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Infrared Study of Deep-Bed Calcined NH_4Y Zeolites

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An infrared spectroscopic study has been made of the hydroxyl groups in so-called ultrastable faujasites and deep-bed calcined NH_4Y samples. The observations include, besides the typical bands at 3650 and 3550 cm^{-1} generally observed in conventional HY, two additional bands around 3700 and 3600 cm^{-1}. The intensity of these bands is high, and the hydroxyls involved do not react with NH_3 or pyridine. The bands persist after treatment with water vapor at 400°C. Extractions with 0.1 N NaOH removed an important fraction of aluminum, but the 3700 and 3600 cm^{-1} bands were not affected. Thus, these bands are considered to be due to framework hydroxyls created during the deep-bed calcination step. The two frequencies may correspond to distinct locations in the framework. The question is raised whether or not these observations require reinterpretation of former work on faujasites saturated with divalent cations.

INTRODUCTION

Thermal decomposition of ammonium-exchanged Y zeolites can yield different products (*1*). Vacuum treatment at moderate temperatures ($<$500°C) results in the formation of a stoichiometric hydrogen Y zeolite, containing almost one hydroxyl group for each ammonium ion decomposed. The hydrogen Y zeolite is generally known to be unstable. Heating above 550°C results in a dehydroxylation. A concomitant formation of trigonal aluminum and even trigonal silicon bearing a positive charge has been postulated. Examples of these reactions can be found in Refs. *1–5*.

McDaniel and Maher (*6*) prepared a so-called ultrastable form of faujasite. The procedure included the usual NH_4^+ exchange at 100°C, heating at 540°C, a second exchange followed by calcination at 815°C. The material remained crystalline and preserved its sorption capacity. It had a very high catalytic activity. The authors postulated a correlation between the enhanced stability and the decreased Na^+ content.

On the basis of DTA and X-ray diffraction results, Ambs and Flank (*7*) concluded that the ultrastable faujasite is not intrinsically different from a common ammonium-exchanged faujasite. The enhancement of stability was ascribed to the low value of the Na content. The intermediate heating was supposed to stimulate the migration of residual Na^+ ions out of the hexagonal prisms towards more accessible sites for exchange.

Kerr (*5, 8, 10, 11*) proved that the removal of tetracoordinated aluminum by the action of H_4EDTA on Y zeolites resulted in a product of increased stability. The effect was maximum for a removal of 30% of the aluminum.

More recently Kerr (*9*) also pointed out the influence of the geometry of the calcination bed. Shallow-bed calcination of NH_4Y produced a typical HY. Deep-bed calcination produced a product that had several properties in common with the ultrastable form of M and M (*6*): a contracted lattice, a greater stability, lower cation exchange capacity, and a lower content of constitution water.

Transfer of aluminum from tetrahedral lattice positions into cation exchange positions was assumed. It was suggested that the formation of new Si–O–Si linkages was at the origin of the increased stability. Kerr (*9*) made the reflection that many reports on catalytic and chemical properties of HY could have described properties of framework-aluminum-deficient zeolites.

The catalytic properties of HY being generally ascribed to the presence of acidic hydroxyls, much work has been devoted to the study of these hydroxyls by infrared spectroscopy. With the reflection of Kerr in mind, we have undertaken a comparison of the ir spectra of conventional hydrogen Y, of a deep-bed calcined NH_4^+ Y and of an aluminum deficient sample prepared by H_4EDTA extraction.

EXPERIMENTAL

A commercial sample of zeolite Y was obtained from the Linde Company. The anhydrous unit-cell composition is given in Table 1. From this we prepared different samples in the following way:

(i) In a conventional ion exchange procedure using a 0.1 *N* solution of NH_4Cl, a NH_4Y sample was prepared with almost 70% of the exchangeable Na^+ ions replaced by NH_4^+: On this sample a "deep-bed" calcination at 550°C was applied following the procedure described by Kerr (*9*). This material will be denoted as YDB. The YDB sample was then exchanged once more with NH_4^+ in order to replace the rest of the Na^+ ions. The sample obtained in this way will be indicated by the symbols $YDBNH_4^+$.

TABLE 1

Sample	Anhydrous unit-cell composition
NaY	$Na_{55}\ (AlO_2)_{55}\ (SiO_2)_{137}$
NH_4^+Y	$Na_{17}\ (NH_4)_{38}\ (AlO_2)_{55}\ (SiO_2)_{137}$
$YDBNH_4^+$	$Na_{0.4}\ (NH_4)_{17}\ Al_x(Al_{1-x}O_2)_{52}\ (SiO_2)_{137}$[a]
AlD	$Na_{49.4}\ (AlO_2)_{49.4}\ (SiO_2)_{137}$
$AlDNH_4^+$	$Na_{13.2}\ (NH_4)_{39.2}\ (AlO_2)_{49.4}\ (SiO_2)_{137}$

[a] A fraction of the aluminum is not in the framework but is supposed to occupy ion-exchange sites. By extraction with 0.1 *N* NaOH, 31% of the aluminum could be extracted from the $YDBNH_4^+$ sample. If this represents the amount of aluminum on ion-exchange sites, x is equal to 0.31.

