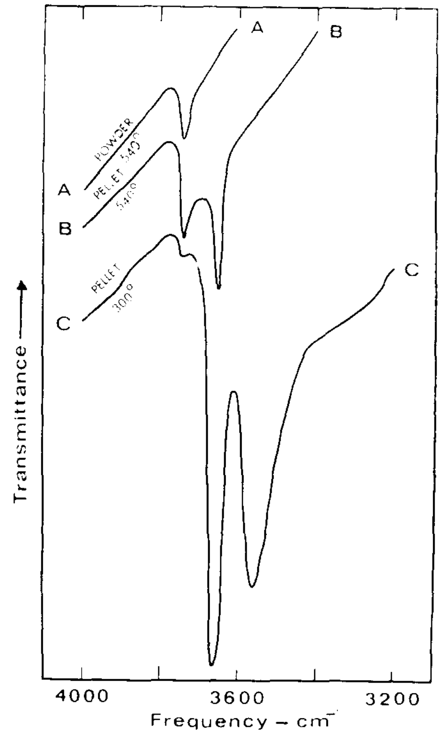


FIG. 9. Effects of geometrical configuration, compactness and temperature of sample during vacuum calcination on extent of dehydroxylation: (A) sample calcined as a powder in vacuum at 540°, 3 hr, then pelleted and calcined in vacuum for 1 hr at 500°C; (B) sample pelleted, then calcined in vacuum at 540°C, 3 hr; (C) sample pelleted, then calcined in vacuum at 300°C, 3 hr.

B. Spectra of NH_4, NaY Zeolites Calcined at 540°C: Framework Region

An analysis of the spectra in the 300 to 1200 cm^{-1} region (Fig. 4) indicates that the changes in the sample's environment during calcination at 540°C affect primarily the T–O asymmetric stretching band. By increasing the amount of moisture in the sample's environment during calcination, the T–O asymmetric stretching band is shifted from 1005 cm^{-1} for the vacuum-calcined sample to 1035 cm^{-1} for the steam-calcined sample.

A shift in frequency in the same direction, although to a smaller degree, is also observed for the other absorption bands in the spectrum.

Flanigen, Khatami and Szymanski (*5*), have shown that an increase in the SiO_2/Al_2O_3 ratio in the Y type framework results in a shift toward higher frequencies of the main asymmetric T–O stretch band, the symmetric stretch band, the double 6-member ring band and the 12-member ring pore opening band. Similar shifts for varying SiO_2/Al_2O_3 ratios in Y type sieves have been observed by Kiselev and Lygin (*12*), Zhdanow *et al.* (*13*) and Wright, Rupert, and Granquist (*14*). The shift of these bands toward higher frequencies observed in our experiments when the environmental moisture content is increased can therefore be related to the increase in the SiO_2/Al_2O_3 ratio in the framework of these materials. Such an increase is the result of partial removal of aluminum from the zeolite framework during calcination in a moist environment. The structural X-ray study by Maher, Hunter and Scherzer (*2*), has shown that in the process of calcining partially ammonium exchanged sodium Y zeolite under self-steaming conditions about 15 aluminum atoms/unit cell were removed from the framework and located in cationic sites S'_I in the form of $Al(OH)_2^+$ cations (Table 4, Structure I).

In view of these data, the shift toward higher frequencies of infrared absorption bands characteristic for the zeolitic skeleton is closely related to the removal of aluminum from the zeolitic framework. This is the effect of interaction between the framework and moisture at high temperature. Mechanisms for such a process have already been suggested (*2*). The higher the moisture content in the system during calcination, the more aluminum will be removed from the framework, resulting in a stronger shift of infrared bands toward higher frequencies. The strongest shift

TABLE 4

FRAMEWORK AND NONFRAMEWORK POSITIONS IN TYPE Y ZEOLITES (*2*)

Position	No. of positions/ unit cell	Structure I[a]		Structure III		Structure IV	
		OP[b]	No. Occ. Pos.[c]	OP	No. Occ. Pos.	OP	No. Occ. Pos.
Si, Al	192	0.92	176.6	0.92	176.6	1.00	192
O_1	96	0.78	74.9	1.00	96	1.00	96
O_2	96	1.00	96	1.00	96	1.00	96
O_3	96	1.00	96	0.74	71.0	0.87	83.5
O_4	96	1.00	96	0.86	82.6	1.00	96
S_{II}[d]	32	0.46	14.7 $Al(OH)_2^+$	0.46	4.9 AlO (OH)	0.23	2.4 AlO (OH)
S_{III}[e]	32	1.00	32 OH^-				
S_V[f]	16	0.32	5.1 Na^+				

[a] Structure I: partially ammonium exchanged Y zeolite, calcined at 540°C for 3 hr under self-steaming conditions.

