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Study of the Decationization of Type A Zeolite

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Some decationized forms of type A zeolite have been studied. The stability of these solids has been measured in terms of the type of thermal pretreatment (under vacuum or in hydrolyzing conditions). Water washing of the NaA forms leads to some decationization and to the appearance of nonacidic OH groups associated with ir bands at 3710 cm^{-1}. These forms are stable up to 800°C. By thermal treatment under vacuum between 220 and 350°C, NH_4A zeolite undergoes structural modifications associated with the appearance of ir bands at 3710, 3670 and 3620 cm^{-1}. The acidic character of the band at 3620 cm^{-1} has been demonstrated by ammonia adsorption. These extensively decationized samples are reactive in catalyzing the isomerization of 1-butene into *cis*- and *trans*-2-butene, when they are pretreated below 500°C. Beyond 500°C gradual breakdown of the lattice diminishes these properties. The NH_4A forms prepared under hydrolyzing conditions do not acquire ultrastability although ir bands are observed at 3600 and 3700 cm^{-1}.

INTRODUCTION

Much work (*1–3*, *25*) has been devoted to the study of the decationization of zeolites with an Si/Al ratio higher than 1.5 (faujasite and mordenite, for example). However, type A zeolites and their decationized forms in particular have been relatively little studied. There are two principal reasons for this: firstly, the low porosity of these molecular sieves restricts their use as catalysts and, secondly, their crystal structure is particularly sensitive to temperature and pH. These solids, nevertheless, constitute interesting surface models, and in recent years there has been a renewal of interest in the crystal structure of type A zeolites (*4*,*5*) and in their thermal stability (*4*,*6*). Some workers have applied themselves to the synthesis of silicon-enriched zeolites A (*7*,*23*). These attempts have in some cases led to new crystalline forms differing slightly from A but with similar properties (*8*).

In this work we have studied the decationization of zeolites NaA and NH_4A. The thermal treatments were performed either *in vacuo* or under hydrolyzing conditions. We have also examined the behavior of a silicon-enriched zeolite (Si/Al = 1.22) called 4 ASi and synthesized by Guth *et al.* (*7*).

EXPERIMENTAL METHODS

Starting with a Linde zeolite NaA type whose formula is $Na_{12}(AlO_2)_{12}(SiO_2)_{12}$ we have prepared our ammonium forms using aqueous ammonium chloride solutions (0.1 *M*). The composition of the NH_4A zeolite obtained is:

$$Na_{6.3}(NH_4)_{5.7}(AlO_2)_{12}(SiO_2)_{12}27H_2O.$$

The crystal structure of our specimens was studied by means of a Compagnie Générale de Radiologie X-ray diffraction apparatus.

The solid state transformations were followed on a differential thermal microanalyzer under an atmosphere of argon or oxygen. The infrared absorption spectra of our solids were determined on Perkin-

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Elmer 421 and 21 spectrometers. Samples analyzed on the PE 421 were mulled in fluorolube.

Catalytic tests (1-butene isomerization) were performed on a pulsed reactor with chromatographic analysis as described previously (*14*).

Depending on the case, our solids were pretreated under different conditions. Five types of thermal treatment were used:

T_1	thermal treatment under vacuum (10^{-4} Torr) during 12 hr.
T_2	thermal treatment in air at 1 atm during 12 hr.
T_3	thermal treatment at constant pressure and flow rate, by Rouquerol's method (*9*).
T_4	treatment as proposed by Kerr (*10*), by thermal shock in deep or shallow beds at high temperature during 4 hr.
T_5	thermal treatment in a current of water vapor and nitrogen, during 8 hr.

RESULTS AND DISCUSSION

I. Decationization of Zeolite NaA by Prolonged Preliminary Washing with Water

The unit cell of zeolite 4 A contains 12 sodium atoms located in a large cavity and in the pores leading to it (*11*). In fact, Yanagida *et al.* (*5*) conclude that there are three types of cationic site: in the oxygen hexagons (8 Na_I per unit cell), in the oxygen octagons making up the pores (3 sodium Na_{II} per unit cell) and in the vicinity of the oxygen squares in the large cavities (1 sodium Na_{III} per unit cell). The most strongly retained sodium ions at the surface are in the oxygen hexagons, whereas the most mobile are in the large cavities and the pores.