(ii) An aluminum-deficient sample (AlD) was prepared from the original NaY by slow addition of H_4EDTA in a Soxhlet extractor following the method of Kerr (*10*). This sample was then also exchanged with NH_4^+ to yield the sample $AlDNH_4^+$. The anhydrous unit-cell compositions of the different samples are listed in Table 1.

Aliquots of the different samples were pressed into thin films between stainless steel plates under a load of 300 kg cm^{-2} of film. The film "thickness" was between 2.5 and 4 mg of dry material solidus cm^{-2}. These films were placed in an infrared cell which could be heated (max. 500°C) and evacuated while mounted in the spectrograph. Full details on the construction of the cell are given elsewhere (*3*). The spectra were recorded on a Beckman IR12 double-beam grating spectrometer in the spectral regions between 3800 and 3000 cm^{-1}, and between 1400 and 1700 cm^{-1}. The slit opening was such that a resolution of better than 3 cm^{-1} was obtained at 3600 cm^{-1}.

The films were outgassed at room temperature until a vacuum of 10^{-6} Torr was obtained, then heated to a fixed temperature (see Results), and cooled to room temperature. The spectra were taken at room temperature.

In special experiments aliquots of the YDB sample were extracted with 0.1 *N* and 0.01 *N* NaOH solutions (*9*). These extractions were carried out in plastic centrifuge bottles. Afterwards the samples were washed free from excess reagent and dried as explained before. The extract was analysed for aluminum and the composition of the extracted sample calculated from the amount of aluminum extracted. Both samples were treated again with 0.1 *N* NH_4Cl solutions at room temperature.

RESULTS

A typical HY has two characteristic OH bands: the high frequency band (HF) at

3650 cm^{-1} and the low frequency one (LF) at 3550 cm^{-1}.

Figure 1 represents the OH stretching spectrum of the sample YDB. Two intense bands at 3675 and 3600 cm^{-1} and a small one at 3750 cm^{-1} are found in the broad envelope of adsorbed water (curves a, b). At 450°C the ν_2 of water around 1645 cm^{-1} has completely disappeared. Supplementary bands at 3665 and 3560 cm^{-1} (shoulder) are resolved (c). These bands are identical to the HF and LF bands in HY. On deuteration with D_2O all the hydroxyls disappear (curve e), and OD bands emerge at the corresponding lower wavenumbers. Adsorbing NH_3 gas at room temperature resulted in the suppression of the 3665 and 3560 cm^{-1} components (d). The bands around 3750, 3675, and 3600 cm^{-1} were insensitive to NH_3.

Similar spectra for $YDBNH_4^+$ are shown in Fig. 2. The same features are observed as for YDB. However, the 3665 and 3560 cm^{-1} bands are more intense.

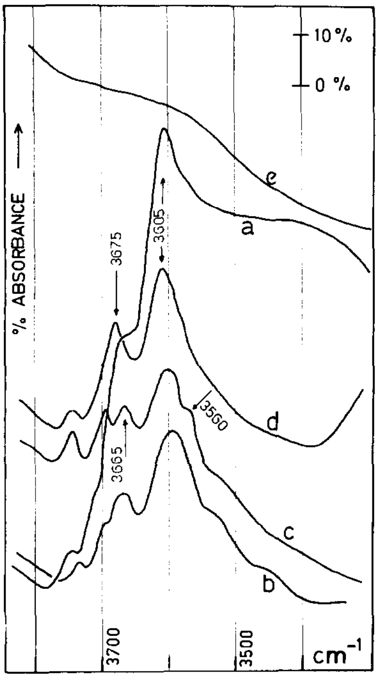


FIG. 1. Sample YDB. IR spectra taken at room temperature after the following pretreatments: (a) outgassing at room temperature; (b) outgassing at 150°C; (c) outgassing at 450°C; (d) sample as for (c) and exposed to NH_3; and (e) sample as for (c) and deuterated.

