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Studies of the Hydrogen Held by Solids

XVI. Infrared Spectroscopy of X- and Y-Type Zeolites Containing Univalent and Divalent Cations

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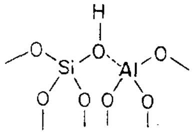
The IR spectra of Linde X- and Y-type zeolites, charge-balanced with different monovalent and divalent cations, were examined in the OH and NH regions after evacuation at various temperatures and when H_2O or NH_3 was added back. Bands near 3650 and 3545 cm^{-1} were identified with decationated sites. With monovalent zeolites only the former band could be detected and it resulted from hydrolysis and corresponded to the base-exchange cation deficiency. With divalent zeolites both bands appeared with the Y zeolites and at high exchange levels with the X zeolites. These bands were too strong to attribute to a deficiency of cations and it is suggested that H_2O molecules are dissociated by the strong electrostatic fields of the Me^{2+} ions, resulting in the formation of decationated sites and ions of the type Me^{+}-OH or Me^{+}-O-Me^{+}. The decationated sites reacted readily with NH_3 to form NH_4^+. A band near 3695 cm^{-1} appeared when small amounts of H_2O were added back. This could be attributed mainly to H_2O bound to the residual Na^+ ions of the preparations, but may have originated partly from a similar interaction with some of the divalent ions as well. Finally, a band near 3605 cm^{-1} was characterized, which could be assigned to Ca^{+}-OH.

INTRODUCTION

The IR spectra of synthetic faujasites, the Linde X- and Y-type zeolites, have been extensively studied in the OH stretching region (*1–15*, *18–21*, *23–28*). The great interest in this subject stems from the fact that the OH groups may act as Brönsted acids in the catalytic cracking of hydrocarbons (*4*, *5*, *18*, *20–27*). The OH bands in decationated zeolites are near 3650 and 3550 cm^{-1} with only minor differences in the frequencies reported by the different authors (*2–10*). Both bands have been attributed to OH groups on sites represented by



and the present authors (*2*) pointed out that at least two bands should appear, because of the several different oxygen sites in the lattice. The formal bond between OH and Al is not required to maintain electrical neutrality but is represented by a dashed line to take into account the requirements of coordination.

Angell and Schaffer (*3*) considered the possibility that the 3550 cm^{-1} band was derived from the band at 3650 cm^{-1} by hydrogen bonding between neighboring OH groups. It now appears more likely, however, that the two bands correspond to OH at different locations in the zeolite framework (*4–9*). White *et al.* (*8*) suggested that the OH groups responsible for the band at 3550 cm^{-1} were located at sites inside the cubooctahedra. Hughes and White (*7*) attributed the 3650-cm^{-1} band to OH groups at O_1 oxygens, i.e., those forming the hexagonal prisms between cubooctahedra. They assigned the 3550-cm^{-1} band to OH groups at those O_1 oxygens where hydrogen bonding could occur with adjacent O_4 oxygen ions. Ward (*5*) presented evidence that the two bands correspond to hydroxyl groups at different crystallographic locations, probably both in the supercages, while the data of Uytterhoeven *et al.* (*9*) suggested that the 3650-cm^{-1} band stems from OH at oxygen ions forming the bridges between cubooctahedra and the 3550 cm^{-1} band to oxygen ion sites which form the body of the cubooctahedra. The former were thought to vibrate inside the supercages while the latter may be either inside or outside.

The IR spectra of zeolites containing different monovalent and divalent cations have been discussed by several authors (*11–15, 19–28*). Bands have been observed at frequencies around 3750, 3690, 3650, 3530, and 3600 cm^{-1}.

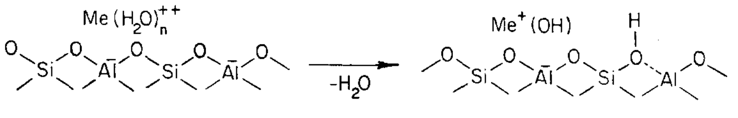
The ubiquitous band at 3750 cm^{-1} has been found by most workers in all preparations and is undoubtedly attributable to SiOH groups either on the faces of the crystals (*2*) or on silica impurities (*3*). Spectra published by Ward (*4*) revealed that the intensity of the band at 3750 cm^{-1} in decationated samples increases for high activation temperatures; therefore, the presence of this band may also be an indication of structural damage.

In a Na-X zeolite Bertch and Habgood (*11*) observed a band at 3695 cm^{-1} the intensity of which increased on adsorption of water. It was therefore attributed to molecules of water associated with the exchangeable ions in such a position that one of the OH vibrations is in a direction where it is not influenced by the oxygens of the zeolite lattice. Kiselev and co-workers (*14, 15*) derived a similar picture.