Structure III: ultrastable zeolite type I.

Structure IV: high-silica ultrastable zeolite.

[b] OP = occupancy parameter.

[c] No. Occ. Pos. = Number of occupied positions.

[d] S_{II} (or S'_I) is within the sodalite cage, close to the 6-member ring shared by the sodalite cage and the hexagonal prism.

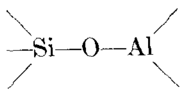
[e] S_{III} (or S'_{II}) is within the sodalite cage, close to the 6-member ring shared by the sodalite cage and the supercage.

[f] S_V is in the center of the 12-membered ring.

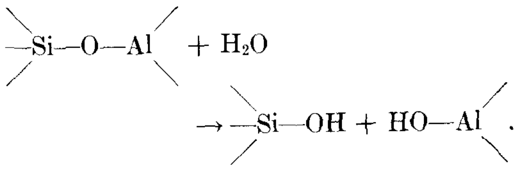
is usually observed for the T–O asymmetric stretching band. The increase of the SiO_2/Al_2O_3 ratio in the framework due to removal of aluminum apparently has an effect on the position of the T–O asymmetric stretching band similar to the one resulting from the increase of the SiO_2/Al_2O_3 ratio by direct synthesis. Data published by Pichat, Beaumont, and Barthomeuf (*15*) and by Lahodny-Šarc and White (*16*) concerning the infrared spectra of aluminum-deficient Y type zeolites support this assumption. Other structural bands whose positions are also affected by the SiO_2/Al_2O_3 ratio of the framework show similar behavior, although the shifts are not as strong.

C. Diversity of OH Groups

It is assumed that partial dealumination of the framework generates new OH groups attached to the framework as well as to the cationic aluminum species (*2*). The new OH groups result from the interaction of steam with



bonds, leading to reactions of the type



The absorption bands observed in the spectra of self-steamed and steamed materials in the 3600 and 3700 cm^{-1} regions are probably due to OH groups resulting from the dealumination process. The strong intensity of these bands in the spectrum of the sample calcined under 100% steam, when advanced dealumination of the framework takes place, supports this assumption. The absence of an absorption band in the 1640 cm^{-1} region, which band is characteristic for the H_2O deformation vibration, excludes the possibility that any of the new bands in the OH stretching region are due to physically adsorbed water. These bands are not visibly affected by pyridine (see Fig. 3) and therefore appear to be nonacidic or inaccessible to pyridine. Treatment of the self-steamed or steamed samples with a 0.1 *N* solution of NaOH at room temperature does not eliminate these two bands from the spectra, but reduces the intensity of the band in the 3600 cm^{-1} region. This could indicate a weak acidity of the OH groups responsible for this band. These finding are in agreement with those of Jacobs and Uytterhoeven (*4*).

The changes in the zeolite under the effect of steam or moisture will affect the local electrostatic field acting upon the structural OH groups. The framework modifications and cationic distributions are not the same in different samples under discussion, and depend strongly upon the moisture content in the calcination environment, calcination temperature, chemical treatment, and other parameters. This could explain why the OH stretching bands assigned to a certain type of OH groups, do not appear at the same frequency, but rather in a "region" covering about 20 or 30 cm^{-1}. The broadness and asymmetric shape of certain adsorption bands in the OH stretching region (see Fig. 2) is probably the result of partial band overlapping. Intensive steaming or high calcination temperatures generate in the 3680–3700 cm^{-1} region a band with a shoulder at its lower frequency end, suggesting that OH groups with similar but not identical absorption frequencies are responsible for the absorption in this region (see Fig. 2 curve D and Fig. 6 curves C and D). Under these conditions, a strong absorption occurs primarily at about 3705 cm^{-1}, whereas the sample calcined at 540°C under self-steaming conditions has a corresponding absorption at about 3680 cm^{-1} (see Fig. 2, curve C). A similar shift toward higher frequencies is shown by the band in the 3600 cm^{-1} region. Such a shift toward higher frequencies seems related to advanced framework dealumination under steam.