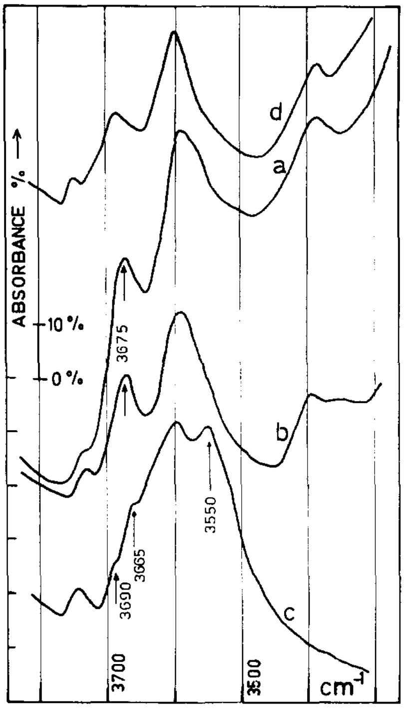


FIG. 2. Sample $YDBNH_4^+$. IR spectra taken at room temperature after the following pretreatments: (a) outgassing at room temperature; (b) outgassing at 180°C; (c) outgassing at 340°C; and (d) sample as for (c) and contacted with NH_3.

In contrast, the $YAlDNa^+$ sample has the same bands as an ordinary NaY (*12*). A concomitant decrease of the sharp band at 3700 cm^{-1} and the deformation band of H_2O is shown in Fig. 3 at increasing temperatures. The $YAlDNH_4^+$ sample heated at 356°C shows a spectrum typical for HY: two intense bands at 3650 and 3550 cm^{-1} (Fig. 4c). Small components at 3675 and 3620 cm^{-1} are seen at lower temperatures (Fig. 4a, b) when there is no overlapping by an intense HF band.

Pyridine adsorption on these samples at room temperature confirms the information obtained from NH_3 adsorption. The bands at 3675 and 3600 cm^{-1} are insensitive to pyridine. Pyridinium ions are formed on the $AlDNH_4^+$, YDB and $YDBNH_4^+$ samples by reaction with the acidic OH groups.

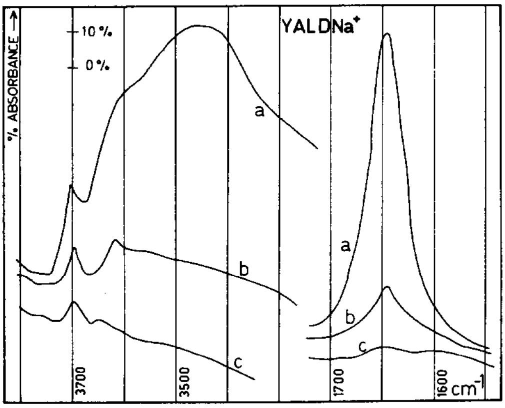


FIG. 3. IR spectra of the sample YAlDNa$^+$ after evacuation at different temperatures; a = room temperature, b = 140°C, and c = 350°C.

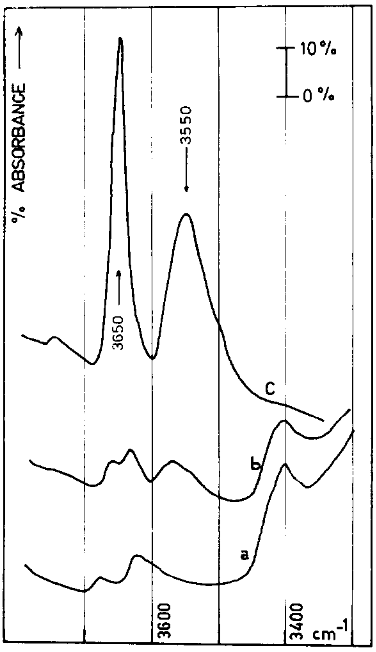


FIG. 4. Sample YAlDNH$_4^+$. IR spectra taken after outgassing (a) at room temperature, (b) at 140°C, and (c) at 350°C.

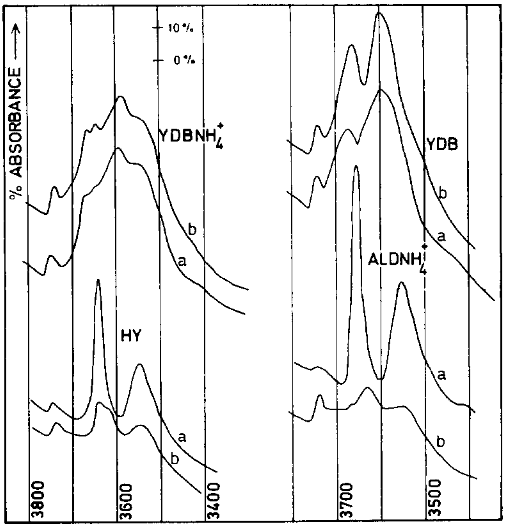


FIG. 5. Infrared spectra of the samples HY, YDBNH$_4^+$, YDB, and AlDNH$_4^+$: Curves (a) after outgassing at 400°C; curves (b), sample as for (a) and treated with water vapor at 400°C, followed by outgassing at 400°C.