In the same spectral region a band was observed by Carter *et al.* (*13*) between 3715 and 3690 cm^{-1}, by Angell and Schaffer (*3*) between 3691 and 3673 cm^{-1}, by Ward (*24, 25*) at 3690 and 3699 cm^{-1}, and by Hall *et al.* (*28*) at 3685 and 3675 cm^{-1} in samples exchanged with a wide variety of divalent and monovalent ions (see Table 1). With one exception (*28*), all of these authors attributed this band to hydroxyls of Al-OH groups by comparison with OH vibration frequencies in alumina. Richardson (*23*) gave this band a similar assignment.

The bands near 3650 cm^{-1} and lower were attributed by Carter *et al.* (*13*) to water molecules associated with the exchangeable ions. More recent authors (*3, 12, 19–28*) have been in general agreement that the bands near 3650 and 3550 cm^{-1}, regardless of the nature of the exchangeable ions, are due to structural hydroxyl groups similar to those in decationated samples (*2*). The frequencies of these bands vary a little from one sample to another, but these variations are not very important and can be understood in terms of the varying electron affinities of the base-exchange cations employed (*23, 28*).

It was demonstrated by Habgood (*12*) that the intensity of the band at 3650 cm^{-1} increased gradually in a Na-X zeolite when the cation deficiency was increased by acid-washing of the zeolite. The intensity of the band near 3650 cm^{-1} in zeolites containing monovalent ions is always small. The second band found in decationated zeolites (at 3550 cm^{-1}) has not been observed in preparations containing only monovalent ions. In zeolites saturated with divalent ions, both bands are observed (*3, 19–28*) with intensities too high to be explained by cation deficiency. It is now generally accepted (*19–28*) that water molecules are dissociated by the electrostatic action of the Me^{2+} ions with the resulting formation of $Me(OH)^+$ and H^+; the latter combine with lattice oxygen to give SiOH groups similar to those in decationated samples. Dissociation of water molecules by the action of the exchangeable ions was first observed in clay minerals by Mortland *et al.* (*16*). Here the dissociation resulted in an increased acidity of the water molecules and did not appear to lead to the formation of structural hydroxyls, except with some particular minerals like saponite (*17*). Hirschler (*18*) suggested that the polarizing action of the exchangeable ion upon water molecules or adjacent hydroxyl groups in zeolites might be responsible for the acidity of these materials. The mechanism of water dissociation in zeolites containing divalent base-exchange cations was formulated by the present authors (*19*, *21*, *28*), and independently by Ward (*24*), as follows:



(I)

Further dehydration may lead to dehydroxylation of both SiOH and Me$^+$(OH) groups. Ward postulated (*24*, *25*) that dehydroxylation results in the formation of neutral molecules of the oxides, MeO. He studied (*25*, *26*) the adsorption of pyridine and water on zeolites which had been exchanged with Me^{2+} ions and activated at high temperatures. In these experiments the adsorption of water resulted in the development of a very intense band near 3585 cm^{-1} in Ca-Y and near 3610 cm^{-1} in Ca-X. Similar observations were made with Mg-Y and Mg-X. These bands increased severalfold in intensity when H_2O was readsorbed. The OH groups responsible for these bands were not reactive with pyridine and therefore were attributed to the hydroxyl groups in ions of type Me$^+$(OH).

An objective of the present work was to provide verification for the occurrence of different OH bands in the ion-exchanged zeolites, and to resolve some of the contradictions in the assignments of bands made by previous workers. A critical comparison will be made between previously published data, supplemented, where needed, with our own experimental observations. Previously published spectra were taken mostly on samples which had been activated by heating to 500°. Prolonged activation at this temperature considerably reduced the intensities of the OH bands. After activation at lower temperature, our spectra showed features which were helpful for correct band assignments. The chemisorption of NH_3 on zeolites has not been as extensively studied as has that of pyridine. Results from this smaller more basic molecule have also been helpful in band assignment.

EXPERIMENTAL

The synthetic zeolites of the X- and Y-type were obtained in the Na$^+$ form from the Linde Company, Tonawanda, New York. The K$^+$, Mg^{2+}, Ca^{2+}, and Ba^{2+} forms were prepared by a repeated exchange with 1 *N* solutions of the acetate salts, followed by washing till free from excess salt and by drying at 60°. To obtain partial exchange, weighed amounts of the original Na$^+$-saturated material were equilibrated with mixed solutions of Na$^+$-Mg^{2+}, Na$^+$-Ca^{2+} or Na$^+$-Ba^{2+} ions, washed and dried as before. The extent of exchange was determined by total analysis. The results discussed herein were obtained from several different lots supplied by Linde. The results from comparable samples from the different lots behaved in a perfectly reproducible manner. Lot numbers and analytical data, expressed as percent of the cation-exchange capacity saturated by ions other than Na$^+$, are given for each particular sample in the captions of the different figures. The percent exchange was calculated from the difference between the aluminum and sodium contents of the samples, expressed as gram atoms per gram of dry sample.

