

Influence of Temperature on the OH-Band Intensity in the Infrared Spectra of Decationated Zeolites X and Y

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The IR spectra of several decationated zeolites X and Y were studied in the OH stretching region, and the influence of temperature on the intensity of the bands near 3650 and 3550 cm^{-1} was investigated. The zeolites were derived from samples initially saturated with Li^+ , Na^+ , K^+ , and Mg^{2+} ions, in case of the Y samples and with Na^+ ions in case of the X samples. Some samples had different contents of residual Na^+ ions. The exact frequency of the band near 3650 cm^{-1} was dependent on the amount more than on the nature of the residual cations. The frequency of the OH bands was interpreted in terms of the electrical field in the zeolite cavities.

A reversible decrease of the band intensity (20-30%) was observed with increasing temperature below 400°C together with a small shift to lower frequencies and a broadening of the bands. All these effects are ascribed to the increased thermal motion of the lattice constituents. The ratio of the intensities of the 3550 and 3650 bands was also dependent on the temperature. This was explained by assuming a redistribution of the protons over the different sites. The effect was dependent on the amount of residual ions and the initial value of the band intensity ratio at room temperature.

INTRODUCTION

The OH groups in hydrogen Y zeolites are generally thought to be Brönsted acids and therefore at the source of the catalytic activity for cracking reactions. This explains the large amount of research devoted to the study of OH groups in so-called decationated zeolites.

By IR spectroscopy two different types of OH groups are recognized, absorbing around 3650 (high frequency-HF) and 3550 cm^{-1} (low frequency-LF). Hughes and White (1) were the first to assign the HF band to OH groups formed on O_1 type oxygen ions, and were followed in this assignment by several others (2-4). Some authors considered the possibility that the LF band was due to hydrogen bonded OH groups (1, 5). However, in view of the distances between the oxygen ions, hydrogen bonding is not likely to occur with the hydroxyls in the zeolites X and Y. It is

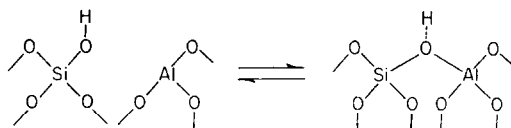
now generally assumed that the LF band corresponds to a distinct location of the OH groups in the zeolite lattice (2, 4, 14). Uytterhoeven *et al.* (2) assign the LF band to hydroxyls on the oxygen ions forming the cubooctahedron cages, without making further distinction between O_2 , O_3 , or O_4 type oxygens. From X-ray diffraction data Olson and Dempsey (4) concluded that the LF type hydroxyls are formed on O_3 oxygens and located inside the hexagonal prisms. Ward and Hansford (3) agreed on the location of the hydroxyls inside the hexagonal prisms. The hexagonal prisms are inaccessible for large molecules. Despite this location the LF type OH groups can react with large molecules like pyridine and piperidine (1, 6, 11). This has been explained by Olson and Dempsey (4) and by Ward and Hansford (3) in terms of a possible migration of the protons over the network of oxygens.

The intensity of the OH bands in the IR spectra of hydroxyl containing minerals shows a reversible decrease in intensity when the minerals are heated at temperatures at which dehydroxylation does not yet occur. This reversible decrease in intensity was associated by Fripiat and co-workers with a possible mobility of the protons. The observation was made on the IR spectra of kaolinite (7), micas (8), and boehmite (9). For boehmite a theoretical explanation of the phenomenon was proposed based on a tunneling of the protons between two symmetrical potential wells associated with distinct positions between a pair of oxygen ions. In the original work on micas (8), the thermal emission of the samples was not taken into account, but this was corrected in a recent work by Rouxhet and Fripiat (10).

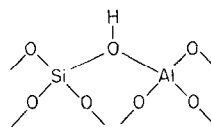
A mobile proton could be a potential active site for hydrocarbon cracking, and therefore several authors have devoted attention to the effect of heating on the intensity of the OH bands in zeolites X and Y (12, 14, 16). There is some controversy about the observation but mainly about the interpretation of this reversible change in intensity. In our previous work (12), a reversible decrease of the OH band intensities up to 30% was reported at temperatures of the order of 300°C. An extrapolation of the data to 100% suggested that the protons were completely delocalized at 400–450°C. Unfortunately, the values in that work were too high, the thermal emission of the samples having introduced an important overestimation of the phenomenon. Eberly (13) did not find evidence for a decrease in intensity of the OH bands upon heating, but the negative result may be due to the low transmission of the samples used for the spectrographic investigation.