Washing a NaA zeolite (100 g) by circulation of 20 liters of distilled water at 25°C for 12 hr with gentle shaking leads to the elimination of small quantities of sodium (*12*). The most mobile sodium ions, Na_{II} and Na_{III}, are probably eliminated preferentially. With NaX and NaY, such treatments affect catalytic activity (*14*).

The ir spectrum of NaA treated in this way is shown in Fig. 1. The well-known spectrum of zeolite 4 A (*1*) can be discerned. There appear to be at least three forms of water at the surface. A sharp band at 3710 cm^{-1} is observed. The most important band centered at 3480 cm^{-1} has a well-defined shoulder at 3420 cm^{-1}. The deformation band of molecular water is found at 1660 cm^{-1}. The sharp band at 3710 cm^{-1} is of particular interest. It is only observed on washed samples, and could be due to the presence of OH groups appearing during the exchange of the most mobile sodium ions with protons from water which would form with the oxygen atoms these OH groups.

Upon adsorption of gaseous ammonia on a washed zeolite outgassed at 450°C under vacuum, the ir spectrum is modified. Bands at 3400, 3365, 3305 and 3260 cm^{-1} appear. They correspond to the presence of physically adsorbed NH_3. The absence of bands at 1450 cm^{-1} and in the frequency range below 3200 cm^{-1} shows

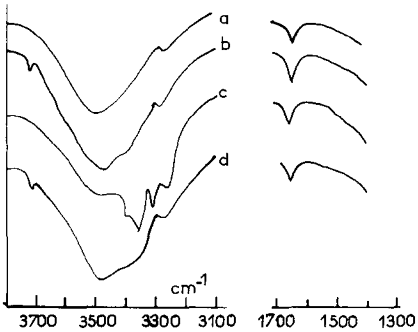


FIG. 1. Effect of washing on the ir spectrum of NaA (all ir spectra are recorded at 25°C). (a) NaA zeolite pretreated at 450°C *in vacuo;* (b) washed NaA zeolite pretreated at 450°C *in vacuo;* (c) as (b) and after NH_3 adsorption and desorption at 25°C *in vacuo;* (d) as (b) after NH_3 adsorption and desorption at 200°C *in vacuo.*

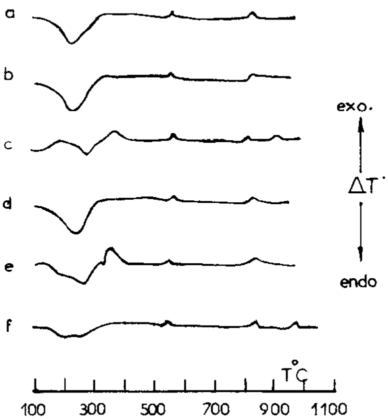


FIG. 2. Differential thermal analysis (heating rate = 8°C/min). (a) NaA; (b) washed NaA; (c) silicon-enriched zeolite 4 ASi (*7*); (d) NH_4A under Ar; (e) NH_4A under O_2; (f) decationized form of zeolite A, obtained by thermal pretreatment of NH_4A at 500°C *in vacuo*.

that NH_4^+ ions are not formed. These specimens are not proton acids. We have not observed bands at 3710 cm^{-1} in the ir spectra of washed 4 ASi samples.

The washing does not modify the stability of the zeolite in any way. Differential thermal analysis (DTA) (see Fig. 2) still shows no recrystallization below 927°C. However, a loss of crystallinity appears well below this temperature and has been followed by X-ray diffraction. Up to 500°C the crystal structure of the zeolite is retained. When the NaA zeolite samples are treated above 500°C, in deep bed conditions, a loss of crystallinity occurs as shown by line broadening. However, the absolute decrease in the intensity of the line is small. At the same time relative intensity variations are observed. On each spectrum can be distinguished two groups of planes; the first is made of the 100, 110, 111, 210 planes, the second corresponds to 221, 311, 321 and 332 planes. When the pretreatment temperature is raised the relative intensities of the 100, 110, 111, 210 planes increase, while those of the second group diminish. Kokotailo and Lawton (*4*) attribute these intensity variations to the progressive passage of the zeolite NaA into an intermediate α-phase before its transformation into carnegieite. Even at 800°C a zeolite treated under these conditions shows only limited crystal damage. The stability of the silicon-enriched zeolite 4ASi (*7*) is not greater than that of the 4 A, quite the opposite. DTA (Fig. 2) reveals a recrystallization peak at 875°C and the crystalline structure is destroyed above 800°C, as against what we have observed for NaA at the same temperature.

