

Fourier transform infrared study of the protonation of the zeolitic lattice- influence of silicon - aluminium ratio and structure

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Fourier-transform Infrared Study of the Protonation of the Zeolitic Lattice

Influence of Silicon : Aluminium Ratio and Structure

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An *in situ* Fourier-transform infrared study is presented for the spectral region from 250 to 1400 cm^{-1} . Using supported samples the changes for the infrared-active lattice modes after protonation are studied for zeolites A, X, L, ZK-5, mordenite and for zeolites Y with Si : Al ratios from 2.4 to 40.

Protonation of the lattice results in a shift to higher wavenumbers for the asymmetric and symmetric T—O stretching modes (where T = Al or Si). These shifts are attributed to coupling between T—O lattice modes and in-plane bending modes of acidic hydroxyls. Inter-tetrahedral and intra-tetrahedral T—O stretching modes show a different coupling. Coupling between T—O lattice modes and out-of-plane hydroxyl bending modes appears to be much weaker. Protonation further results in changes of the infrared band intensities for the symmetric T—O stretching modes and for several modes in the region below 650 cm^{-1} .

The changes observed for the asymmetric T—O stretching modes are a function of the proton concentration and do not depend significantly on the lattice structure. Changes after protonation for the symmetric T—O stretching modes and especially for the modes in the region below 650 cm^{-1} are most sensitive to variation in zeolite structure.

Zeolites are a class of aluminosilicates with an open lattice structure. The silicon or aluminium atoms (T atoms) are connected *via* oxygen atoms to form cages and channels and different zeolitic structures can result. Such lattices are not rigid.¹⁻³ Interactions with cations, protonation of the lattice or substitution of the T atoms cause the structure to deform. Different techniques can be used to study these phenomena. X-Ray diffraction (XRD) provides information directly on bond angles and bond lengths, but lattice relaxation is also observed with NMR.^{4,5} The zeolitic lattice vibrations are also influenced by this relaxation of the structure. In a previous study we investigated the interactions of cations and acidic protons with the lattice of non-dealuminated Y zeolites using *in situ* Fourier-transform infrared (FTIR) spectroscopy.⁶ We found that dehydration of divalent cations resulted in a migration of these cations, leading to stronger electrostatic interactions with the zeolitic lattice. The observed lattice modes were strongly affected by these interactions. Protonation of the lattice also changes markedly the IR spectra. Unlike dehydration, protonation results in a shift to higher wavenumbers for the symmetric and asymmetric T—O stretching modes and the intensities for several modes are affected. In this paper we will study *in situ* the protonation of the lattices of X and Y zeolites having different silicon : alumina ratios, using FTIR transmission spectroscopy. Finally, we will discuss the influence of structure by studying the protonation of the lattices of the zeolites A, L, ZK-5 and mordenite.

Experimental

Samples of zeolites Y with different Si : Al ratios were prepared from the sodium form of zeolite Y (LZ-Y52 with Si : Al = 2.4 and Akzo PA42611B with Si : Al = 2.8). Non-dealuminated sodium-free ammonium-exchanged zeolites were obtained after repeated exchange with an excess of NH_4NO_3 at 353 K. Dealuminated zeolites with Si : Al ratios from 2.8 to 40 were prepared by dealuminating an 85% ammonium-exchanged zeolite Y with $(\text{NH}_4)_2\text{SiF}_6$ at 343

K^{7,8} or by dealuminating the sodium form with SiCl_4 during 15 to 60 min at temperatures ranging between 473 and 673 K.⁹⁻¹² In the latter case the ammonium form was obtained after repeated exchange in a solution containing the dealuminated product and an excess of NH_4NO_3 . According to chemical analysis the sodium content in the dealuminated samples was negligible. The ammonium form of zeolite A was prepared by exchanging the starting material, obtained from Proctor and Gamble, at room temperature with a solution containing NH_4NO_3 and NaNO_3 in a 1 : 1 ratio. Zeolites X (Exxon Chemical AT1005) and ZK-5 (Exxon Chemical AT385-51) were converted to the ammonium forms by exchange with NH_4NO_3 at room temperature.