In contrast to the report by Eberly, Ward (14) observed a 29% decrease in absorbance of the HF band when a HY zeolite is heated from 120 to 450°C. The decrease of the LF band in the same sample was less important. The experiments were carried out with a Cary-White 90 spectrometer, where the chopping of the radia-

tion before and not after the sample avoided the interference of the thermal emission of the sample. Ward (14) attributed the decrease in intensity of the OH bands and the concomitant shift in frequency to a probable interaction of the silanol groups with neighboring atoms, invoking the scheme suggested by Liengme and Hall (11) and by one of the present authors (J.B.U.) (15).



The increase in temperature would shift this equilibrium to the right. However, since that scheme was proposed, Olson and Dempsey (4) presented evidence from X-ray diffraction experiments that the aluminum ions in deammoniated faujasites remain in a tetrahedral configuration with respect to the oxygen lattice. The architecture of the hydroxylated sites is therefore



as proposed earlier by Uytterhoeven *et al.* (2). In the article cited above (14), Ward considered the protons in the activated hydroxyls as mobile or delocalized. He further suggested that the protons "delocalized" at higher temperature are the active sites for catalytic reactions.

Cant and Hall (16) made a critical review of the experiments quoted here. They made experiments on micas, on η -alumina and on decationated Y zeolites as well. Great care was taken in avoiding the interference of thermal emission, and they arrived at the conclusion that most of the results published at the time their paper was submitted (7–9, 12) were too high because of this emission. However, they still agreed on the observation that a reversible decrease of the OH bands of less than 20% occurs upon heating of the different samples to moderate temperatures. Nevertheless they conclude that "this change is

insufficient to necessitate a special explanation and thus our measurements do not demonstrate that dissociation of OH groups is responsible for the mobility of hydrogen in these solids."

Recently Rouxhet and Fripiat (10) made a theoretical treatment of the O-H...O oscillating system. They showed that the thermal activation of O-O vibrations could alter the shape of the OH stretching band, without changing the true band area. The effect is such that for reasonable variations of the O-O distances there is a considerable broadening of the band at the base. An important part of the band area could thus be lost in the base line of the spectrum, and this could account, at least semiquantitatively, for the band decrease.

At the present moment it seems uncertain that the reversible decrease in intensity observed in the OH stretching bands of hydroxyl containing minerals upon heating can be associated with a mobility of the protons. In this work we have studied the shape and the area of the OH absorption bands as a function of temperature on a wide variety of decationated samples, differing in the degree of decationation and the nature of the residual exchangeable ions. The relative variation of the area of the OH bands at 3650 and at 3550 cm^{-1} is discussed in terms of a variation of the population of the different sites, thus giving an indirect proof for the migration of the protons.

EXPERIMENTAL SECTION

Materials

Zeolite samples were obtained from the Linde Co. Two different X samples (lot nos. 1340080 and 137396) and a Y sample (lot no. 51-53) were used. Samples containing the ions Na^+ , Li^+ , K^+ , and Mg^{2+} were prepared from the materials as received by a conventional ion exchange procedure using 2N solutions of NaCl , LiCl , KCl , and MgCl_2 , followed by washing until free from excess electrolyte. Samples with different proportions of Na^+ and NH_4^+ ions were then prepared from the Na sam-

ples by stirring with NH_4Cl solutions of different concentrations followed by decantation and washing. The Li^+ , K^+ , and Mg^{2+} samples were exchanged with NH_4^+ to the maximum possible extent, using a 1N NH_4Cl solution. After that, the samples were dried in an electric oven at 60°C to minimize losses of NH_3 . Even at that low temperature some of the X samples suffer decomposition of the NH_4^+ ions. To obtain constant weight, the samples were stored in a desiccator over a saturated NH_4Cl solution. The samples were analyzed, and the degree of decationation was calculated from the differences between the aluminum content and the content in exchangeable ions other than NH_4^+ . The analytical data are expressed in Table 1 in terms of unit cell composition.