The band in the 3680–3700 cm^{-1} region is probably generated by OH groups attached to the framework. The band in the 3600 cm^{-1} region is presumably due to OH groups close to cationic aluminum. This could account for the weakly acidic nature of this band (polarization effect). The inertness of the band at 3600 cm^{-1} toward pyridine and its interaction with sodium hydroxide suggest that the corresponding OH groups are not located in the zeolite supercage. This is also in line with structural X-ray data (*2*) which show that cationic aluminum is located in the sodalite cage. However, further information is required for a more accurate localization of these groups.

We have seen that at 540°C, a moderate increase in moisture content in the calcination environment tends to suppress the dehydroxylation process of the zeolite. Moderate dealumination of the zeolitic framework (up to 25–30% alumina removed) and the resulting increase in its silica–alumina ratio will also increase the thermal stability of the OH groups and retard the dehydroxylation process. This is in agreement with the findings by Uytterhoeven *et al.* (*6*), who showed that in the case of ammonium exchanged sieves, the X type zeolites (low SiO_2/Al_2O_3 ratio) are easier to dehydroxylate than Y type zeolites (high SiO_2/Al_2O_3 ratio).

However, intensive framework dealumination under steam or high temperatures, while enhancing the intensity of the bands at 3600 and 3700 cm^{-1}, will suppress the acidic absorption band at 3650 cm^{-1}. The suppression of this band is a result of the drastic reduction in tetrahedrally coordinated aluminum in the framework.

D. Spectra of Y Zeolites Calcined at 820°C

We have seen that when calcined NH_4, NaY sieves were ammonium exchanged to remove the remaining sodium ions (to less than 0.2 wt % Na_2O) and then calcined at 820°C for 3 hr under the same conditions as in their previous thermal treatment, the materials resulting from calcination under vacuum or under 10% moist air collapsed. The materials resulting from calcination under self-steaming and steaming conditions are ultrastable zeolite type I (US-YI), and high silica ultrastable zeolite (HS US-YI), respectively.

Despite the presence of moisture in the zeolite's environment, these stabilized zeolites are almost totally dehydroxylated as a result of the high calcination temperature. The strong shift towards higher frequencies of the infrared bands characteristic for the framework vibrations indicates a significant increase of the SiO_2/Al_2O_3 ratio in the framework. This can result from further aluminum removal from the framework. However, structural X-ray studies have shown (*2*) that in the material exposed to intensive steaming (high silica ultrastable zeolite), the vacancies left in the framework due to removal of aluminum during the first calcination are filled during the final high temperature calcination under steam (see Table 4, Structure IV). Most of the oxygen atoms missing from the framework after the first calcination are also replaced during the final calcination.

These data indicate that besides aluminum removal from the framework, the presence of steam at high temperatures facilitates a structural rearrangement in the zeolite. Such a rearrangement could be viewed as a recrystallization process involving silica migration into the vacancies created by dealumination. The silica could originate from amorphous silica gel trapped in the zeolite during its synthesis or from other portions of the sample (e.g., from regions with structural breakdown; smaller crystallites are likely to collapse). Wyart and Sabatier (*17*) have shown that at 400°C and for a steam density of 0.56, the amount of amorphous silica volatilized is 1200 mg/kg of steam. Therefore, it is obvious that under intense steaming and at higher temperatures the transport of silica will be significantly enhanced as compared to self-steaming conditions. The higher silica content of the structure obtained by calcination under 100% steam accounts for the stronger shift toward higher frequencies of characteristic infrared absorption bands. It could also explain the high thermal stability, low ion exchange capability and the unusually small unit cell size of this material.