The sodium form of mordenite (Laporte Industries Limited CLA26723) was converted to the ammonium form by exchange at 353 K with a NH_4NO_3 solution.

The protonated form of zeolite L was obtained from Amoco. This sample contained some residual potassium (K : Al = 0.34).

The crystallinity of each sample was checked by XRD. The Si : Al ratios of the samples have been determined from ²⁹Si MAS NMR spectra obtained on a Bruker CXP 300 or MSL 400 spectrometer, according to the procedure used by Thomas and Klinowski.¹³

IR spectra (250–4000 cm^{-1}) were recorded on a Bruker IFS 113v FTIR-spectrometer equipped with a heatable *in situ* transmission cell connected to a vacuum system, which produced a vacuum better than 10^{-4} Pa. All spectra (250–4000 cm^{-1}) were recorded at room temperature after evacuation at 573–823 K, readsorption of anhydrous ammonia (UCAR, purity 99.997%) at room temperature and evacuation at room temperature. To study the intense lattice vibrations the zeolitic samples were supported on a silicon disc.⁶ The *in situ* cell was equipped with KRS-5 windows. Typically 500 scans were co-added at a resolution of 4 cm^{-1} using a standard mid-IR DTGS detector, a globar light source and a germanium-coated KBr beamsplitter. The region below 700 cm^{-1} was recorded with a far-IR DTGS detector and a Mylar beamsplitter.

Results

In the region above 1400 cm^{-1} weak bands due to ammonium ions and adsorbed water can be found. The deformation modes of the ammonium ions are observed around 1450 cm^{-1} . A second, less intense deformation mode is present around 1670 cm^{-1} . The latter band has become IR active because of a distortion of the tetrahedral symmetry of the ammonium ions. The deformation mode of adsorbed water is normally observed near 1650 cm^{-1} . In our spectra this band is only just visible indicating that most of the zeolitic water has desorbed even after evacuation at room temperature. The stretching modes of ammonium ions and residual water molecules are both observed as a broad band extending from 2000 to 3800 cm^{-1} . Heating *in vacuo* results in desorption of ammonia and water. In our spectra the features due to ammonium ions and adsorbed water then have disappeared and weak bands due to the acidic Brønsted sites can be observed near 3600 cm^{-1} .

We will concentrate on the region below 1400 cm^{-1} where the more intense zeolitic lattice modes can be observed. In Fig. 1(a) and (b) four representative spectra of the lattice modes of Y zeolites with different Si : Al ratios are presented for the region from 250 – 1400 cm^{-1} . In Fig. 1(b) the protonated forms resulting after heating *in vacuo* are shown. The spectra in Fig. 1(a) and the results presented in Table 1 are obtained after adsorbing anhydrous ammonia onto the proton forms. The spectra for the ammonium forms are similar to those obtained after evacuating the starting material at room temperature. However readsorption of ammonia results in somewhat better resolved bands. This

Table 1 Lattice vibrations of ammonium-exchanged Y zeolites with different Si : Al ratios

IR vibrations/ cm^{-1}							
2.4	2.8	4.5	6.7	7.7	16	33	40
1122	1131	1126	1190	1206	1207	1209	1208
				1170	1173	1175	1174
1018	1023	1038	1078	1078	1082	1085	1090
779	787	795	819	830	831	833	834
			781	790	789	789	794
721	728	738	738				
631	634	654	666	679	678	681	684
574	578	581	591	606	607	610	612
509	509	517	523	526	528	529	528
			476	481	481	483	482
453	455	457	457	459	460	460	462
393	394	391	393	397	399	400	401
				352	348	350	352
306	310	312	316	317	314	319	325
			287	291	285	291	289

may be due to the absence of zeolitic water after readsorption of ammonia. In Fig. 2(a) and (b) the spectra obtained after readsorption of ammonia onto the protonated forms and the spectra of the protonated forms resulting after heating are shown for the zeolites mordenite, ZK-5, L and A.