TABLE 1
UNIT CELL COMPOSITION OF THE DIFFERENT
SAMPLES, ANALYZED IN THE NH_4^+ FORM
BEFORE DECATONATION

Sample	Anhydrous unit cell composition
Y Mg-H	$(\text{NH}_4)_{39.1}\text{Mg}_{4.95}(\text{AlO}_2)_{55}(\text{SiO}_2)_{137}$
Y K-H	$(\text{NH}_4)_{41.2}\text{K}_{13.5}\text{Y}^a$
Y Li-H	$(\text{NH}_4)_{42}\text{Li}_{13}\text{Y}$
Y Na-H ₁	$(\text{NH}_4)_{49.6}\text{Na}_{6.4}\text{Y}$
Y Na-H ₂	$(\text{NH}_4)_{43.7}\text{Na}_{11.3}\text{Y}$
Y Na-H ₃	$(\text{NH}_4)_{30.9}\text{Na}_{24.1}\text{Y}$
Y Na-H ₄	$(\text{NH}_4)_{24.9}\text{Na}_{30.1}\text{Y}$
Y Na-H ₅	$(\text{NH}_4)_{24.8}\text{Na}_{30.2}\text{Y}$
Y Na-H ₆	$(\text{NH}_4)_{17.4}\text{Na}_{37.6}\text{Y}$
X Na-H ₁	$(\text{NH}_4)_{64.5}\text{Na}_{20.5}(\text{AlO}_2)_{35}(\text{SiO}_2)_{107}$
X Na-H ₂	$(\text{NH}_4)_{60.3}\text{Na}_{22.7}(\text{AlO}_2)_{33}(\text{SiO}_2)_{109}$
X Na-H ₃	$(\text{NH}_4)_{35.6}\text{Na}_{49.4}(\text{AlO}_2)_{35}(\text{SiO}_2)_{107}$
X Na-H ₄	$(\text{NH}_4)_{24.2}\text{Na}_{58.8}(\text{AlO}_2)_{33}(\text{SiO}_2)_{109}$

^a $\text{Y}-(\text{AlO}_2)_{55}(\text{SiO}_2)_{137}$

Spectrographic Equipment and Sample Preparation

The infrared cell used in this work was connected to a high vacuum system and allowed to heat *in situ* during the scanning of the spectrum. Full details on the design are described elsewhere (2). The spectrograph was a Beckman IR12 grating instrument. To avoid the effect of thermal emission the chopper between the sample and the detector was stopped. In this way

any radiation emitted either by the sample or by the furnace is not observed, because the detection system is sensitive only towards a modulated beam of light. The decrease in energy resulting from the suppression of the second chopper is compensated by a larger slit width. In order to obtain absolute absorbance measurements, the slit width was selected so that a resolution was obtained better than 10% of the half-width of the narrowest band (3650 cm^{-1}). Period, gain setting, and scanning speed were adapted to the selected slit following the instruction manual of the instrument.

The zeolite samples were pressed into thin wafers between two steel plates at a maximum load of 1000 kg cm^{-2} of film. Films of approximately $2 \times 3\text{ cm}$ were cut from this wafer, the weight and area of which were carefully measured. Film thickness ranged between 3 and 5 mg cm^{-2} . Thicker films were discarded: if the amount of material in the spectral beam was higher than 5 mg cm^{-2} , the energy transmitted in the OH stretching region was very low and the results became less reliable.

Spectrographic Procedure

The NH_4^+ zeolites were decationated following a flash procedure. The stabilizing effect of such a flash-pretreatment has been discussed elsewhere (2). Y zeolites were pretreated at 400°C , the X samples at 300°C , both at a vacuum of 10^{-5} – 10^{-6} Torr. After cooling to room temperature, the spectrum was recorded between 3300 and 3750 cm^{-1} . The temperature was then gradually raised, using intervals of 30 – 40°C . When thermal equilibrium was reached at each interval the spectrum was recorded two or three times before passing to the next step. The procedure was continued till the temperature of pretreatment was approached. In order to control the reversibility of the process, the temperature was lowered to room temperature in two or three steps; and at each step spectra were taken again.

Various procedures for quantitative interpretation of IR spectra of the zeolites are found in the literature. The band area

rather than the peak height must be used here because the shape of the bands changes with temperature. Hughes and White (1) integrated the high-frequency half of the bands and considered the band area as twice the integrated portion. For our purposes this procedure was found to be not accurate enough. Cant and Hall (16) calculated the area of the HF band from the peak height and half-width, and applied to these values a correction for slit width effects as proposed by Ramsey (17). The area of the LF band was integrated by Cant and Hall using a rolling disc planimeter.