The hydrothermal stability of the hydroxyl groups is demonstrated in Fig. 5. The curves (a) show the OH spectra after outgassing at 400°C. These samples were then contacted with water vapor (±20 mm) at 400°C for several hours. After a prolonged outgassing at this temperature, the (b) spectra were scanned at room temperature. This procedure will be referred to as steaming. The hydrolytic stability of the hydroxyls on the HY and AlDNH$_4^+$ samples is small. The bands at 3650 and 3550 cm^{-1} are completely suppressed. A small band is observed at 3620 cm^{-1}. For the YDB and YDNH$_4^+$ samples all bands increased slightly in intensity.

The crystallinity of the different samples was tested by X-ray diffraction. The unit-cell dimensions decreased as follows:

NaY, 24.764 ± 0.003 Å;
AlD, 24.697 ± 0.003 Å;
YDB, 24.550 ± 0.003 Å.

This is in agreement with Kerr's findings. The crystallinity of the hydrothermally treated samples could be compared with the ir results. The HY and AlDNH$_4^+$ samples become completely amorphous after steaming, while the YDB and YDBNH$_4^+$ remain crystalline.

Kerr (*9*) reported that aluminum could be extracted from the DB samples by 0.1 *N* NaOH. From our YDB sample 17.1Al atoms per anhydrous unit cell are extracted. This extracted sample has been exchanged with NH$_4^+$, treated with 0.01 *N* NaOH and back-exchanged with NH$_4^+$. The treatment with 0.01 *N* NaOH did not extract any more aluminum. Also during the NH_4^+ exchange no Al was extracted. The ir spectra of the different samples of this cycle are shown in Fig. 6. Table 2 gives a semi-quantitative estimation of the intensities of the different bands.

In each case the two bands characteristic of the YDB sample are observed. After the NaOH treatments, the bands shifted from 3680 to 3700 and from 3600 to 3620 cm^{-1}. The exchange with NH_4^+ (Fig. 6 B and D) returned the bands to their original positions. Some differences in intensities of the spectra in Fig. 6 are due to the difference in film thickness. Therefore, comparison of the intensities must be based on the values reported in Table 2. In the absence of physically adsorbed water, the band at 3700–3680 cm^{-1} has almost the same intensity on all the samples described in Fig. 6. The band at 3600–3620 cm^{-1} had practically disappeared after the treatment with 0.1 *N* NaOH, and was reduced to about half the original intensity after the treatment with 0.01 *N* NaOH. This band regained the original intensity after exchange with NH_4^+ (see Fig. 6, parts A, B, C, and D).

Thus the intensity of the 3600–3620 cm^{-1} band depends on the concentration of the NaOH solution. This could mean that these hydroxyls are weakly acidic, and that their protons can be replaced by Na^+ in strongly alkaline solutions. Nevertheless, in the dry state, the hydroxyls involved in that band are insensitive to the bases NH_3 and pyridine. Samples intermediate between YDB and conventional HY were also prepared. A conventional NH_4Y was treated under vacuum in a Pyrex tube, i.d., 10 mm; the height of the sample was 50 mm. In this way DB geometry was realized, but the evacuation of gases was accelerated by the vacuum treatment. Spectra of this sample are shown in Fig. 7. The components at 3675, 3600, and 3550 cm^{-1} are clearly re-

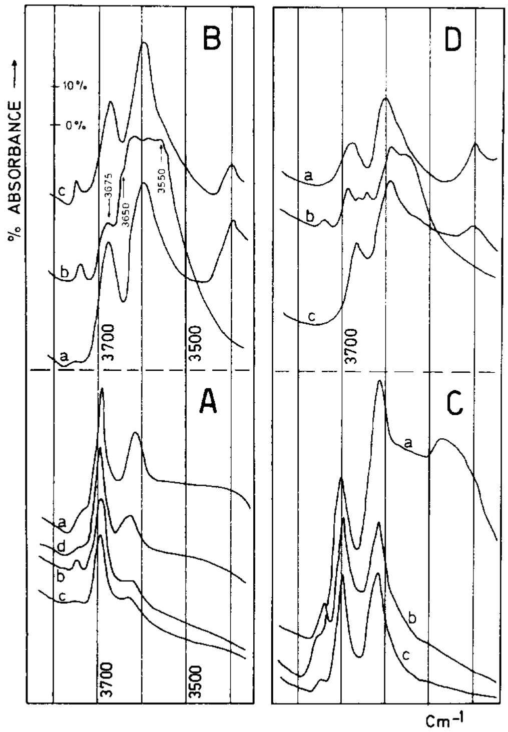


FIG. 6. Infrared spectra of the sample YDB: A = after extraction with 0.1 *N* NaOH; B = sample as for A saturated with NH_4^+; C = sample as for B treated with 0.01 *N* NaOH; and D = sample as for C saturated with NH_4^+. The spectra were taken after the following film pretreatments *in vacuo*: a = room temperature, b = 400°C, c = sample as for (b) treated with NH_3, d = sample as for (a) and outgassed at 200°C.