Discussion

The zeolitic lattice modes have been studied extensively with IR spectroscopy using mainly the KBr technique.^{14–18} According to these studies asymmetrical T–O stretching modes are found at 950 – 1250 cm^{-1} (intra-tetrahedral) and at

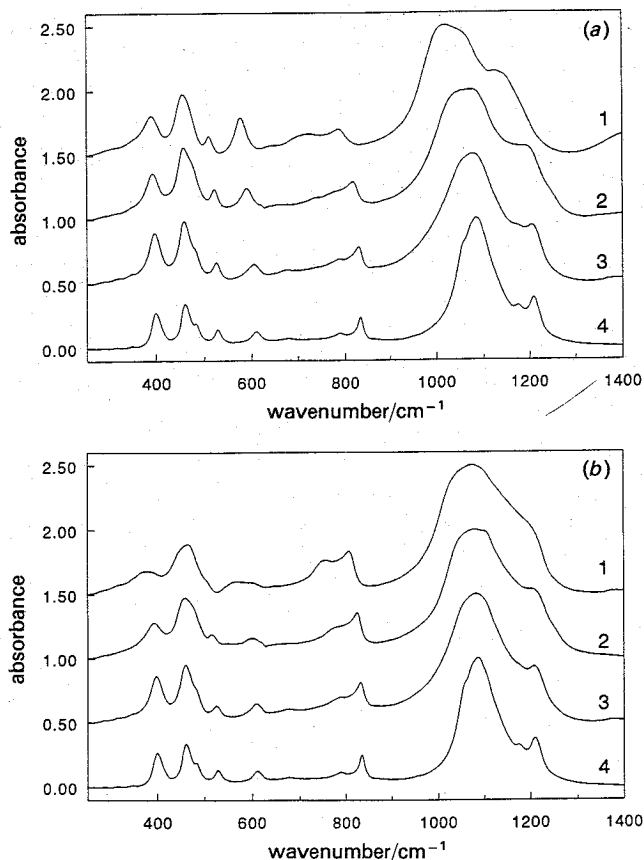


Fig. 1(a) IR spectra of ammonium Y zeolites with different Si : Al ratios: 1, 2.8; 2, 6.7; 3, 7.7 and 4, 33. Sample 1 is non-dealuminated, sample 2 is dealuminated with $(\text{NH}_4)_2\text{SiF}_6$ and sample 3 and 4 are dealuminated with SiCl_4 . **(b)** IR spectra of protonated Y zeolites obtained for the samples in (a) after heating at 1.2, 723 and 3.4, 773 K.