In parallel with X-ray diffraction, study of the ir spectra in the frequency range between 400 and 1200 cm^{-1} can provide information on the structural behavior of the solid. Figure 3 shows the change in the ir spectrum of zeolite NaA when these structural modifications appear. Bands at

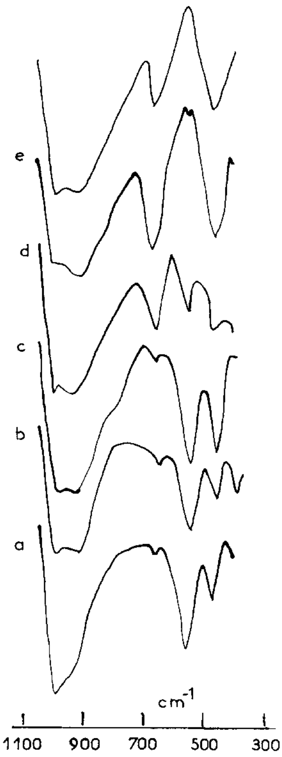


FIG. 3. Infrared spectra in the 1100 to 400 cm^{-1} range. Effect of the pretreatment temperature *in vacuo*. (a) NaA (25°C); (b) NaA (300°C); (c) NaA (600°C); (d) NaA (700°C); (e) NaA (900°C); (f) NaA (1000°C).

1000, 660, 550 and 460 cm^{-1} have been observed. When the temperature goes from 600 to 1000°C the band at 550 cm^{-1} decreases while the vibration band of SiO_4 tetrahedra at about 680 cm^{-1} increases. Some authors (*24*) consider that the band near 550 cm^{-1} corresponds to Si-O-Al chain vibrations: others (*16*) think that the existence of this band is related to the presence of connecting prisms (cubes) or large pore openings (8 oxygen-rings) in the crystal. If this is so, the decrease in the intensity of the 550 cm^{-1} band could be due to the increasing loss of crystallinity of the specimen.

II. Study of the Decationization of Zeolites NH_4A by Thermal Treatment Under Vacuum

The ammonium zeolites which we have studied contain about equal numbers of Na^+ and NH_4^+ ions in exchange sites. The surface of nontreated zeolite NH_4A can be represented by the approximate structure (a) in the scheme shown below.

Even though the exchange of Na^+ by NH_4^+ in these forms is extensive, the crystal structure of the ammonium zeolite remains well defined up to 300°C. At 500°C, the crystallinity is reduced. The lines broaden much more than in the case of NaA zeolites. These modifications are particularly noticeable for samples calcined above 500°C, whatever the pretreatment conditions. The intensities of the lines corresponding to the planes of the first group are, as in the case of the NaA zeolites, less perturbed by thermal pretreatment than those of the second.

1. Samples Heated in Vacuo *at Temperatures below 200°C*

The spectra (Fig. 4) show the vibration bands of the NH_4^+ ion; stretching bands (ν_3 at 3200 and 2990 cm^{-1}) and deformation bands (ν_4 at 1450 and 1400 cm^{-1}, ν_2 at 1680 cm^{-1}). The position of these bands is comparable to those observed by Uytterhoeven *et al.* (*2*) in a study on decationized zeolites X and Y. The molecular water band at 1660 cm^{-1} is relatively unimportant.