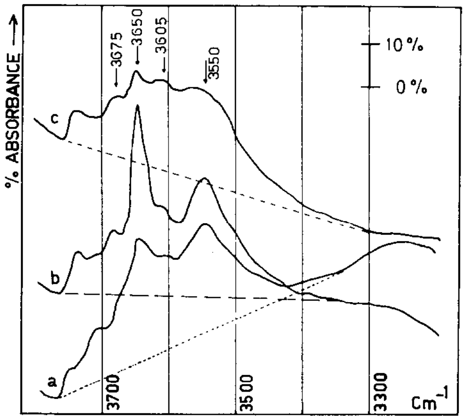


FIG. 7. IR spectra of the sample YNH_4^+ heated *in vacuo* in a tube (Ø 10 mm, sample height, 5 cm): The temperature was raised very slowly to 500°C under continuous evacuation. The spectra were taken on a film pretreated *in vacuo* at: (a) 150°C, (b) 350°C, (c) 400°C in the presence of water vapor and then evacuated at 400°C.

TABLE 2

Intensity of the OH Bands in Arbitrary Units, Calculated From the Peak Height Divided by the Film Thickness (mg/cm^2 of Film)

Sample (YDB = 1)	Film pretreatment	cm^{-1}	Intensity	cm^{-1}	Intensity
1 = YDB	Outgassing 350°C	3680	11.9	3600	19.6
	Water vapor 400°C	3680	18.4	3600	19.6
	Outgassing 450°C	3680	14.8	3600	20.2
2 = Sample 1 treated with 0.1 N NaOH	Outgassing 100°C	3697	16.7	3618	12.7
	Outgassing 150°C	3697	13.2	3620	6.6
	Outgassing 400°C	3697	8.6	3620	1.8
	Water vapor 400°C	3700	13		
	+NH$_3$	3700	13.7		
3 = Sample 2 treated with 0.1 N NH$_4$Cl	Outgassing 150°C	3682	16.4	3595	19.4
	Outgassing 375°C	3685	8.9	3605	22.8
	Water vapor 400°C	3675	17.2	3600	22.6
4 = Sample 3 treated with 0.01 N NaOH	Outgassing 150°C	3695	14.1	3605	15.4
	Outgassing 400°C	3700	13.2	3620	12.3
	Water vapor 400°C	3700	13.2	3618	12.7
5 = Sample 4 treated with 0.1 N NH$_4$Cl	Outgassing 150°C	3680	12.5	3600	25.4
	Outgassing 420°C	3685	10.7	3600	23.9
	Water vapor 400°C	3675	11.4	3600	21.8

solved. From the relative intensities of both kind of bands, it can be deduced that the sample is predominantly HY. Steaming (Fig. 7, curve c) reduces the components typical for HY, while the DB bands remain unchanged.

Discussion

The Origin of the Stability

The similarity in the results of the infrared experiments and the X-ray diffraction data is an important observation. It seems indeed that the collapse of the structure and the suppression of the hydroxyl bands in Fig. 5 are concomitant phenomena. In this discussion we will, therefore, interpret the suppression of hydroxyl bands as an indication of structure collapse.

The decrease of the Na$^+$ content was considered by McDaniels and Maher (*6*) to be the possible origin of the increased stability. This was supported by Ambs and Flank (*7*). They developed the hypothesis that there is an inverse relation between the content of residual Na$^+$ ions and the lattice stability for all the NH$_4^+$ exchanged faujasites. Kerr (*11*) suggested that the stability is related to the Al deficiency of the samples. Our present data allow us to clarify some of these divergences.