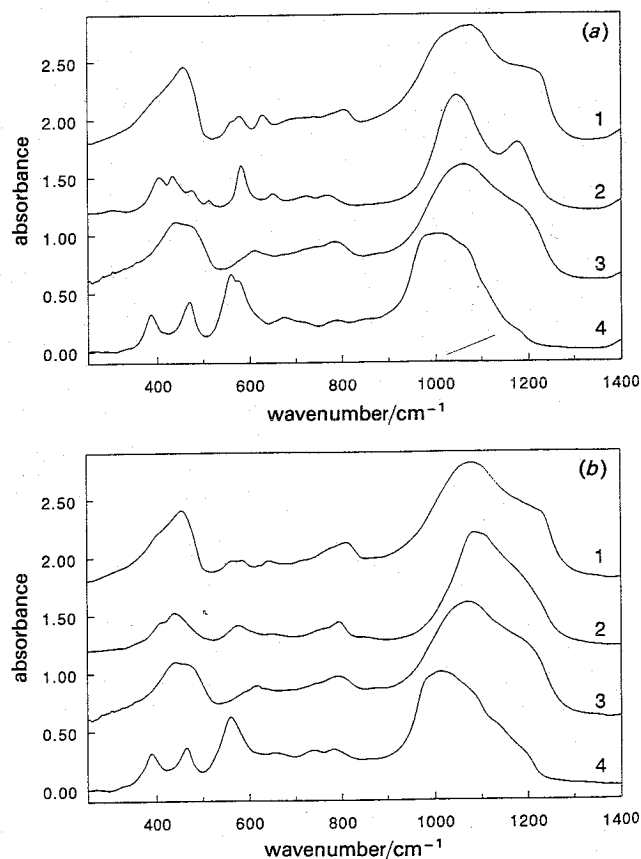


Fig. 2(a) IR spectra of ammonium zeolites: 1, mordenite; 2, ZK-5, 3, L and 4, A. **(b)** IR spectra of the protonated forms obtained for the samples in (a) after heating at: 1, 823; 2, 823; 3, 773 and 4, 573 K.

1050–1150 cm^{-1} (inter-tetrahedral), while the corresponding symmetrical T–O stretching modes are found at 650–720 cm^{-1} and at 750–820 cm^{-1} respectively.^{14,19,20} The region below ca. 650 cm^{-1} is mainly of T–O bending character.²⁰

Zeolite Y, Influence of Si : Al

Dealumination of Y zeolites results in a shift to higher wavenumbers for the T–O stretching modes due to an increase in the average T–O bond strength.^{14,21} This is in agreement with our observations (Fig. 1(a) and Table 1). From the results presented in Table 1 we can further conclude, that the modes observed below 690 cm^{-1} still possess some T–O stretching character, since these modes are also shifted to higher wavenumbers upon increasing degree of dealumination. However, the T–O stretching character becomes less important for the modes at lower wavenumbers.

Protonation of the zeolitic lattice induces changes in the IR-active lattice modes. The broad features due to the symmetric and asymmetric T–O stretching modes are shifted to higher wavenumbers. The magnitudes of these shifts are determined by the proton concentration X_H as can be seen in Fig. 3, where the proton concentration is defined as:

$$X_H \approx \frac{2N_{\text{Al}}}{N_{\text{Al}} + N_{\text{Si}}} = \frac{2}{1 + \frac{N_{\text{Si}}}{N_{\text{Al}}}}$$

Here we have used the approximation that at high levels of ammonium exchange the number of protons is almost equal to the number of aluminium atoms. The shifts are determined from the average band positions for the symmetric and asymmetric T–O stretching modes of the protonated and ammonium zeolites. These average positions are calculated by:

$$\nu_{s, a} = \frac{\int_{x_1}^{x_2} \nu A(\nu) d\nu}{\int_{x_1}^{x_2} A(\nu) d\nu}$$

with ν the frequency in wavenumbers, $A(\nu)$ the absorbance at wavenumber ν and x_1, x_2 the edges of the T–O stretching bands. From Fig. 3 it can be concluded that protonation results in a larger shift for the asymmetric mode. For this mode a linear relation between the shift $\Delta\nu_a$ and the proton

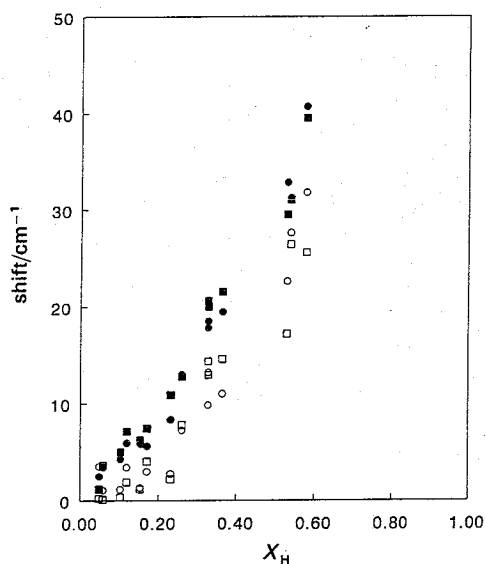


Fig. 3 Shift of the symmetric and asymmetric stretching band due to protonation of the lattice of zeolite Y. The ammonium forms are those after evacuation at room temperature (\square and \blacksquare) or after readsorption of ammonia (\circ and \bullet).