In our experiments both the HF and LF bands were integrated using a rolling disc planimeter. In order to do this a base line was drawn tangent to the spectrum at 3300 and 3700 cm^{-1} . In the region of overlapping the bands were individualized and drawn in such a way that at each particular frequency the sum of the absorption of each individual band was equal to the recorded absorption. The values thus obtained were compared in many cases with values calculated following Ramsey's (17) procedure. The values obtained with the planimeter were always lower than the calculated intensities, the differences being between 5 and 9% for the HF band, and between 14 and 22% for the low frequency band.

However, Ramsey's method (17) was elaborated for a prism spectrometer, and the actual correction on our spectra is lower because of the higher resolution power of the grating instrument used in this work. On the other hand, the differences between the intensities obtained by graphical integration and by the Ramsey calculation were, for each individual film, independent of temperature to a limit better than 3%. Therefore the values obtained by graphical integration are completely reliable. A possible inaccuracy in drawing the base line was kept to a minimum by the repeated scanning at each temperature.

RESULTS

The notation and the chemical composition of the samples are indicated in Table 1. The observations made in this work in-

clude the band frequencies for the different samples, the shift and the broadening of the bands as a function of temperature, and the band intensity of both the HF and LF bands at different temperatures under the conditions described in the experimental section.

The frequency of the OH bands in zeolites has been reported to be a function of the electron affinity of the saturating ions (18, 19). In order to compare this with our results, the band frequencies observed at room temperature in samples with different kinds of residual ions (Na^+ , K^+ , Li^+ , Mg^{2+}) are plotted in Fig. 1 (lower) as a function of the electron affinity of the residual ions. The three points, enclosed by broken lines, represent Y zeolites with different amounts of residual Na^+ ions. In Fig. 1 (upper) we compare the band frequencies for the different decationated samples prepared from the Na^+ form as a function of the amount of residual Na^+ ions. These correlations are only shown for the HF band. Similar observations on the LF band were inaccurate and are not shown.

When the samples are heated, a broaden-

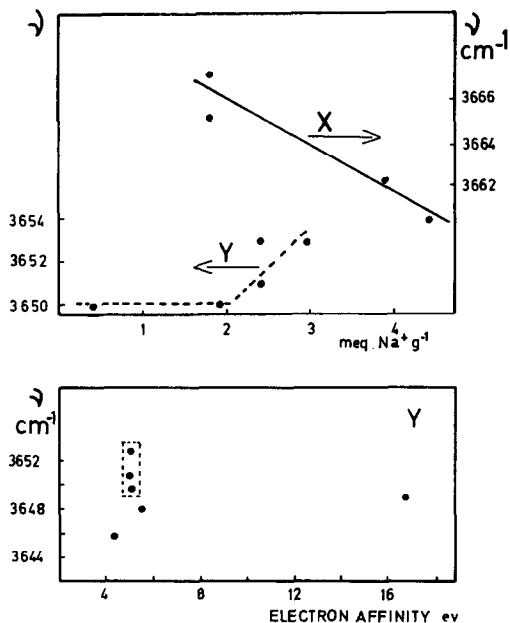


FIG. 1. (lower) Frequency of the HF band in Y samples as a function of the electron affinity of the residual cations; (upper) Frequency of the HF band as a function of the amount of residual Na ions for X (left) and Y (right) zeolites.

ing of the OH bands and a shift to lower frequencies occurs. At 425°C the average shift of the HF band in the different samples was 17 cm⁻¹, and a broadening of 15 to 20 cm⁻¹ was observed at the same temperature. The LF band showed the same tendencies, but accurate determinations were not possible because of the broadness of this band.

Figure 2 contains some typical examples of the variation of the band area as a function of temperature. The X Na-H₄ sample, which had only the HF band, shows no significant decrease in band intensity up to temperatures close to dehydroxylation (Fig. 2A, curve 3) and a similar observation has been made on the X Na-H₃ sample. For X Na-H₁ (Fig. 2A, curves 1 and 2) and also for X Na-H₂, both LF and HF bands show a linear decrease in intensity with increasing temperature. The Y samples, with both the HF and LF bands well developed, show for both bands an exponential decrease in intensity. This is

