

## Fourier-transform infrared and inelastic neutron-scattering study of hy zeolites

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# Fourier transform infrared and inelastic neutron scattering study of HY zeolites

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A combination of FTi.r. and INS spectroscopy is used in a vibrational study of the bending and stretching vibrations of the acidic hydroxyl groups of Y zeolites. The influence of the number of acidic Brönsted sites and the Si/Al ratio is discussed. Out-of-plane hydroxyl bending modes are assigned to vibrations centered around  $419\text{ cm}^{-1}$  and in-plane hydroxyl bending modes are assigned to vibrations centered around  $1089\text{ cm}^{-1}$ . Upon dealumination, these bands are shifted by approximately  $30\text{ cm}^{-1}$  to lower values. The less intense bands at  $319, 470, 565, 765,$  and  $1130\text{ cm}^{-1}$  are assigned to proton-coupled framework vibrations. Upon dealumination, the mode at  $319\text{ cm}^{-1}$  is shifted to lower frequencies and the modes at  $565$  and  $1130\text{ cm}^{-1}$  are shifted to higher frequencies.

**Keywords:** FTi.r., INS, zeolite HY, Brönsted acidity; hydroxyl groups; dealumination

## INTRODUCTION

In catalysis zeolites play an important role. One of the reasons is the possibility to create acidic protons inside these materials. In the past, the acidic character of the zeolites has been extensively studied<sup>1,2</sup> using a variety of different techniques including infrared<sup>3,10</sup> and nuclear magnetic resonance<sup>11-15</sup> spectroscopy, and temperature-programmed desorption methods.<sup>16-19</sup> Infrared spectroscopy has been used to characterize the stretching frequencies of the zeolitic hydroxyl groups both for the acidic Brönsted sites as for the nonacidic terminal Si-OH groups. Near-infrared (n.i.r.) spectroscopy has been used to study overtones and combinations of stretching and bending vibrations for the hydroxyl groups.<sup>20,21</sup> A direct observation of the bending vibrations for these hydroxyls is not possible with infrared spectroscopy. A reason for this is that the spectral region where these bending vibrations are situated is dominated by intense vibrations due to the zeolitic framework.<sup>22-24</sup>

Inelastic neutron scattering can be used in a vibrational study of zeolites.<sup>25-28</sup> Because of the large incoherent cross section of hydrogen atoms, this technique is especially sensitive for zeolitic vibrations in which hydrogen atoms participate. This offers the possibility to study directly the bending vibrations of the hydroxyl groups in zeolites.

In this paper, we present a study of the bending

and stretching vibrations of hydroxyl groups in HY zeolites using a combination of Fourier transform infrared (FTi.r.) and inelastic neutron scattering (INS) spectroscopy. We discuss the influence of the amount of acidic groups and the influence of dealumination on the vibrational spectra. Also, a distinction between vibrations of hydroxyl groups and proton-coupled framework vibrations will be made.

## EXPERIMENTAL

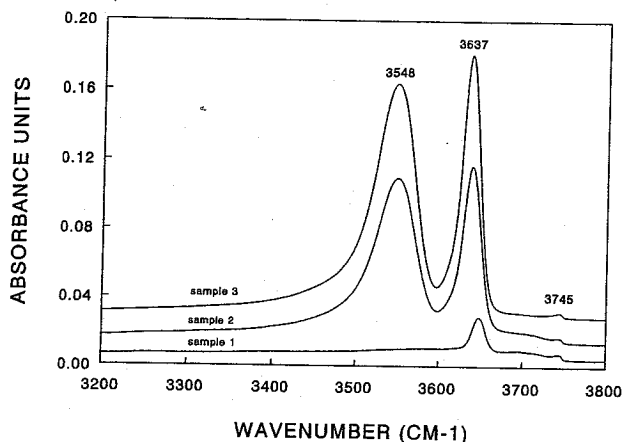
Starting material was Na<sub>56</sub>Y (Union Carbide) and Na<sub>51</sub>Y (Akzo). Sample 1 with a low degree of exchange was obtained after exchange with NH<sub>4</sub>NO<sub>3</sub> at room temperature. Samples 2 and 3, both with a high degree of exchange, were obtained after repeated exchange with an excess of NH<sub>4</sub>NO<sub>3</sub> at 350 K. Sample 4 was obtained after dealumination of Na<sub>51</sub>Y with SiCl<sub>4</sub> for 3 h at 523 K.<sup>29-32</sup> Succeedingly, the sample was repeatedly exchanged with an excess of NH<sub>4</sub>NO<sub>3</sub> at 350 K.