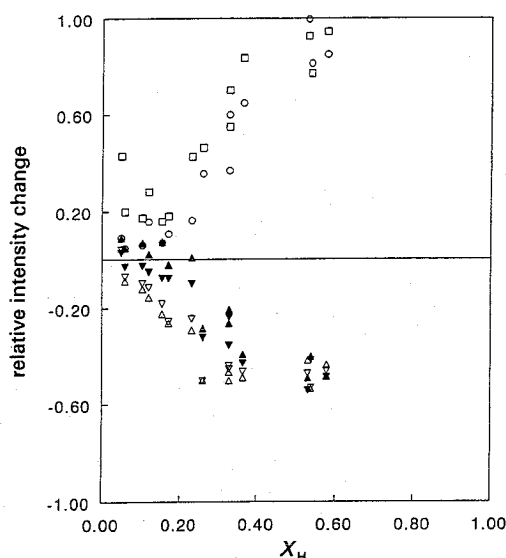


Fig. 4 Change in the relative band intensity due to protonation of the lattice of zeolite Y. The ammonium forms are those respectively after evacuation at room temperature or readsorption of ammonia: symmetric stretching band (\square, \circ), band near 574 cm^{-1} (Δ, ∇), band near 391 cm^{-1} ($\blacktriangle, \blacktriangledown$).

concentration X_H is observed:

$$\Delta\nu_a = 58X_H$$

For the symmetric mode the observed dependence of the shift on the proton concentration is not linear. Also, smaller shifts are observed for the modes located near 509 and 453 cm^{-1} . The former is shifted to lower wavenumbers, the latter is shifted to higher wavenumbers. For zeolites with high proton concentrations this results in a collapse of these two bands upon protonation.

In the preceding section we calculated a mean value for the shift of the intra-tetrahedral and inter-tetrahedral stretching modes. However from the spectra obtained, especially from those for zeolites with intermediate dealumination levels (Si : Al = 5–10), it can be seen that for the asymmetric T–O stretching modes the low-frequency part of the band (intra-tetrahedral) has a larger shift upon protonation, compared to the high-frequency part of this band (inter-tetrahedral). For the less intense symmetric T–O stretching band this difference is less pronounced.

Besides these shifts protonation induces changes in the intensities for the symmetric stretching modes and for the modes observed near 574 and 391 cm^{-1} . The total intensity for the asymmetric T–O stretching mode however is not changed after protonation. In Fig. 4 the changes in the relative intensities, defined by:

$$\Delta A = \frac{A_{\text{H}^+} - A_{\text{NH}_4^+}}{A_{\text{NH}_4^+}}$$

where A , the band areas for the protonated and ammonium zeolites, are given with respect to the proton concentration X_H . With increasing proton concentration, the gain in intensity for the symmetric stretching band upon protonation becomes larger. These changes in intensity are linearly related to the proton concentration ($\Delta A = 1.7X_H$). The decrease in intensities after protonation, observed for the modes near 574 and 391 cm^{-1} respectively, is also related to the proton concentration. For the mode near 574 cm^{-1} the observed decrease is linear in the proton concentration for values of X_H less than 0.4 ($\Delta A = -1.4X_H$).

The acidic protons are bonded to the bridging oxygen atoms, the resulting bonds give rise to IR-active stretching