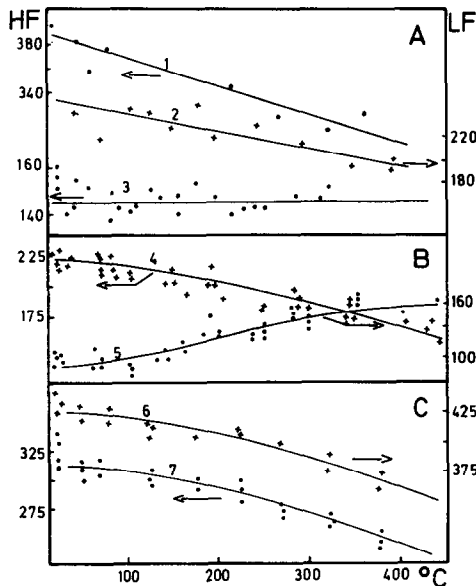


FIG. 2. Decrease of the OH band area as a function of the temperature for a few samples. The ordinate scale is in arbitrary units. The scale on the left applies to the HF band, the right scale to the LF band. (A) data on the samples X Na-H₁ (curves 1 and 2) and X Na-H₄ (curve 3); (B) curves 4 and 5 give the evolution of the HF and LF band of sample Y Na-H₅; Curves 6 and 7 are for the LF and HF band of sample Y Na-H₁.

shown in Fig. 2C for the sample Y Na-H₁. For the Y samples with a low initial intensity of the LF band, an exponential decrease of the HF and a concomitant increase of the LF band are observed (Fig. 2B). All the phenomena reported in Fig. 2 are absolutely reversible. Whatever the mechanism of the decrease in intensity, it can be represented by a relationship of the form $(1 - \alpha) = \beta \exp(-E/RT)$, as proposed by Fripiat and co-workers (8, 12). In this relation α is the ratio of the integrated band intensities at temperature T and at room temperature. A temperature factor can be calculated from an Arrhenius plot. For those samples where such a calculation was possible the data are given in Table 2. The accuracy of the determination

TABLE 2
ACTIVATION ENERGY FOR THE DECREASE IN
INTENSITY OF THE HF AND LF BANDS IN THE
DECATONATED Y SAMPLES

Sample	HF band	LF band
Y Mg-H	3.39	4.07
Y K-H	2.75	2.65
Y Li-H	2.47	2.75
Y Na-H ₁	2.47	2.31
Y Na-H ₂	2.66	4.3
Y Na-H ₃	2.56	2.7
Y Na-H ₄	3.94	—
Y Na-H ₅	2.32	—
Y Na-H ₆	3.80	—
Av	2.6	3.13

is of the order of 1 kcal, and thus the difference between the values listed in Table 2 is not significant. The average value of the temperature factor is 2.6 kcal/mole for the HF and 3.13 kcal for the LF band. From the data published by Ward (14) we calculated an energy of 3.4 kcal. The values published so far for other minerals (7, 10, 12) range between 2 and 5 kcal.

A relation exists between the intensity changes of the HF and LF bands. To point this out the ratio of the intensities of the LF and HF bands are plotted as a function of the temperature in Fig. 3. A family of lines is obtained, the slope of which depends on the relative intensities of the two

bands. The experimental points are given only for a few lines. In any case the regression of the lines was calculated and the correlation between the LF/HF ratio and the temperature was found to be highly significant. The scattering of the points shown for curves 1, 2, and 3 indicates that a high number of experimental points is desirable to obtain meaningful quantitative data from IR spectra.

The sudden breakdown of curve 2 at 400°C is due to dehydroxylation. This confirms that the protons responsible for the LF band are more sensitive to dehydroxylation than the HF protons.

DISCUSSION

Frequency of the OH Bands

Richardson (19), Christner *et al.* (18) and Ward (28) reported a correlation between the frequency of the band near 3650 cm⁻¹ in samples of zeolite Y exchanged with different ions and the electron affinity of these ions. The examination on hydrogen Y zeolites with different contents of residual ions made in this work does not reveal a similar trend (Fig. 1, lower) but shows that the influence of the number of residual ions is more important than the nature of the ions itself. The influence is not the same for the two types of zeolites, and is more important for the X than for the Y samples. There is no contradiction between our observations and the reports by Richardson (19) and by Christner and co-workers (18). These authors reported data for samples with a high content of exchangeable ions for which the differences in electron affinity may have a significant effect. Our observations are made on samples with a low content of exchangeable ions and the amount of residual ions becomes equally important as the difference in electron affinity. All these data support the hypothesis advanced by White *et al.* (20) and supported by several others (2, 18, 19) that the frequency of the OH bands depends on the charge distribution through the lattice. White and co-workers (20) attempted a quantitative interpretation of the OH frequencies in zeolites, based on a

theory developed by Coggeshal (21). Applying the same theory on the average difference between the frequency of the HF band in our decationated X and Y zeolites, we estimate that the field in the large cavities of the X sample is lower by about 0.5 V \AA^{-1} as compared to the Y samples. This is of the same order of magnitude as the difference between the values calculated by Dempsey for NaX and NaY zeolites (28). The frequency shift as a function of the Na^+ content observed for our Y samples may not be very significant as it is of the same order of magnitude as the resolution. For the X samples the shift to lower frequencies is significant and leads to the conclusion that the field in the large cavities increases with the Na^+ content.