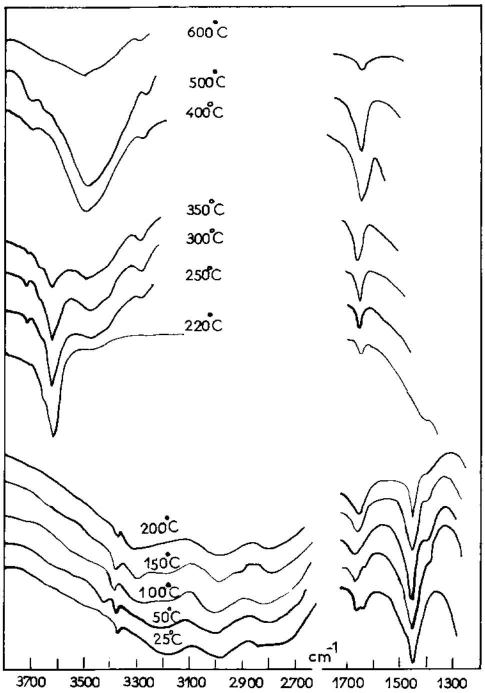
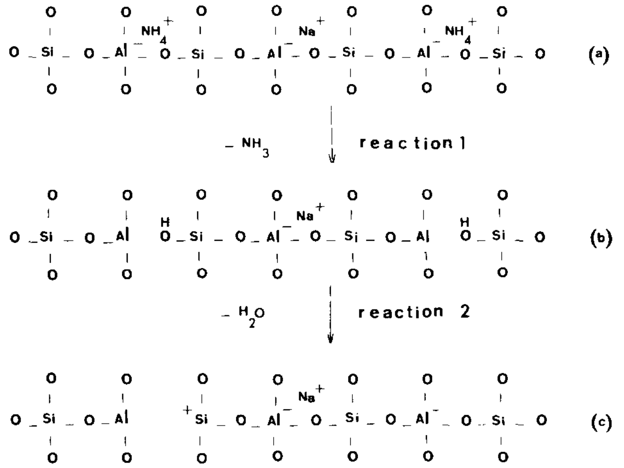


FIG. 4. Infrared spectra of zeolite NH_4A (treated *in vacuo* between 25 and 600°C).

2. Samples Treated in Vacuo *at Temperatures Between 220 and 350°C*

Between 200 and 220°C zeolite NH_4A suffers considerable modification. The bands due to ammonium disappear totally from the spectrum and new bands appear at 3700, 3670 and 3620 cm^{-1} (Fig. 4). The band at 3620 cm^{-1} is the most intense while the band at 3710 cm^{-1} is sharp and weak, and that at 3670 cm^{-1} is only a shoulder. Bands due to molecular water are seen to be virtually absent for the lower temperatures in this range. The form of the spectra varies little between 250 and 350°C. The appearance of new bands related to the loss of NH_4^+ ions is very probably explained by the formation of OH groups arising from the action of the proton formed in the destruction of the ammonium ion on the different oxygen atoms located in the cavity (reaction 1).



Above 300°C the intensity of the 3620 cm^{-1} band diminishes and that of the molecular water bands increases. DTA gives different results depending on whether the vector gas is argon or oxygen. In the presence of oxygen in addition to large endothermic peak at 250°C, exothermic peaks are observed (see Fig. 2). Venuto *et al.* (*17*) attribute these exothermic peaks to the reaction of oxygen with the NH_4^+ ions. We have verified that these peaks no longer appear when the sample is swept with argon or when the zeolite is first raised to 500°C. It seems therefore that the exothermic peak is related to the interaction of oxygen with the ammonium ion.

The zeolite $NH_4$4ASi gives the same type of differential thermal analysis spectrum. In addition its stability *in vacuo* is reduced and above 200°C it loses its crystallinity.

Effect of ammonia adsorption on the intensity of the OH bands. The adsorption of ammonia on a zeolite NH_4A previously outgassed at 300°C *in vacuo* makes the band at 3620 cm^{-1} disappear completely (Fig. 5). The ir spectrum has numerous bands of physically adsorbed ammonia and the ammonium ion. It is often difficult to distinguish the NH_3 bands from those of NH_4^+ in the stretching vibration range. However, the deformation bands at 1400 and 1450 cm^{-1} identify clearly the NH_4^+ ion. By thermal treatment *in vacuo* the band at 3620 cm^{-1} as well as the two other bands at 3710 and 3670 cm^{-1} can easily be made to reappear from 220°C upwards. We have noticed a slight shift of the frequency of the 3620 cm^{-1} band towards higher values, as long as the desorption of ammonia is not complete. The 3620 cm^{-1} band reappears when the sample is outgassed up to 280°C.