vibrations near 3550 cm^{-1} [low frequency (LF)-OH] and near 3650 cm^{-1} [high frequency (HF)-OH].²²⁻²⁴ The locations of these protons have been obtained from neutron diffraction experiments.²⁵ According to these experiments the protons are mainly located near the O(1) and O(3) positions. A smaller number of protons is located near the O(2) position. The HF-OH band is assigned to protons bonded to O(1), while the LF-OH band is assigned to protons near O(2) and O(3). With inelastic neutron spectroscopy the corresponding OH bending vibrations can be observed.^{26,27} Two types of bending modes are present. The in-plane bending modes were observed near 1090 cm^{-1} and the out-of-plane bending modes near 420 cm^{-1} . Additionally in the inelastic neutron spectra the lattice modes of HY zeolites are enhanced in intensity compared with those of NaY zeolites. This is caused by coupling between the T—O lattice modes and the O—H bending modes.^{26,28} This coupling affects the IR-active lattice modes and so the observed shifts of the stretching modes may be due to the coupling between the lattice modes and the in-plane bending modes. The heterogeneous shifts for the T—O stretching bands may be due to a different coupling of the in-plane hydroxyl bending modes with the inter-tetrahedral or intra-tetrahedral modes. At lower wavenumbers a coupling between lattice modes and out-of-plane bending modes may exist. However, the changes after protonation in this spectral region are similar to those observed after dehydration of non-dealuminated Y zeolites containing divalent cations.^{1,6} These changes were attributed to structural relaxation, caused by migration of the cations into the double-six rings, where solvation of the cation by the oxygen atoms of the lattice is most favourable. Solvation of these cations was the driving force for the deformation of the lattice. Also protonation of the lattice induces relaxation of the zeolitic structure. Quantum chemical *ab initio* calculations indicated that protonation results in a lengthening of the T—O bonds at the Brønsted site, due to the formation of a covalent O—H bond.^{2,3,29,30} So we conclude that the intensity changes in the spectral region below *ca.* 650 cm^{-1} are mainly caused by structural relaxation effects. Further, we note that the lengthening of the T—O bond results in a decrease in the value of the corresponding stretching force constant. This should result in a downward shift of the stretching modes in contradiction to our observations. However, the mean value for the T—O force constant will not change very much, because it is very likely that the weakening of one T—O bond upon protonation is compensated by the strengthening of the three other T—O bonds. Recently, the vibrational density of states was calculated for four-ring clusters, containing one aluminium atom, with and without protonation of the cluster.³⁰ These calculations showed upward shifts upon protonation which are similar to those observed in our experiments.

In the preceding section we have discussed the changes in the IR spectra upon protonation of zeolite Y in relation to the Si : Al ratio. Zeolite X (Si : Al = 1.25) and zeolite Y both have the faujasite structure. Protonation of the lattice of zeolite X shifts the stretching modes to higher wavenumbers. However, the observed shifts are relatively small. For the symmetric and asymmetric stretching modes mean shifts of 20 and 33 cm^{-1} were obtained, corresponding to a proton concentration of 0.5. However, the intensity for the symmetric stretching mode apparently does not change after protonation. In the T—O bending region changes in intensities for various bands (565 , 460 and 390 cm^{-1}) are observable. The nature of these changes are similar to those for the Y zeolites. From the literature it is known that heating of ammonium-containing zeolite X samples results in considerable dehydroxylation and a loss of acidic sites.^{31,32} Therefore

the observed changes in the IR spectra upon protonation, especially the shift of the stretching modes, reflect the number of acidic sites still intact. The different behaviour for the intensity of the symmetric stretching mode may be caused by the fact that this band is not completely resolved and may contain contributions from T—O bending modes.

Zeolites A, L, ZK-5 and Mordenite

In the past the IR spectra of zeolites have been studied for various structures.¹⁴⁻¹⁸ Some spectral features have been attributed to structural sub-units, *e.g.* the double-six ring mode.¹⁵ Recently, de Man and van Santen²⁰ showed that there was no evidence for correlating spectral features with large structural sub-units. However, in this work, protonation of the lattice was not considered. Since the location of the protons is also determined by the structural sub-units present, it is interesting to study the protonation of the lattice for different zeolitic structures.

For zeolite A (Si : Al = 1) the shift of the asymmetric stretching mode and the change in the relative intensity of the symmetric stretching mode are similar to those obtained for Y zeolites with a proton concentration $X_H = 0.5-0.6$. Again the intensity for the asymmetric stretching mode is not influenced by protonation. For the symmetric stretching mode, a weak band in the region $640-840\text{ cm}^{-1}$, an abnormally large shift (78 cm^{-1}) is observed. Also the intensity changes in the banding region are different to those found for zeolite Y. After protonation the modes near 385 and 570 cm^{-1} decrease only slightly in intensity. Unlike zeolite Y the mode near 470 cm^{-1} decreases in intensity due to protonation. Readsorption of ammonia results in a spectrum similar to the one obtained for the starting ammonium form. Therefore the procedure followed has not induced severe damage to the lattice.