For the IR spectroscopic investigations, the samples were pressed into thin wafers between stainless steel blocks. Wafer "thickness" was between 4 and 10 mg/cm^2. They were mounted on a stainless steel slider in a vacuum IR cell (*2*), which was fitted with NaCl windows at one end. The other end was made of fused quartz and the mounted wafer could be transferred readily from one end (for heating and treatment with gases) to the other (for spectroscopic examination). Vacuum pretreatments at different temperatures and adsorption of NH_3 or H_2O were performed with the cell attached to a conventional vacuum apparatus. After pretreatment, the cell was isolated from the vacuum and mounted in the spectrometer.

The location of the wafer in the IR beam was reproducible.

Some of the spectra were taken using a Beckman IR-7 spectrometer and were recorded as percent transmission. Others were determined with a Beckman IR-12 grating instrument in absorbance units. Because of the poor transmission, slit widths five times the standard slit settings of the instruments were frequently required. The resolution was still better than 2 cm^{-1} at 3650 cm^{-1}. The spectra were scanned at room temperature at 20 cm^{-1}/min.

RESULTS

In agreement with Bertch and Habgood (*11*), the data of Fig. 1 showed that the intensity of the 3695-cm^{-1} band was very sensitive to hydration. The 3695-cm^{-1} band in Na$^+$-X and Na$^+$-Y became undetectable after 2 hr outgassing at 290° to 10^{-6} torr. The band was regenerated when H_2O was readsorbed (Fig. 1a), and the concomitant evolution of the H_2O deformation band at 1660 cm^{-1} in the dehydration–rehydration cycle (Fig. 1b) was observed.

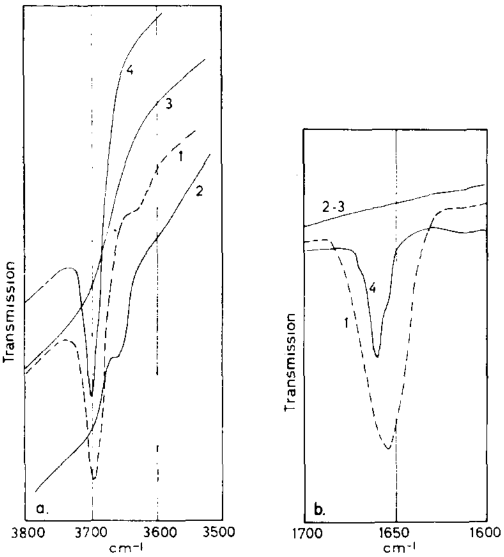


FIG. 1. Evolution of the OH stretching bands (a) and H_2O deformation band (b) in a Linde NaX zeolite (Lot No. 13-7396). Curve 1, after outgassing overnight at room temperature. Curve 2, after 2 hr further outgassing at 290°C. Curve 3, after 2 hr further outgassing at 550°C. Cuive 4, sample of Curve 3 after readsorption of 8 μmoles of water.

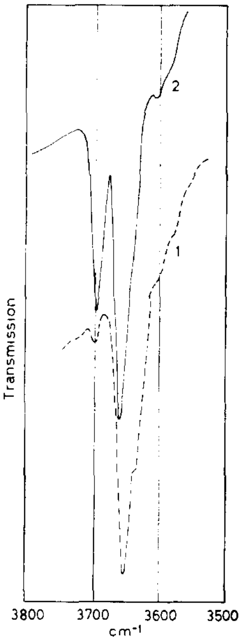


FIG. 2. OH stretching bands in a partially (45%) decationated Linde X zeolite (Lot No. 13-7396). Curve 1, after 1 hr outgassing at 490°C. Curve 2, sample of Curve 1 after readsorption of 8 μmoles of water.

Figure 2 illustrates the evolution of the stretching bands in a partially decationated (45%) X zeolite upon rehydration. Outgassing for 1 hr at 490° gave rise to a very sharp band at 3650 cm^{-1}, while the 3695-cm^{-1} band had almost completely disappeared. Readmission of a small amount of water (8 μmoles on a 10-mg film) at room temperature hardly affected the 3650-cm^{-1} band, but markedly increased the intensity of the 3695-cm^{-1} band. In similar experiments with decationated samples having a low Na$^+$ content, the 3695-cm^{-1} band was not evident.