The behavior of the YDB and YDBNH$_4^+$ samples indicates that the residual Na$^+$ is not the major factor. Indeed, an important fraction of Na$^+$ ions (31%) is still present in the YDB sample, although the stability of this sample in hydrothermal conditions is identical to that of sample YDBNH$_4^+$ in which the Na$^+$ content is extremely low. The aluminum deficiency of itself is also not immediately responsible for the stability: The AlDNH$_4^+$ samples, with a slightly lower Na$^+$ content than the YDB sample, collapse in hydrothermal circumstances where the YDB and YDBNH$_4^+$ samples remain stable. The AlDNH$_4^+$ sample is Al-deficient and the YDB and YDBNH$_4^+$ samples, as far as the overall chemical composition is considered, are not. However, the contraction of the lattice of the YDB sample indicates that a fraction of the aluminum is not in tetrahedral lattice positions. The extraction test with 0.1 N NaOH solution proves that 17.4 aluminum atoms per unit cell ($\approx$31%) are easily extracted. According to Kerr (*9*) this aluminum is located on ion-exchange sites, probably not as Al^{3+} ions, but as a hydroxy ion of the type $Al(OH)_x{}^{(3-x)+}$. Taking into account the work of Kerr (*8–11*), but comparing the behavior of the sample $AlDNH_4{}^+$ with that of the samples YDB and $YDBNH_4{}^+$, we conclude that the stability cannot be attributed to the aluminum deficiency *per se* but probably to the fact that hydroxy–aluminum ions occupy an important fraction of the ion exchange positions during the thermal treatment. It is not possible to state which type of exchange sites is occupied by these ions. The fact that the total amount of Na^+ ions becomes available after a deep-bed calcination could indicate that the hexagonal prisms are involved. The parallelism between the structure collapse and the suppression of hydroxyl bands further suggests that the lattice destruction is due to the hydrolytic activity of the protons and not to the influence of the Na^+ ions. The behavior of the YDB sample after the extraction with NaOH indicates that the stabilizing action of the hydroxy–aluminum ion is only required during the first calcination step. This interpretation is not in agreement with the excellent work by Ambs and Flank (*7*). However, in that work the conclusions are mainly based on DTA results. It could well be that the experimental conditions of the DTA technique are comparable to deep-bed conditions. In that case a differentiation between so-called ultrastabilized and conventional $NH_4{}^+$ exchanged zeolites could not be made. Indeed, in our experiments the YDB sample behaves essentially in the same way as the $YDBNH_4{}^+$ sample.

The Infrared Spectra

In all the samples exchanged with $NH_4{}^+$, bands are observed around 3650 and 3550 cm^{-1}. They are typical for the so-called decationated zeolites. Their assignment to hydroxyls formed by a proton of the decomposed $NH_4{}^+$ ion entering the oxygen lattice has been discussed by many authors (*2–4, 12–18*) and needs no further comment. The intensity of these bands is high in the $AlDNH_4{}^+$ sample but relatively low in the YDB and $YDBNH_4{}^+$ samples. This is due to the considerable dehydroxylation that took place during the DB calcination procedure. The $AlDNH_4{}^+$ sample is in fact comparable to a conventional HY. It is known (*3*) that the 3550 cm^{-1} band is more sensitive to dehydroxylation. Therefore, the 3650 cm^{-1} is in all cases better resolved than the 3550 cm^{-1} band which in some spectra (YDB) is only present as a small shoulder in the envelope of other bands. The identity of these bands is further supported by their acidic character and their reactivity towards NH_3 and pyridine as discussed in a previous section.

Typical for the "stable" sample are the bands around 3620–3595 cm^{-1} and around 3675–3705 cm^{-1}. These bands are present only in the YDB and $YDBNH_4{}^+$ samples. The band around 3600 cm^{-1} is especially intense, (Figs. 1 and 3) and remarkably resistant to hydrothermal treatment (Fig. 5). The frequency of these bands are dependent on the presence or absence of exchangeable ions as will be explained later. The hydroxyls involved in these bands do not react with ammonia and pyridine and are, therefore, qualified as non-acidic, as compared to the 3650 and 3550 cm^{-1} bands in conventional HY. A discussion of the assignment of the bands near 3600 and 3695 cm^{-1} in the "stable" samples requires care, because other bands occurring at the same frequencies are reported in earlier work. A review of that literature was recently made by Uytterhoeven *et al.* (*19*). A list of spectra taken from that review is given in Table 3.