Protonation of the lattice of zeolite L (Si : Al = 3) results in a shift of respectively 18 and 12 cm^{-1} for the symmetric and asymmetric modes, while the intensity for the symmetric modes now decreases slightly. Similar to zeolite A the symmetric T—O stretching mode has the largest shift. Taking account of the residual potassium cations we obtain a value of 0.3 for the proton concentration, so the observed shift for the asymmetric mode has a similar magnitude as for the Y zeolites. In the T—O bending region the changes after protonation are small. In the region below 530 cm^{-1} no intensity changes are observed. A clear decrease in intensity, as was observed for two bands of zeolite Y, is not present. For zeolite ZK-5 (Si : Al = 3.4) the changes for the stretching modes upon protonation are comparable to those for zeolite Y with a proton concentration $X_H \approx 0.5$. This is in agreement with the Si : Al ratio of zeolite ZK-5. Further, we observe a heterogeneous shift for both the T—O stretching bands, similar to that observed for zeolite Y. Owing to protonation the modes near 515 and 650 cm^{-1} decrease strongly in intensity. The decrease in intensity for the mode near 580 cm^{-1} is a little smaller than found for Y zeolites. The total intensity for the range $310-530\text{ cm}^{-1}$ is not much affected by protonation of the lattice.

After protonation of the lattice of mordenite (Si : Al = 6.7) the symmetric stretching mode has shifted by 24 cm^{-1} and has gained intensity. The asymmetric stretching mode has shifted by 18 cm^{-1} without any intensity change. The shift of the asymmetric band is comparable to that measured for dealuminated Y zeolites with a similar Si : Al ratio. The shift for the symmetric band, however, is much larger. Also we observe that the shifts for the low-frequency parts of the stretching bands are again greater than for the high-frequency parts. The mode near 630 cm^{-1} and the band in the region $520-600\text{ cm}^{-1}$ decrease in intensity after proto-

nation of the lattice. The magnitudes of these changes are comparable to those for the bands near 574 and 391 cm^{-1} for zeolite Y. The region below 520 cm^{-1} is not much affected by protonation of the lattice.

When comparing the results for the different structures, we see that the shift of the asymmetric stretching mode is not influenced by the lattice structure and the intensity does not change after protonation. However, for the symmetric stretching band the changes in band position and intensity after protonation are both structure sensitive. Zeolite Y and ZK-5 show a similar shift, but the shifts for zeolite A, L and mordenite are larger. The changes in the intensity for this band are similar except for zeolite L. In the region below ca. 650 cm^{-1} the changes in the spectra after protonation are different for the zeolites studied. The zeolites Y, ZK-5 and mordenite possess some bands in this region, which are clearly influenced by protonation of the lattice. For zeolite A and especially L, however, the induced changes are much smaller. As with zeolite Y we observe increase and decrease in band intensities simultaneously. We attribute these intensity changes again to changes in the vibrational motion of the T atoms and oxygen atoms, caused by relaxation effects. The extent of structure relaxation depends on the zeolite structure, explaining the differences in intensity changes observed. Apparently, protonation of the structure of zeolite L does not result in strong relaxation effects.