An experiment was carried out using an X zeolite in which 64% of the Na$^+$ ions were replaced with Ca^{2+} (Fig. 3). After outgassing for 30 min at 175° some water was still present as indicated by the deformation band at 1650 cm^{-1} (Curve 1). Stretching bands at 3640, 3605, and 3540 cm^{-1} began to develop. The 3695-cm^{-1} band was absent, but this band appeared when 10 μmoles of H_2O was introduced into the cell (Curve 2).

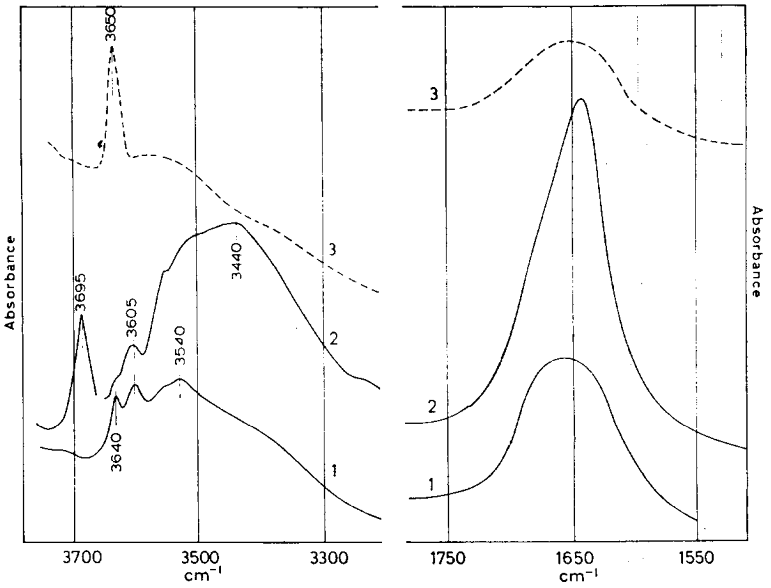


FIG. 3. Evolution of the OH stretching and H_2O bending bands on outgassing and water readsorption in a Linde X zeolite 64% saturated by Ca^{2+} (Lot No. 13-50080). Cuive 1, after 30 min outgassing at 175°C. Curve 2, sample of Curve 1 after cooling and readsorbing 10 μmoles of water. Curve 3, sample of Curve 2 after 3 hr outgassing at 175°C.

The 3695-cm^{-1} band disappeared when the rehydrated sample was outgassed again (Curve 3). Outgassing at higher temperature (250–300°) resulted in a complete disappearing of the H_2O deformation band and a decrease in intensity of the band at 3650 cm^{-1}. Once activated at this temperature the multivalent ion-exchanged zeolites alter their behavior toward rehydration; it has been our experience that all the well-resolved bands of the zeolites saturated with divalent ions diminish in intensity or vanish when water is introduced into the cell, and that a band due to hydrogen-bonded water develops in the 3460-cm^{-1} region. In agreement with Angell and Schaffer's finding (*3*), the 3695-cm^{-1} band could not be regenerated by water adsorption after pretreatment at 300°. In a rehydration experiment of a Ca^{2+}-Y and a Mg^{2+}-Y outgassed at much higher temperature than was used in this instance, Ward (*25*) observed the increase of the bands at 3640 and 3585 cm^{-1}, but did not observe the increase of the band at around 3690 cm^{-1}.

The data presented in Figs. 3 and 4 show the evolution of the bands at 3650, 3540, and 3605 cm^{-1} in a Ca^{2+}-X zeolite upon outgassing. The concomitant decrease of the H_2O deformation band makes it probable that hydration water is involved in the formation of the OH species responsible for these bands. The 3650-cm^{-1} (and 3540-cm^{-1}) band in both figures can be assigned to hydroxyls of the same nature as those in decationated zeolites; the 3605-cm^{-1} band cannot.