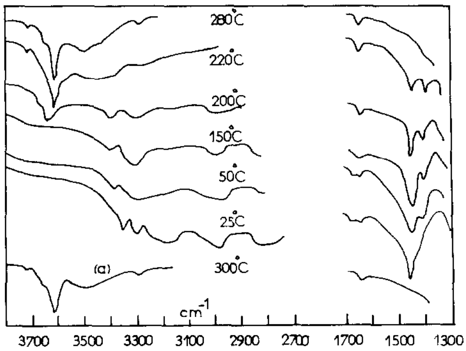


FIG. 5. Influence of ammonia gas on zeolite NH_4A, previously outgassed between 25 and 280°C.

3. *Temperature Range Above 350°C*

Above 350°C the band at 3620 cm^{-1} disappears totally and the shoulder at 3670 cm^{-1} becomes very weak. As for the band at 3710 cm^{-1}, it disappears or is hidden by a broad band whose maximum is at 3700 cm^{-1} and stretches from 3720 to 3680 cm^{-1}. The molecular water bands are very strong, with maxima at 3480 and 3280 cm^{-1}. It looks as though the water freed by the condensation of two surface OH groups remained inside the cavities (reaction 2).

Study of zeolites NH_4A treated under hydrolyzing conditions. Decationized zeolites of the A type are not thermally stable except for thermal treatment temperatures below 800°C, at best. In recent work (*3,10,18,19*) on the stabilization of zeolites Y, the role played by the water which is present in the crystal during thermal treatment has been clearly demonstrated. In the present work we have examined the NH_4A forms treated in hydrolyzing conditions, by the methods enumerated above (treatments T_2, T_3, T_4 and T_5).

It appears, from the X-ray diffraction spectra, that the less destroyed structures are those which were subjected to the highest partial pressure of water during calcination. The stablest sample was obtained by the T_5 treatment. These treatments are accompanied by a diminution of the intensities of the planes of the second group relative to those of the planes constituting the first group. Decreasing crystallinity causes broadening of the lines.

All the ir spectra show, in addition to the molecular water bands, a band at 3750 cm^{-1} (Fig. 6). This band is always visible, except for samples pretreated at 600°C. When the material is calcined at 300°C, the band at 3620 cm^{-1} is observed (strong shoulder). In the frequency range 400 to 1100 cm^{-1}, it is observed that the greater the contact with water vapor the stronger is the band at 550 cm^{-1} (Fig. 7).

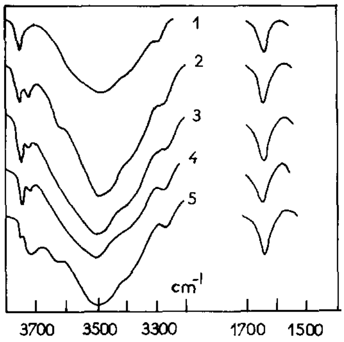


FIG. 6. Infrared spectra of NH_4A zeolites treated under hydrolyzing conditions. (1) T_5 treatment at 600°C followed by T_1 treatment at 300°C; (2) T_5 treatment at 300°C followed by T_1 treatment at 300°C; (3) T_4 treatment of the initially water saturated NH_4A zeolite at 500°C, in deep bed, followed by T_1 treatment at 300°C; (4) T_2 treatment followed by T_1 treatment at 300°C; (5) T_3 treatment at 20 Torr and 500°C.

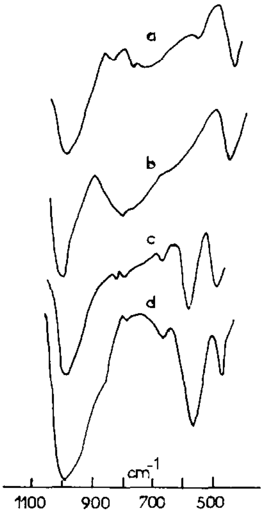


FIG. 7. Infrared spectra of NH_4A zeolites treated under hydrolyzing conditions (400 to 1100 cm^{-1} range). (a) T_4 treatment at 300°C in deep bed; (b) T_4 treatment at 500°C in deep bed; (c) as (b) but with samples initially saturated with water; (d) T_5 treatment followed by T_1 treatment at 500°C under vacuum.