In the preceding section IR spectra for zeolites with different framework structures are discussed. Zeolite X and Y both have the faujasite structure.³³ In this structure sodalite cages are connected tetrahedrally to each other *via* double-six rings. In this way the supercages are formed. Each supercage is surrounded by ten sodalite cages. Zeolite A has structure type LTA. Each sodalite cage is now connected *via* double-four rings to six other sodalite cages.³³ In this way large rhombi-cuboctahedra are formed by eight sodalite cages placed at the corners of a cube. Zeolite ZK-5 has structure type KFI. Here also three different cages can be differentiated: the large rhombi-cuboctahedra, the paulingite cages and the double-six rings.³³ In this structure the rhombi-cuboctahedra are connected with each other *via* paulingite cages or *via* double-six rings. Zeolite L possesses structure type LTL and contains only two types of cages: cancrinite cages and double-six rings are alternately linked together.³³ Six such chains are linked together forming pores comprised of twelve membered oxygen rings. These pores are connected by smaller eight membered channels. The mordenite structure (MOR) contains only one type of cage. These cages are faced by four five-membered rings and are connected in such a way that twelve-membered and eight-membered channels are formed.³³

When studying the spectral changes due to protonation it seems impossible to relate these changes to structural subunits (cages). Sodalite cages are present in both the zeolites A and Y, but the changes in the region below 650 cm^{-1} after protonation are different. Further, double-six rings are present in the structures for zeolite Y, ZK-5 and L. Both zeolite Y and ZK-5 possess IR bands which decrease upon protonation. For zeolite L such behaviour is not observed, whereas for mordenite similar decreases in intensities are observed. Therefore the presence of double-six rings is not a necessary condition for the occurrence of spectral changes upon protonation. Our conclusions are then in agreement with the results of de Man and van Santen,²⁰ who showed that a correlation between spectral features and large structural elements does not exist.

In the preceding section we concluded that the changes for the lattice modes observed after protonation were caused by two factors: relaxation of the zeolitic structure and coupling

of the lattice modes with the bending modes of the acidic hydroxyl groups. For the symmetric stretching modes the changes after protonation are structure sensitive. It is possible that different zeolitic structures give rise to a different coupling between the symmetric stretching modes and the hydroxyl bending modes resulting in a different shift. On the other hand the larger shift found for the symmetric stretching mode may partly be caused by relaxation effects, which are also responsible for the intensity changes.

Conclusion

Protonation of zeolitic lattices is successfully studied by FTIR spectroscopy using supported samples. Protonation results in an upward shift for the average frequencies of the asymmetric T—O stretching modes without changing the intensities. The magnitude of the shift is governed by the amount of acidic protons present in the zeolite structure. No influence due to structural differences is observed. However, a heterogeneous shift for the asymmetric stretching band is observed. Protonation results in a larger shift for the low-frequency part of this band. A linear relation between the shift in mean frequency for the asymmetric band and the proton concentration is obtained, which can be used to estimate the proton concentration in other zeolitic samples.

The changes in the symmetric stretching modes after protonation are structure sensitive. For zeolite Y after protonation this band is shifted heterogeneously to high frequencies and gains intensity. Again the magnitudes of these changes are governed by the proton content.

The changes in the region below 650 cm^{-1} are determined strongly by the zeolitic structure. For zeolite Y an upward and also a downward shift is observed after protonation for modes near 453 and 509 cm^{-1} . At the same time the bands near 391 and 574 cm^{-1} decrease in intensity. Also for zeolites A, ZK-5 and mordenite intensity changes are clearly observed in this spectral region. When comparing the spectral changes after protonation for the zeolites A, Y, L, ZK-5 and mordenite no relation between the observed changes and the zeolitic structures is found.

The origin of the shifts of the stretching modes may be attributed to coupling of the in-plane bending modes of the acidic hydroxyls with the T—O lattice modes. The T—O stretching bands show a heterogeneous shift due to a different coupling of the in-plane bending modes of the acidic hydroxyls with the inter-tetrahedral and intra-tetrahedral stretching modes. A contribution due to lattice relaxation upon protonation may be present, especially for the region below 650 cm^{-1} . The out-of-plane bending modes may couple with lattice modes in the T—O bending region, but this interaction seems to be very small. The downward shift of the mode at 509 cm^{-1} may be caused by such an interaction.

The intensity changes in the T—O bending region are explained by lattice relaxation effects. The magnitude of these effects are determined by the proton concentration but also by the zeolitic structure.

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