The spectra of partially hydrated samples are somewhat complicated. The band at 3640 cm^{-1} on Curve 1 in Fig. 3 is thought to be identical with the 3650-cm^{-1} band. No interpretation can be given to the band at 3620 cm^{-1} in Curves 1 and 2 of Fig. 4, but the overlapping of several bands could be responsible for the shift in the maxima which later develops at 3650 cm^{-1}. The occurrence of these bands is highly dependent on the outgassing conditions and on the exchange level of the samples. With the sample in which 64% of the exchange capacity was occupied by Ca^{2+} (Figs. 3 and 4) the two bands at 3650 and 3545 cm^{-1} were observed. For a Ca-X (42% exchanged) the band at 3540 cm^{-1} never appeared. This observation was confirmed with other X zeolites exchanged with Ca^{2+}, Mg^{2+}, and Ba^{2+}. The

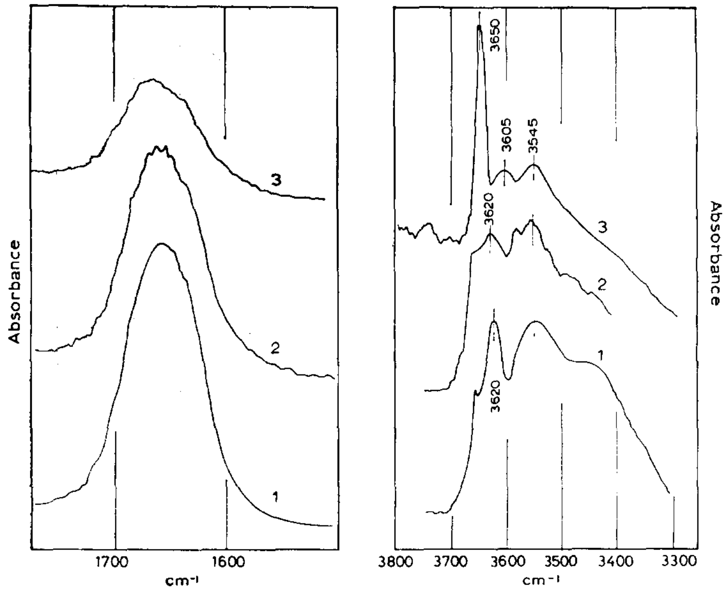


FIG. 4. Evolution of H_2O bending and OH stretching bands as a function of outgassing temperature in a Linde X zeolite 64% saturated by Ca^{2+} (Lot No. 13-50080). Curve 1, after outgassing at room temperature. Curve 2, after 1.5 hr further outgassing at 80°C. Curve 3, after 1.5 hr further outgassing at 160°C.

X zeolites with high levels of exchange yielded IR spectra with both decationation bands clearly developed. The same samples with lower contents of divalent ions gave only the high-frequency band near 3650 cm^{-1}. In Y samples both bands were detected for all the exchange levels tested.

Comparison of Curves 3 of Figs. 3 and 4 demonstrates the sensitivity to pretreatment. Bands at 3650, 3605, and 3545 cm^{-1} appeared in Fig. 4 while only the 3650-cm^{-1} band is evident in Fig. 3. The latter sample was outgassed at only a slightly higher temperature than the former. On heating to 350°, all OH bands disappeared from the sample of Fig. 4.

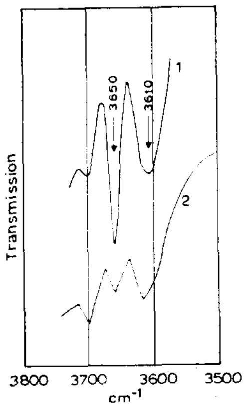


FIG. 5. Dependence of OH stretching band intensity on temperature of outgassing in a Linde X-zeolite, 42% saturated by Ca^{2+} (Lot No. 13-50080). Curve 1, after outgassing at 240°C. Curve 2, after further outgassing at 290°C.

In a Ca-X sample (42% exchanged) of Fig. 5, the intensity of the 3610-cm^{-1} band was much higher than that of the corresponding 3605-cm^{-1} band in Fig. 4, Curve 3. As stated above, no 3550-cm^{-1} band was observed for the sample with low Ca^{2+} content. Again a rapid decrease of the band intensity on raising the temperature was observed (Curve 2), the bands disappearing on evacuation at 350°.

NH_3 gas was adsorbed on 42% Ca-X previously outgassed at 175°C to test the acidity of the 3605 to 3610-cm^{-1} hydroxyl. The results are shown in Fig. 6. The 3650 cm^{-1} band decreased in intensity gradually as NH_3 was adsorbed with a concomitant development of the NH_4^+ deformation band (ν_4) at 1485 cm^{-1}. A shift in the maximum of the 3605-cm^{-1} band to lower wave numbers (reminiscent of solvation) was evident, but there was no measurable decrease in intensity. It