The crystallinity of the samples was checked by XRD prior to the i.r. and INS experiments. From chemical analysis, the compositions of the samples as listed in Table 1 were obtained. Here, also, the Si/Al ratios are listed, which were obtained from <sup>29</sup>Si MAS n.m.r. measurements using a Bruker CXP 300 spectrometer.

Infrared spectra were recorded on a Bruker IFS 113v FTi.r. spectrometer equipped with a heatable vacuum cell. All measurements were performed in the transmission mode. The spectra were recorded by coadding at least 125 scans at a resolution of  $1\text{ cm}^{-1}$  using a standard d.t.g.s. detector. Self-supported

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**Figure 1** Room temperature infrared absorbance spectra in the O-H stretching region for the nondealuminated samples

discs of 2–6 mg/cm<sup>2</sup> were used for the measurements. The samples were pretreated in the cell for 1 h at 723 K *in vacuo* before the room temperature spectra were recorded.

The INS measurements were performed on the spectrometer TFXA (ISIS, Chilton, UK),<sup>33</sup> and for the dealuminated sample, on the spectrometer INFB (ILL, Grenoble, France).<sup>34</sup> Typically, an amount of 10 g of zeolite was dehydrated and deammoniated by increasing the temperature at a rate of 0.2 K/min up to 623 K under flowing dry oxygen. After reaching this temperature, the flow of oxygen was maintained for 2 h, followed by evacuation at the same temperature for 12 h. For the dealuminated sample, a heating rate of 5 K/min and a temperature of 723 K was used. After cooling to room temperature, the evacuated ampullae containing the samples were sealed off. The thus-obtained ampullae were opened inside a glove box containing dry argon just before the measurements. The zeolites were transferred to an aluminum container for the measurements. One of the samples (no. 3, Table 1) was transferred to aluminum sachets to reduce the scattering from the aluminum.

## RESULTS AND DISCUSSION

### Nondealuminated Y zeolites with different levels of exchange

In Figure 1, the results for the infrared measurements in the hydroxyl stretching region are presented for samples 1, 2, and 3. For the highly exchanged samples 2 and 3, both the high-frequency (HF) and low-frequency (LF) hydroxyl vibrations can be observed at 3637 and 3548 cm<sup>-1</sup>. These vibrations are assigned to the Brønsted sites.<sup>3–5</sup> The protons are, respectively, located at the O<sub>1</sub> oxygen atoms pointing into the supercage and at the O<sub>2</sub> or O<sub>3</sub> oxygen atoms pointing into the sodalite cage.<sup>5,8,35</sup> Also, a small feature at 3745 cm<sup>-1</sup> is present that is due to terminal hydroxyl groups.

For sample 1, the LF hydroxyl groups are almost completely absent because of the low level of ex-

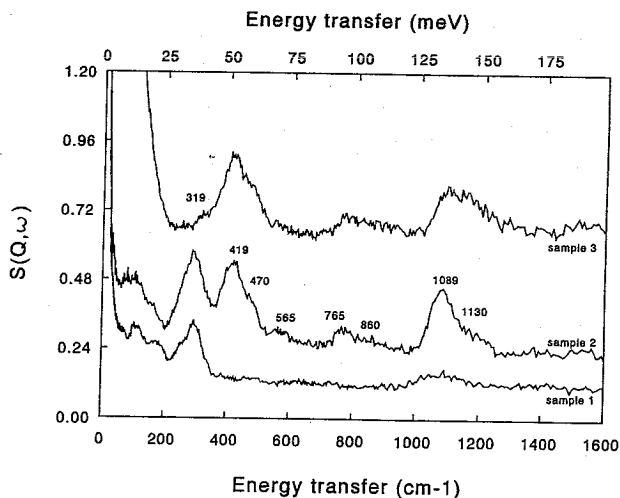
change. The HF hydroxyls are observed at 3640 cm<sup>-1</sup>.

The results for the INS measurements are presented in Figure 2 for samples 1, 2, and 3. Comparing the spectra for samples 1 and 2 with the spectrum for sample 3, it can be seen that below 350 cm<sup>-1</sup> considerable scattering due to the aluminum container is observed. This scattering is almost negligible for the experiment performed with sachets.