The structural rearrangement and elimination of framework vacancies could explain the sharper absorption bands in the framework vibrational spectrum of steamed zeolites. Sharper absorption bands would indicate a higher degree of crystallinity or a higher "degree of ordering" in the framework. The progression of absorption maxima to higher frequencies and of increasing band sharpness is illustrated by Fig. 10 which compares the low frequency spectrum of NaY (4.2), the starting material, with ultrastable zeolite, type I, and high silica ultrastable zeolite. A somewhat similar effect of the "degree of ordering" on the infrared bands has been observed by Laves and Hafner (*18*) for aluminosilicates of the feldspar type.

The high SiO_2/Al_2O_3 ratio of the stabilized zeolitic framework resulting from both alumina elimination and the structural rearrangement accounts also for the significant shortening of the average T–O bond distance in the framework. In the partially ammonium exchanged NaY zeolite, calcined under self-steaming conditions at 540°C, the T–O bond distance has a mean value close to 1.69 Å, while in the high silica ultrastable zeolite that distance is 1.61 Å (*2*). The value assigned by Jones (*19*) for a pure Si–O bond distance is 1.603 Å. Similarly, the position of the asymmetric T–O stretch band of the steamed zeolite at 1082 cm^{-1} is much closer to that observed for pure silica (in the 1100 cm^{-1} region) than to that of the original NaY zeolite (995 cm^{-1}). All these data indicate that in the zeolite calcined under 100% steam, the majority of tetrahedral aluminum atoms have been removed from the framework. This is in excellent agreement with structural X-ray data obtained for high silica ultrastable zeolite.

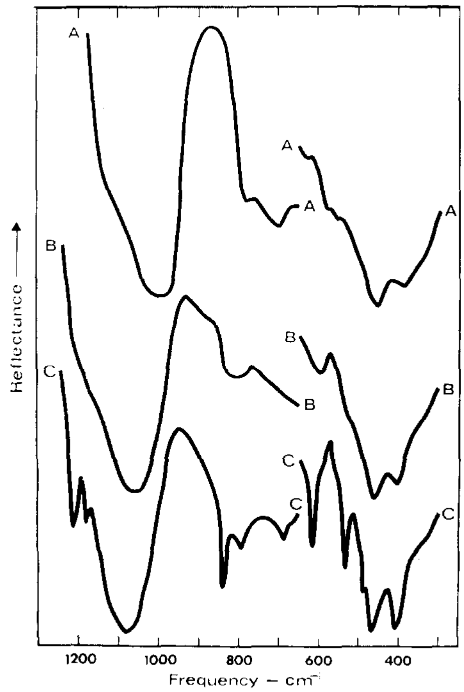


FIG. 10. Framework bands of (A) NaY (4.2), (B) ultrastable zeolite, type I, and (C) high silica ultrastable zeolite.

However, the possibility that other processes occur during the structural rearrangement in the zeolite, besides silica migration, should not be excluded. This high-temperature restructuring process still requires further investigation.

If no or insufficient moisture is present in the zeolite environment during calcination at 820°C, neither the dealumination process nor any structural rearrangement can take place to a significant degree. In this case, due to the relatively low SiO_2/Al_2O_3 ratio of the framework, it becomes unstable at high temperatures and collapses. This explains the collapse of the samples with a final calcination at 820°C under vacuum or under 10% moist air. Such is the behavior of a normal hydrogen Y zeolite, which has low thermal stability.

The infrared spectrum in the 300 to 1200 cm^{-1} region of the ultrastable zeolite, type I, prepared from NaY (4.75) under self-steaming conditions occupies somewhat an intermediate position between the spectra of stabilized sieves obtained from NaY (4.2) under self-steaming conditions and under 100% steam. The peaks in the spectrum of US-Y I (4.75; Sst) sieve are sharper and stronger than those in the spectrum of US-Y I (4.2; Sst), yet not as strong as those obtained for US-Y I (4.2; St). A comparison between US-Y I (4.2) and US-Y I (4.75) is shown in Fig. 11. The unit cell size has also an intermediate value: 24.31 Å for the US-Y I (4.75; Sst) vs 24.37 Å for the US-Y I (4.2; Sst) and 24.24 Å for the High Silica US-Y I (4.2;