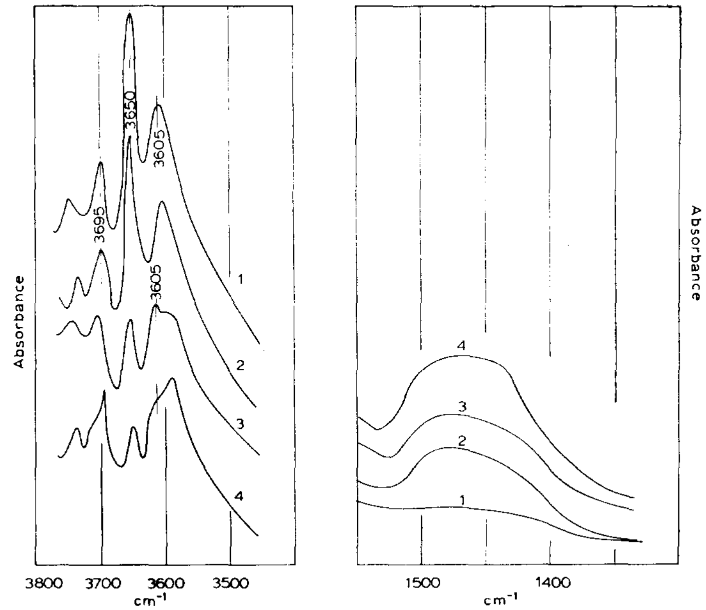


FIG. 6. Evolution of the OH stretching and NH_4^+ bending bands on adsorption of small amounts of NH_3 on a Linde X zeolite 42% saturated with Ca^{2+} (Lot No. 13-50080). Curve 1, after 1 hr outgassing at 175°C. Curve 2, sample of Curve 1 after adsorption of 7 μmoles of NH_3. Curve 3, sample of Curve 1 after adsorption of 14 μmoles of NH_3. Curve 4, sample of Curve 1 after adsorption of 28 μmoles of NH_3.

is of course possible that a new OH species was formed, providing a new strong band, but in view of the limited possibilities, this seems unlikely. The 3695-cm^{-1} band was not affected by NH_3. NH_3 adsorption on samples having both the 3650- and the 3540-cm^{-1} bands resulted in a decrease of both bands, thus demonstrating the identity of these OH species with the OH groups in decationated zeolites.

Our observations with Mg^{2+}- and Ba^{2+}-exchanged samples were comparable to those described for Ca-X except for the 3610-cm^{-1} band. This band was observed in a Y zeolite 72% exchanged with Mg^{2+} ions, but this observation could not be systematically repeated. In Ba-X and Ba-Y, the 3650- and 3550-cm^{-1} bands were observed as in Ca-X and Ca-Y, but the 3605-cm^{-1} or an equivalent band was never evident.

DISCUSSION

Data taken from the works of Carter *et al.* (*13*), Ward (*24*, *25*), Angell and Schaffer (*3*), and Hall and co-workers (*28*) are assembled in Table 1 for comparison. The available data appear self-consistent and in agreement with those presented herein.

The 3750-cm^{-1} band needs no comment because of the general agreement among authors on both observation and assignment.

The bands near 3650 cm^{-1} and near 3550 cm^{-1} are undoubtedly identifiable with those of similar frequency in decationated samples. The 3650-cm^{-1} band escaped observation in only a few cases (Table 1), e.g., with the Ca X zeolite in refs. (*3*), (*13*), (*25*), which is at variance with the results reported herein. Angell and Schaffer (*3*) missed the 3650-cm^{-1} band with Sr-Y, but Carter *et al.* (*13*) observed it with Sr-X.

The 3550-cm^{-1} band was not observed by Carter *et al.* (*13*) with X zeolites, which is again at variance with our findings (Fig. 4). It was absent in spectra from Ca-Y and Sr-Y preparations made by Angell and Schaffer (*3*), but was observed in similar samples by Ward (*24*). We are convinced that these discrepancies are due to minor differences in outgassing conditions and stability of the preparations, and that the absence of the 3550- and/or 3650-cm^{-1} bands