The best crystallized samples can have a band at 3750 cm^{-1} in their ir spectra. This band which is often mentioned in ir spectroscopic studies of zeolites is generally attributed to Si–OH groups formed on the

TABLE 1
CATALYTIC ACTIVITY AND SELECTIVITY OF ZEOLITES A IN 1-BUTENE ISOMERIZATION[a]

Zeolite	T_1 (°C)	T_2 (°C)	% 2-butene obtained	R
NaA	500	280	0.8	0.5
4 ASi	500	280	1	0.5
Washed NaA	500	280	4	4
NH_4A	500	280	10	1.5
NH_4A	300	200	26.4	5

[a] T_1: temperature of pretreatment *in vacuo;* T_2: temperature of reaction; R: *trans*-2-butene (%)/*cis*-2-butene (%).

faces of the crystal, or to silica impurities (*20*). Ward (*21*) thinks that the intensity of the 3750 cm^{-1} band is related to crystal breakdown of decationized zeolites.

Catalytic activity of decationized A zeolites in the isomerization of 1-butene to cis *and* trans-*2-butene* (see Table 1). It has been shown that isomerization of 1-butene to *cis*- and *trans*-2-butene involves the Brønsted acid sites constituted by the OH groups located insides the cavities of A, X and Y zeolites (OH located in the oxygen hexagons) (*13,14*). The high values of the *trans*/*cis* ratio (R) obtained for isomerization by type A molecular sieves have been attributed to the polarization of the different isomers of butene in the electric field of the crystal (*15*).

We investigated the catalytic activity of the different zeolites studied in this work (NaA, washed NaA, silicon-enriched zeolite 4ASi and NH_4A).

It was observed that just like the NaA, the zeolite 4ASi, though less rich in sodium does not allow much diffusion of the reactants toward the cavities. Although gas diffusion is better than in the zeolite NaA, the absence of internal active centers makes it unsuitable for isomerization; however, the very low activity found is due to the contribution of the external surface and is associated with an isomer ratio (R) less than unity. Slight decationization of the NaA zeolite by washing with water leads to a solid of low activity and a selectivity R greater than unity. It seems likely that some of the sodium ions which obstruct the pores are eliminated and that the reactant can approach some active centers in the large cavities. The low concentration of these centers and the magnitude of the water band in the ir spectra make difficult their identification.

The decationization of NH_4A zeolites produces very active forms. The catalytic activity measurements are fairly reproducible when the solids are pretreated at temperatures below 300°C. However, above 450°C the activity and the catalytic selectivity diminish considerably, due to breakdown of the crystal structure.

CONCLUSION

The decationization of zeolites NaA leads to a loss of thermal stability which is more or less important depending on the degree of decationization. For a low degree of decationization the stability is retained up to 800°C, in deep bed and at 1 Torr. For extensive decationization (but less than 50%) the zeolite loses its crystallinity during thermal treatment *in vacuo* at temperatures above 500°C. Under the same conditions $NH_4$4ASi is destroyed from 200°C upwards *in vacuo.* A preliminary treatment with distilled water probably eliminates the most weakly attached sodium ions from the surface of the zeolites NaA; that is, those which are in the pores or in the large cavities in the vicinity of the oxygen squares. The OH groups formed in this decationization could be associated with the existence of a band at 3710 cm^{-1}. These OH groups are not acidic and, just like the NaA and the 4ASi, the washed zeolite NaA has very little catalytic activity for the isomerization of 1-butene.