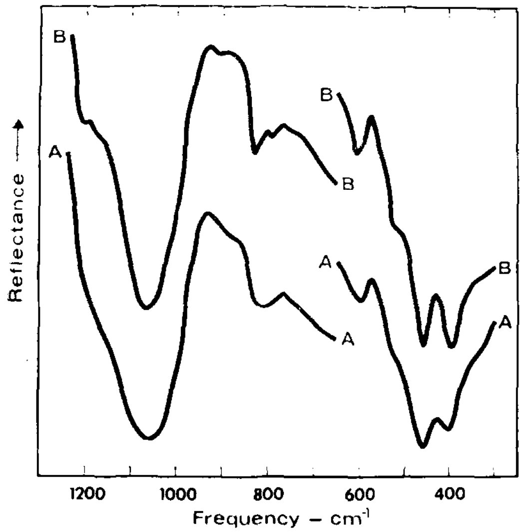


FIG. 11. Framework bands of (A) ultrastable zeolite, type I, prepared from NaY (4.2) and (B) ultrastable zeolite, type I, prepared from NaY (4.75).

St). These data indicate that the SiO_2/Al_2O_3 ratio and the "degree of ordering" in the framework of US-Y I (4.75; Sst) is higher than in US-Y I (4.2; Sst), yet lower than in High Silica US-Y I (4.2; St).

E. Spectra of NH_4, NaY Zeolites Calcined At 760°C

We have seen that when the calcination temperature for the partially ammonium exchanged Y zeolite is increased from 540 to 760°C, only the sample calcined under self-steaming conditions or under moist air did not collapse. The former case corresponds to the preparation of ultrastable zeolite, type II, as recommended by McDaniel and Maher. A comparison between the spectra of the samples calcined at 540 and 760°C in a similar environment clearly shows that an increase in temperature enhances the buildup of absorption bands in the 3600 and 3700 cm^{-1} region (see Fig. 6) and causes a stronger shift of absorption bands in the framework region toward higher frequencies (see Fig. 7).

It indicates that for similar moisture content in the calcination environment, an increase in temperature enhances the dealumination process of the framework. This enhanced dealumination results in a smaller unit cell size for the samples calcined at higher temperatures. The similarity of the spectra in the hydroxyl region of NH_4, NaY calcined at 540°C under 100% steam and at 760°C under self-steaming conditions (compare Fig. 2D with 6D) suggests that a similar degree of dealumination can be achieved either at lower temperature and higher moisture content, or higher temperature and lower moisture content.

Partial dealumination of the framework stabilizes the zeolitic structure. When the calcination of the partially ammonium exchanged zeolite is carried out at 760°C under 100% steam, the degree of dealumination of the framework is too high, so that the remaining structure is unstable and collapses. On the other hand, where the calcination is carried out under vacuum, the lack of dealumination prevents the stabilization of the framework and results in the collapse of the zeolite. The optimum stabilization appears under self-steaming conditions, resulting in a material of fairly high crystallinity.

The instability of the sodium-containing sieve at 760°C under steam is probably related not only to advanced dealumination of the framework, but also to the interaction of the sodium ions with the framework. That interaction between sodium ions and adjacent framework bonds is enhanced by both high temperatures and the presence of steam and results in the breaking of these bonds.

An increase of the initial silica–alumina ratio in the zeolite framework will obviously increase its overall stability and could prevent the collapse under the above described conditions.

The transformations taking place in the zeolitic materials under different calcination conditions are schematically summarized in Fig. 1.

F. Pyridine Adsorption on Ultrastable Zeolites

In view of the structural changes taking place in the zeolite framework during the preparation of the ultrastable zeolites, the rehydration of these materials does not regenerate Bronsted acid sites to a significant degree (see Fig. 8). The spectrum of pyridine adsorbed on a rehydrated ultrastable zeolite, type I, (under 4 mm H_2O pressure) does not show any significant difference from that obtained for pyridine adsorbed on the initial ultrastable zeolite. If we assume that the presence of an absorption band at 1545 cm^{-1} is indicative for the existence of Bronsted acid type sites in these materials, then the spectra obtained suggest that this type of acidity exists in the ultrastable zeolite in spite of the absence of both HF and LF hydroxyl stretching bands. Such a phenomenon has also been observed by others [cf. (*8*)]. A more detailed study of pyridine adsorption on different materials investigated in this paper is now in progress.

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