OH Band Decrease

It results from our experiments that the OH band intensity in the zeolites decreases reversibly with increasing temperature. At 400°C the effect is close to 25% and important enough to attempt an explanation. It seems unlikely to us at this moment that this reversible decrease can be correlated with the mobility of the protons. This would indeed suggest that an important fraction of the hydroxyls is jumping from oxygen to oxygen with a frequency so high that the lifetime of the hydroxyls is too short to contribute to the IR absorption. In a recent review Rouxhet *et al.* (22) estimated this jump frequency between 10^9 and 10^{11} sec^{-1} . Such a high jump frequency seems not to be in agreement with the low value of the diffusion coefficient for protons. In the case of the mica muscovite this diffusion coefficient at 400°C , determined by Rouxhet *et al.* (22) using the technique of H-D exchange, was found to be $1.6 \times 10^{-18} \text{ cm}^2 \text{ sec}^{-1}$. This corresponds to a jump frequency of $5 \times 10^9 \text{ sec}^{-1}$. This suggests that another mechanism than proton jumping is determining the rate of migration of the protons.

Gallagher and Phillips (23) studied the diffusion of protons in α FeOOH. The jump frequency derived from their diffusion coefficient, extrapolated to 400°C , amounts to 10 sec^{-1} . They assume a diffusion mecha-

nism involving hydrogen bond rupture and a rotation of a defect water molecule within the solid. The rotation of water molecules was also found to be the rate-determining step for proton diffusion in dilute acid solutions (27). This rotation reflects the necessity of bringing the orbitals of the oxygens in the right direction to allow the proton migration. If this is a general condition applicable also to the zeolites, a jump frequency of 10^9 – 10^{11} sec^{-1} seems to us unrealistically high.

In hydrogen bonded systems O-H...O, such as exists in boehmite, it is still possible to assume that an oscillation of the proton between the two oxygen ions influences the band intensity, and that this oscillation is not a real diffusion (22). It seems unlikely to us that such a distinction can hold in zeolites where the hydroxyls are not involved in hydrogen bonding. Unfortunately, diffusion coefficients for protons in decationated zeolites are not available.

From these considerations we conclude that there is very little evidence to explain the reversible decrease in OH band intensity entirely by the mobility of the protons. If this mobility has such an effect, other factors such as O-O distances are at least equally important. This has been shown by Rouxhet and Fripiat (10). In agreement with Cant and Hall (16) we feel that the increased thermal motion and the slightly higher distances between the lattice constituents at higher temperature offer sufficient explanation for the observed changes in bandwidth and frequency shifts, and that the same phenomena explain also the apparent decrease in band intensity.

Repopulation of Hydroxyl Sites

Our negative conclusions do not imply that the protons are immobile, but only that the reversible decrease of the OH band intensities is not a good method to study such mobility. The increase of the electrical conductivity of boehmite with increasing temperature, investigated by Mata and Fripiat (24) supports such proton mobility.

Evidence for the migration of protons in the HY zeolites is found in the variation

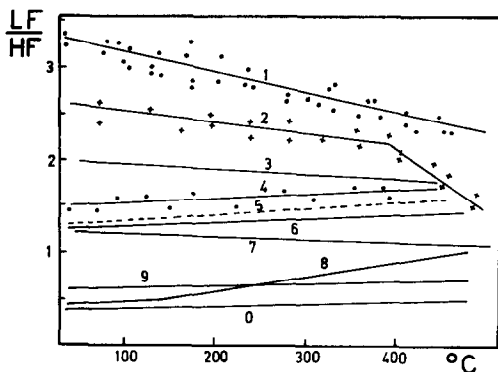


FIG. 3. LF/HF ratio as a function of the temperature for different samples: (1) Y Mg-H; (2) Y Li-H; (3) Y K-H; (4) Y Na-H₁; (5) Y Na-H₂; (6) Y Na-H₃; (8) Y Na-H₆; (9) X Na-H₁; and (0) X Na-H₂. Curve 7 was obtained with data from the paper by Ward (14).