The Band near 3700 cm^{-1}

Many authors reported a band at 3700 cm^{-1} for various ion-exchanged forms of zeolite Y. It was emphasized by Habgood (*20*), by Ward (*21, 22*), and by Uytterhoeven *et al.* (*19*) that in NaX and NaY a very narrow band at 3695 cm^{-1} must be attributed to water molecules associated with the cations, probably monovalent but possibly also divalent cations. Ward (*21, 22*) and Uytterhoeven *et al.* (*19*) suggested that the presence of a band around 3695 cm^{-1} could indicate incomplete dehydration,

TABLE 3
WAVENUMBERS (CM^{-1}) OF THE OH STRETCHING BANDS IN ION-EXCHANGED ZEOLITES TYPES X AND Y[a]

Carter, Lucchesi and Yates (*25*)

NaX	3695	3655	—	—
Li-X	—	3660	—	—
KX	3715	3650	—	—
AgX	3685	3630	—	—
CaX	3695	—	—	3590
SrX	3700	3660	—	3605
BaX	3695	3620	—	—
CdX	3690	—	—	3600

Angell and Schaffer (*12*)

NaY	—	3652	—	—
LiY	—	—	—	—
MgY	3688	3643	3540	—
CaY	—	3645	—	—
SrY	3691	—	—	—
BaY	—	3647	—	—
MnY	—	3644	3545	—
CaY	—	3646	3540	—
NiY	3682	3643	3544	—
ZnY	3673	3642	3542	—
AgY	—	3634	3550	—
NaX	—	—	—	—
CaX	—	—	—	—

Ward (*21*)

LiY				
NaY	No fine bands			
RbY	Broad bands, due to physically			
KY	adsorbed H_2O, removed at			
CsY	various temperatures			
BaY	between 250–400°C.			
MgY	3690	3645	3530	—
CaY	3688	3642	3520	3582
SrY	3691	3645	3560	3580

Ward (*22*) after addition of H_2O

CaY	3688	3642	3540	3585
CaX	3690	—	—	3610 and 3510
MgY	3690	3639	—	3610
MgY(H_2O)	3690	3639	3595	—

Christner, Liengme and Hall (*24*)

BaY	—	3645	—	—
MgY	3685	3642	3550	—
ZnY	3675	3645	3550	—
CaY	—	3640	3550	—

TABLE 3 (*Continued*)

Uytterhoeven *et al.* (*19*)

CaX(64%)	3695	3650	3550	3605
CaX(42%)	3695	3650	—	3610
CaY	3695	3650	3550	—
MgX	—	3650	(3550)	—
MgY	3690	3650	3550	(3610)
BaX	—	3650	(3550)	—
BaY	—	3650	3550	—

[a] A band around 3750 cm^{-1}, systematically present in all zeolite samples, is not included in this table.

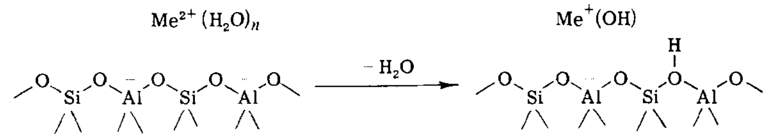
and X-ray data obtained by Olson (*23*) supported that suggestion. However, the band at 3700–3675 cm^{-1} observed in this work is very intense even after a vacuum treatment at 400°C for several hours. At that temperature the deformation band of water around 1645 cm^{-1} is no longer present. Moreover, the band has a comparable intensity in both the YDB and YDBNH$_4^+$ samples. The former still has Na$^+$ ions, whereas the YDBNH$_4^+$ sample is entirely decationated. Therefore, the assignment to residual water molecules associated with the exchange cations cannot be valid for these samples.

It appears then that bands of different nature can occur in these zeolites at the same frequency. The observation and interpretation made by Habgood (*20*), Ward (*22*), and Uytterhoeven (*19*) on hydrated samples is certainly valid. However, a band near 3695 in samples pretreated at high temperature must not necessarily be interpreted as evidence for incomplete dehydration. At this point a reconsideration of the data in Table 3 is useful. It is remarkable that for samples pretreated at high temperature the band around 3690 cm^{-1} was seldom observed with samples saturated with monovalent ions, but was almost systematically present in samples with divalent ions. The papers by Angell and Schaffer (*12*) and by Christner *et al.* (*24*) are the most significant in this respect. Taking into account the high pretreatment temperatures applied in those studies (500°C), together with the evidence provided by the present work, we believe that the band around 3695 cm^{-1} cannot be systematically attributed to water molecules. Our observations on the YDB and $YDBNH_4^+$ suggest that during the calcination procedure structural changes occur which produce hydroxyls incorporated in the lattice. This is indeed suggested by the constancy of the band intensity after various treatments (Table 2). We have no arguments to decide on the exact nature of the hydroxyls involved in this band. They are probably hydroxyls created by the extraction of aluminum but fixed to the zeolite lattice. If they were associated with the hydroxy-aluminum ions, the NaOH extractions would have suppressed this band. It could well be that in the samples saturated with divalent cations the weak bands at slightly variable frequencies, observed after pretreatment at high temperature (*12*, *24*), could have a similar origin. A given concentration of acidic hydroxyls absorbing at 3650 and 3550 cm^{-1} is indeed present in the faujasites saturated with divalent ions (*vide infra*), and a dehydroxylation certainly takes place during the pretreatment at 500°C (*19*).