TABLE 1
WAVE NUMBERS OF THE OH STRETCHING BANDS IN ION-EXCHANGED ZEOLITES TYPES X AND Y

Carter, Lucchesi, and Yates (13)					
Na-X	3750	3695	3655	—	—
Li-X	3740	—	3660	—	—
K-X	3750	3715	3650	—	—
Ag-X	3750	3685	3630	—	—
Ca-X	3750	3695	—	—	3590
Sr-X	3750	3700	3660	—	3605
Ba-X	3750	3695	3620	—	—
Cd-X	3750	3690	—	—	3600
Angell and Schaffer (3)					
Na-Y	3748	—	3652	—	—
Li-Y	3744	—	—	—	—
Mg-Y	3745	3688	3643	3540	—
Ca-Y	3746	—	3645	—	—
Sr-Y	3746	3691	—	—	—
Ba-Y	3744	—	3647	—	—
Mn-Y	3748	—	3644	3545	—
Ca-Y	3748	—	3646	3540	—
Ni-Y	3746	3682	3643	3544	—
Zn-Y	3744	3673	3642	3542	—
Ag-Y	3745	—	3634	3550	—
Na-X	3744	—	—	—	—
Ca-X	3744	—	—	—	—
Ward (24)					
Li-Y Na-Y Rb-Y K-Y Cs-Y Ba-Y	No fine bands Broad bands, due to physically adsorbed H_2O, removed at various temperatures between 250°C–400°C				
Mg-Y	3739	3690	3645	3530	—
Ca-Y	3739	3688	3642	3520	3582
Sr-Y	3739	3691	3645	3560	3480
Ward (25) after addition of H_2O					
Ca-Y	3739	3688	3642	3540	3585
Ca-X	—	3690	—	—	3610 and 3510
Mg-Y	3740	3690	3639	—	3610
Mg-Y(H_2O)	3740	3690	3639	3595	—
Christner, Liengme, and Hall (28)					
Ba-Y	—	—	3645	—	—
Mg-Y	3745	3685	3642	3550	—
Zn-Y	3745	3675	3645	3550	—
Ca-Y	3745	—	3640	3550	—
This work					
CaX (64%)	3740	3695	3650	3550	3605
CaX (42%)	3740	3695	3650	—	3610
CaY	3740	3695	3650	3550	—
MgX	3740	—	3650	3550[a]	—
MgY	3740	3690	3650	3550	(3610)[b]
BaX	—	—	3650	3550[a]	—
BaY	—	—	3650	3550	—

[a] Only in samples with high Mg^{2+} or Ba^{2+} exchange level. [b] Not systematically reproducible.

must be ascribed to dehydroxylation (see below).

The band near 3690 cm^{-1} was detected by Carter, Lucchesi, and Yates (*13*) in all of their preparations except Li-X. Ward (*24*) reported it in Ca-, Mg-, and Sr-exchanged Y samples. Angell and Schaffer observed a similar band at wave numbers between 3691 and 3673 cm^{-1} in Y zeolites containing Mg, Sr, Ni, and Zn but not with Ca. Hall *et al.* reported bands at 3685 and 3675 cm^{-1} in a Mg-Y and a Zn-Y evacuated at 460°.

The experiments of Bertch and Habgood (*11*) on Na-X together with the present dehydration–rehydration experiments (Figs. 1–3) constitute undeniable evidence favoring the assignment of the 3695-cm^{-1} band to water molecules associated with monovalent cations. Since all divalent preparations so far reported have contained substantial quantities of unexchanged Na^+, it seems reasonable to make the same assignment for these (e.g., Fig. 3). A problem arises, however, when some of these materials are pretreated at high temperatures, i.e., the band is retained after evacuation to 500° (*3*, *28*). This led Christner, Liengme, and Hall (*28*) to suggest that a similar interaction may occur between H_2O and divalent ions. In view of the present evidence, two possibilities present themselves: (a) that the interaction is between H_2O and Me^+-OH or (b) between residual H_2O and residual Na^+ whose adsorption characteristics have been drastically altered by some unspecified rearrangement during the high-temperature pretreatment. The assignment (*13*) to Al-OH groups, based only on the argument that bands near this frequency occur in different kinds of alumina is very unconvincing. Indeed, in view of the present knowledge concerning the chemistry of these materials, it is difficult to see how the introduction of divalent ions can create Al-OH groups. Moreover, comparison of the available data (Table 1) reveals that not all the divalent ions generate this band.

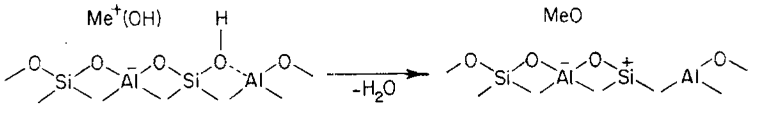
Bands at 3610 to 3580 cm^{-1} have been reported in the earlier work of Carter *et al.* (*13*), and more recently by Uytterhoeven (*19*) and by Ward (*24*, *25*). In the present work this band was observed with X zeolites with 45% (Fig. 6) and with 64% (Fig. 4) of the Na^+ replaced with Ca^{2+} but only in the presence of hydration water. The band was attributed by Uytterhoeven (*19*) and also by Ward (*24*, *25*) to OH groups in ions of the type $Me^+(OH)$. This assignment is strengthened by the present results. The insensitivity of this band towards addition of pyridine (*25*) or ammonia, as reported herein, suggests that this OH group has basic, rather than acidic character.