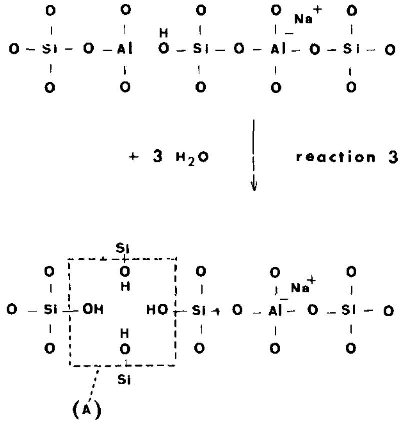
When the ammonium zeolites are treated *in vacuo* between 200°C and 350°C absorption bands at 3710, 3620 and 3670 cm^{-1} appear. It is difficult to say whether these three bands correspond to OH groups located at well-defined sites of the crystal. Let us remember, however, that there are three types of cationic site initially occupied by sodium ions in the crystal. The band at 3710 cm^{-1} could be attributed to the OH groups located in the octagons or the squares of oxygen atoms whereas the band at 3620 cm^{-1}, by far the most intense, could owe its origin to the OH formed in the oxygen hexagons which are the most numerous of the sites in the cavity. These hydroxyl groups (band at 3620 cm^{-1}) are acidic, in contrast to the band at 3710 cm^{-1}. The high catalytic activity of NH_4A outgassed at 250°C *in vacuo* is probably due, at least to a large extent, to the acidity of these OH (*14*).

The molecular water which appears as the band at 3620 cm^{-1} disappears can only arise from the condensation of two OH groups. This water, once formed, appears to remain in the molecular state in the cavities, even though the thermal treatment is performed under vacuum.

The presence of a rather broad band situated at 3700 cm^{-1} and stretching from 3680 to 3720 cm^{-1} for ammoniated samples calcined above 350°C is probably the sum of several bands, in particular the band at 3710 cm^{-1} and another band at 3680 cm^{-1} attributed to molecules of water attached to monovalent ions (*26*).

Ammonium zeolites heated under hydrolyzing conditions by means of thermal shocks in deep bed (treatment T_4) do not acquire high stability, in contrast to what happens in the case of zeolite Y (*10*). The zeolites treated under these conditions retain molecular water even after calcination under vacuum performed after the hydrolyzing treatment. The OH bands at 3620 cm^{-1} are sometimes observed even after a final treatment, at 500°C *in vacuo*. It could be suggested that the water bands simply hide the OH bands, but another explanation which takes account of the reaction models proposed by Kerr can be proposed.

When the zeolite NH_4A is calcined in the presence of excess water, it is possible that a significant part of the OH formed by the loss of ammonia does not condense to give water molecules. These same OH groups could, on the other hand, react with the water present and lead to the formation of motifs A [see Eq. (d)] and aluminum hydroxide by reaction 3.



It could be proposed, in agreement with Ward (*21*), that the silanol groups formed in this way correspond to the band at 3750 cm^{-1} which we have observed only with samples treated under hydrolyzing conditions. We have moreover never detected aluminum ions (except in trace quantities) in sodium citrate solutions placed in contact with the zeolite desorbed under hydrolyzing conditions. This negative result is consistent with the fact that the aluminum is present in the form of hydroxide and not as an exchangeable cation. Reaction 3 can continue and lead to the dehydration of the structure A shown in Eq. (d) and the formation of an excess of Si-O-Si bonds. In this case, the crystal structure is destroyed and the measurements of the decrease of the cell parameters which we observe no longer have any meaning.

Generally speaking, it is difficult to identify the groups responsible for the ir bands observed, and we only propose here a working hypothesis. Consider the band at 3700 cm^{-1}, for example; according to previous work this band is of special importance. In the opinion of many authors, this and the band at 3600 cm^{-1} are associated with ultrastability. In the case of our zeolites we consider that we have shown that it does not have this meaning. The hydrolyzing treatments used provoke the appearance of only one supplementary ir band, that at 3750 cm^{-1} which is not necessarily associated with crystal breakdown.

Attempts to extract aluminum by chemical methods, using acetylacetone for example, have so far been unsuccessful. It would appear that the best way of increasing the stability of zeolites A is by synthesizing silicon-enriched forms (*7*,*8*). However, it is not certain that a small increase in the Si/Al ratio is enough to produce a stabler form. We have not observed any such increase in our study of the slightly silicon-enriched zeolite 4ASi.

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