The Band near 3600 cm^{-1}

This band also cannot be ascribed to water molecules, because it persists at high temperatures when no evidence for water is left in the deformation region. It cannot be associated with exchangeable cations, because it is present in the YDB and in the $YDBNH_4^+$ samples with comparable intensities. The latter sample is completely decationized, while in the YDB sample residual Na^+ ions are the only cations. It cannot be associated with hydroxy-aluminum cations: in that case it would irreversibly disappear from the spectra after the extraction with 0.1 *N* NaOH solution. The hydroxyls involved in this band are slightly acidic. The treatment with 0.1 *N* NaOH affects the intensity of the band, but it can be restored by an ion exchange with NH_4^+ (see Figs. 6 and Table 2). The frequency of this band is sensitive to the environment; it is at 3600 cm^{-1} when protons are present (Fig. 6B and 6D) and around 3620 cm^{-1} when Na^+ ions are introduced (Fig. 6A and 6C). This band must also be attributed to structural OH groups created when the structure of NH_4^+Y or HY is altered by the dehydroxylation and the extraction from the lattice of some aluminum ions by calcination. The 3695 and 3600 cm^{-1} bands could be due to hydroxyls, similar in nature but at different locations in the lattice. In the absence of better data on the structure of ultrastable faujasites, a better assignment cannot be given.

The observation of the 3600 cm^{-1} band in the DB calcined samples also brings into question some former interpretations. Bands were indeed reported between 3580 and 3610 cm^{-1} in several zeolites saturated with divalent cations (see Table 3). These bands have been attributed to hydroxyls belonging to cations of the type $Me^+(OH)$, resulting from the dissociation of water molecules following the reaction:



The evidence presented in this work is not sufficient to reject this interpretation, but is strong enough to stimulate some doubts. Indeed, the frequency of the 3600 cm^{-1} band in divalent exchanged zeolites is rather constant. Reported values are between 3610 and 3580 cm^{-1} for the different types of Me^{2+} ions in the $Me(OH)^+$ species (*21*, *22*). In our samples (Fig. 6), a simple replacement of Na^+ by NH_4^+ was reported to cause a shift from 3620 to 3595 cm^{-1}. Therefore, a greater variability in frequency would be more in favor of an assignment to $Me(OH)^+$ cations. Furthermore, in this work the development of the 3700 and of the 3600 cm^{-1} bands were seen to be concomitant phenomena. When a component around 3600 was reported in zeolites containing divalent ions, the 3700 cm^{-1} band was also present (*19, 21, 25*). This point strengthens the suspicion that the bands around 3600 and 3700 cm^{-1} in deep-bed calcined faujasites and in faujasites saturated with polyvalent cations could have a common origin.

CONCLUSIONS

This note shows that the deep-bed calcination is an essential step in the preparation of ultrastable faujasites. The mechanism of stabilization seems not to be influenced in the first instance by the Na^+ content or the aluminum deficiency. A partial dehydroxylation and the presence of hydroxy–aluminum ions on some ion-exchange sites during this dehydroxylation seem to be more essential. Most probably, the ultrastable faujasites have a typical structure, deficient in aluminum and with hydroxyl groups at distinct places in the lattice. These hydroxyls absorb around 3700 and 3600 cm^{-1}. It is not known whether or not the ultrastabilized samples correspond to a well-defined crystalline phase. It could be that the hydroxyls are located at defect parts of the normal faujasite lattice. The existence of samples intermediate between HY and ultrastable faujasites, and the occurrence of bands around 3600 and 3700 cm^{-1} in zeolites saturated with polyvalent cations seem to support the latter hypothesis. Further evidence for this assumption may be found in the fact that the YDB and related samples still contain a small amount of hydroxyls absorbing at 3650 and 3550 cm^{-1}, and that these hydroxyls also have an increased stability towards hydrothermal conditions as compared to the conventional HY.

Hitherto, the catalytic activity of zeolite Y has been ascribed to the acidic protons in decationated samples or to the carbonogenic action ascribed to the cations in zeolites saturated with polyvalent ions. In accordance with Kerr (*9*) we want to emphasize that most of the catalytic work has been and is done on samples pretreated in deep-bed conditions, whereas the conclusion about the acidity of the OH groups has been based on infrared work in which the pretreatment of extremely thin wafers predominantly produces HY samples. Furthermore, in every faujasite sample containing protons, introduced by NH_4^+ ions or by exchange with polyvalent ions, structural rearrangements of the type DB calcination are possible at some spots in the structure. Therefore, it seems still worthwhile to look further for a common type of acid site in the different faujasite catalysts.

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