Recently, Olson (*29*) demonstrated the presence of "residual water oxygens" associated with Ca^{2+} in zeolites outgassed at 500°. These Ca^{2+} ions are located at sites S-II′, which are within the cubooctahedra on the six rings of oxygen ions adjacent to the large cavities. Olson's work constitutes a very strong argument in favor of the sequence of reactions proposed by the present authors (*19, 21, 28*) and by Ward (*24*) for the dehydration of zeolites containing divalent base-exchange cations. The conclusions of Olson are based on X-ray diffraction data, and do not allow the distinction of whether oxygens are present as H_2O molecules associated with the ions, as OH groups in an ion of type $Me(OH)^+$, or as neutral oxide molecules. What his data do show is the position of the Ca^{2+} inside the oxygen six-ring with an additional oxygen in a nearly tetrahedral position, beyond the Ca^{2+}. Moreover, this oxygen either bears an H or is linked to another Ca^{2+} in an S-I′ position on an adjacent six-ring. The formation of MeO molecules in Me^{2+} zeolites has been postulated (*19*, *21*, *24*, *28*) to account for the low thermal stability of the band near 3600 cm^{-1}. In view of Olson's data it now seems more likely that the end result is Me^+-O-Me^+.

Some comments can be made here on the stoichiometry of the different reactions. If reaction (1) occurred stoichiometrically on each Me^{2+} ion present, the band near 3600 cm^{-1} could be reasonably expected to be comparable in intensity with those at 3650 and 3550 cm^{-1}, whereas it is either weak or not observed. It is obvious, therefore, that the $Me^+(OH)$ ions are unstable and suffer a dehydroxylation reaction even at relatively low temperatures. The data appear to be best satisfied by Eq. (1) followed by

$$Ca^+{-}OH + Ca^{2+}\ (\text{adjacent}) \rightarrow Ca^+{-}O{-}Ca^+ + H^+ \quad (2)$$

where the freed proton reacts with lattice oxygen to form another decationated (Brönsted) site. If dehydroxylation of the latter takes place independently, no special stoichiometry is required. Contrast this with the variation proposed by Ward (*24*), i.e.,



(3)

Accordingly, the 3650- and 3550-cm^{-1} bands would disappear at the same time as the 3600-cm^{-1} band. Contrary to this the 3600-cm^{-1} species is absent in most samples, while the 3650- and 3550-cm^{-1} bands are still present. This indicates that $Me(OH)^+$ ions are more sensitive to dehydroxylation than the —Si-OH groups. The data of Table 1, and our experiments as well, also show that the OH groups responsible for the 3650-cm^{-1} band are more resistant to dehydroxylation than those responsible for the 3550-cm^{-1} band. This relative stability is consistent with the observations by Uytterhoeven *et al.* (*9*) with decationated zeolites, but the difference in stability seems to be more pronounced in the samples exchanged with divalent ions than with decationated samples.

An attempt was made to evaluate the concentration of OH groups in the 3650- and 3550-cm^{-1} bands of different Ca-Y samples evacuated at 300°, using the corrected* adsorption coefficients published by Uytterhoeven *et al.* (*9*). In the most favorable cases the OH content was close to the theoretically possible amount, but the figures were not reproducible from one experiment to another.

Pickert *et al.* (*30*) attributed the catalytic activity of Me^{2+}-exchanged zeolites for hydrocarbon cracking reactions to the electrostatic action of the charge imbalance

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* The absorption coefficients published in ref. (*9*), after correction for a decimal error and conversion into integrated intensities are 5.281 and 3.123 (X zeolite) or 2.525 cm $\mu mole^{-1}$ (Y zeolite) for the 3650- and 3550-cm^{-1} bands, respectively.

created when multivalent ions are introduced. In agreement with other workers (*24*), our results suggest that the first molecules affected by this high potential are the water molecules which are already present, prior to a catalytic experiment. It is apparent from the results reported here, that dissociation of the residual water molecules upon dehydration gives rise to OH groups having essentially the same properties as those in decationated zeolites, and that the dehydroxylation results in the formation of electrophillic sites also identical with those in decationated zeolites. The catalytic activity of the alkaline earth faujasites can therefore be explained on the same basis as that given for the decationated zeolites. The hydroxyls in Me^{2+} zeolites are manifestly less stable than the hydroxyls in decationated samples. If the hydroxyls are considered to be the catalytically active groups, the concentration of active sites would be considerably lower in Me^{2+}-exchanged zeolites. However, as discussed by Hall and co-workers (*28*), in the presence of both H_2O and a proton-accepting molecule, the electrostatic potential may effect proton transfer directly to the base, and this process may be favored over the reaction of the base with decationated sites.

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