of the relative intensities of the two kinds of OH bands in the IR spectra presented in this work. The LF/HF intensity ratio changes with temperature as indicated in Fig. 3. This reflects a variation in the population of the sites corresponding to these two bands. As shown in Fig. 3, for samples with a high proton content, having a very intense LF band and thus a high LF/HF ratio, this ratio decreases definitely indicating that the LF band is influenced more by an increase in the temperature than the HF band. On the other hand, for samples with a low proton content, having a low initial LF/HF ratio, the slope of the lines becomes positive indicating that the HF band is more affected by a change in temperature than the LF band. A gradual change in the slope of the lines can be seen for samples with intermediate initial LF/HF ratios.

Several authors have indicated that the relative intensity of the two OH bands is a function of the amount of residual Na⁺ ions (2, 3). Ward and Hansford (3) have studied an extensive series of hydrogen Y zeolites with increasing amounts of protons. It was shown that the HF band develops regularly with decreasing Na⁺ content, but that the LF band occurs to any extent only during the replacement of the last 22 to 25 Na⁺ ions. The development of the 3550 cm⁻¹ band was therefore associated

with the removal of the ions from the hexagonal prisms. In an earlier work Uytterhoeven *et al.* (2) also correlated the development of the HF band with the removal of ions in the large cavity, while the development of the LF band was thought to start when an important part of six-membered rings of oxygen ions, either inside the large or inside the small cavities, was liberated from Na⁺ ions. In any case, the location of the residual Na⁺ ions is considered to influence the distribution of the protons, and a migration of the Na⁺ ions at higher temperature will therefore influence the redistribution of the protons over the HF and LF bands.

The migration of the Na⁺ ions in zeolites X and Y was studied by Schoonheydt and Uytterhoeven (25) by electrical conductivity. They showed that the migration path of the Na⁺ ions in the large cavities, from one six-ring of oxygens to another, goes over the square faces. The O₁ oxygen ions, i.e., the sites responsible for the HF band, are part of these square faces. The samples with low initial LF/HF ratios are those with a high amount of residual Na⁺ ions, some of them probably still located inside the large cavities. When the temperature is raised, these ions can migrate over the square faces and induce a migration of protons away from O₁ oxygens. A proton leaving an oxygen ion of type I can only go to an oxygen belonging to the cage of a cubooctahedron and thus to sites contributing to the LF band. In this way we understand that the samples with the highest content of residual Na⁺ ions show a decrease of the HF and a concomitant increase of the LF band.

Unfortunately this hypothesis cannot be tested by the study of the X zeolites. In the X samples with a high content of residual Na⁺ ions (Fig. 2, curve 3) no significant decrease in band intensity upon heating was observed. On the other hand, considerable dehydroxylation takes place during the initial decationation of X samples (2). This means that the results with the X samples were less reproducible and could not be interpreted.

For samples low in Na⁺ content, the re-

distribution of the protons may be a simple matter of statistics. It was shown by Uytterhoeven and co-workers (2) that the OH's of the HF band are more stable than those of the LF band. It is most likely that upon heating a given fraction of the protons start migrating and depopulate the less stable sites in favor of the most stable. It is impossible to make exact calculations on the population of each site, because the effect of apparent decrease in band intensity with increasing temperature superposes on the effect of repopulation of the sites. In any case, the reversibility of the phenomena described here indicates that the distribution of the protons over the different lattice sites corresponds to an equilibrium state, and that this equilibrium is dependent on external factors like temperature and content in residual cations.

These considerations are important from the viewpoint of catalysis. Many investigators have tried to correlate the catalytic activity with the acidity of the hydroxyl groups. Especially the reactivity toward bases like pyridine and piperidine has been used (1, 11, 13, 14, 18). The difference in reactivity of the two kinds of hydroxyls toward these molecules is probably a matter of accessibility of sites rather than a difference in acid strength. In a recent study, Ward (26) demonstrated that only the OH groups of the 3650 cm^{-1} band take part in the catalytic dealkylation reaction of cumene. We conclude from our experiments that the presence of molecules with basic properties may influence the equilibrium distribution of the protons over the different crystallographic sites, especially at temperatures where the protons acquire a certain mobility.

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