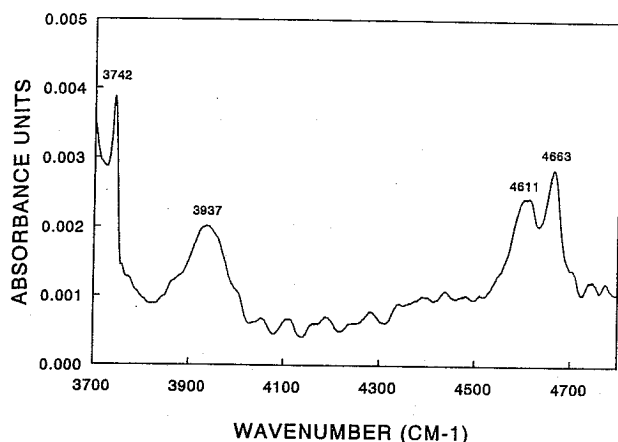
For the highly exchanged samples, the INS spectra are characterized by strong vibrations at 419 and 1089 cm<sup>-1</sup> including shoulders at 319, 470 and 1130 cm<sup>-1</sup>. Weaker features can be found at 765 cm<sup>-1</sup>, with a shoulder extending to the higher energy side, and at 565 cm<sup>-1</sup>. For the low-exchanged zeolite (sample 1), only the feature at 1089 cm<sup>-1</sup>, with a much reduced intensity, could be observed.

The vibrations at 419 and 1089 cm<sup>-1</sup> have been assigned by Jobic<sup>28</sup> to the out-of-plane ( $\nu_{OH}$ ) and in-plane ( $\delta_{OH}$ ) bending modes of the acidic hydroxyl groups. The observed influence on degree of exchange on these modes strongly supports this view.

The frequencies for these bending modes can also be deduced from the position of the infrared bands due to the combinations of the stretching ( $\nu_{OH}$ ) with the bending ( $\nu_{OH}$ ,  $\delta_{OH}$ ) vibrations. In Figure 3, the infrared spectrum of sample 3 for the combination region is presented. The combinations of stretching and out-of-plane vibrations ( $\nu_{OH} + \nu_{OH}$ ) are centered at 3937 cm<sup>-1</sup>, and the combinations of stretching and in-plane vibrations ( $\nu_{OH} + \delta_{OH}$ ) are centered at 4611 and 4663 cm<sup>-1</sup> for, respectively, the LF and HF hydroxyl groups. The assignment for the combinations with the in-plane bending modes is based on CO adsorption experiments performed at 90 K after evacuating the sample at 723 K. Because of the interaction with CO, only the bands at 3637 and 4663 cm<sup>-1</sup> are shifted to lower wavenumbers. These results are in agreement with the results obtained by Kustov et al.<sup>21</sup> using diffuse reflectance near-infrared spectroscopy. Neglecting anharmonicity and using



**Figure 2** Inelastic neutron scattering spectra for the nondealuminated samples at 20 K



**Figure 3** Room temperature infrared absorbance spectrum in the O-H combination region for the nondealuminated sample 3

our INS and infrared results, the bending vibrations are calculated at  $344\text{ cm}^{-1}$  for the out-of-plane modes and at  $1063\text{ cm}^{-1}$  (LF hydroxyl) and  $1026\text{ cm}^{-1}$  (HF hydroxyl) for the in-plane modes. The thus-calculated frequencies are up to  $75\text{ cm}^{-1}$  lower than measured in the INS experiments. This difference is partly caused by anharmonicity effects, the estimated experimental error being approximately  $10\text{ cm}^{-1}$  for the INS experiment. Because of anharmonicity, the observed combination bands are located at a frequency lower than the sum of frequencies for the hydroxyl stretching and bending modes. Using infrared results for terminal Si-OH groups, Kustov et al.<sup>21</sup> deduced an anharmonic contribution of  $5\text{ cm}^{-1}$  or less. Cluster calculations performed by Sauer and co-workers<sup>36</sup> gave a similar value.

For the out-of-plane modes, only one component could be resolved. For the in-plane modes, two components could be assigned corresponding to the HF and LF hydroxyls. Interestingly, the HF hydroxyls now have the lower bending frequency.

The assignment for the in-plane and out-of-plane bending vibrations of the hydroxyl groups given here are in good agreement with the values derived by nonempirical quantum chemical cluster calculations performed by Sauer.<sup>37</sup> In these cluster calculations, the in-plane bending mode is predicted at  $1110\text{ cm}^{-1}$  and the out-of-plane bending mode is predicted at  $420\text{ cm}^{-1}$ .

The bands at  $765$  and  $1130\text{ cm}^{-1}$  are located in the region where the symmetric and asymmetric stretching T-O modes can be found. The feature at  $470\text{ cm}^{-1}$  is mainly of O-T-O bending character and can be observed for any zeolite, together with the pore opening mode at  $319\text{ cm}^{-1}$ .<sup>38</sup> The band at  $565\text{ cm}^{-1}$  is also due to framework vibrations. It is located in the region where according to Flanigen et al.<sup>22,23</sup> vibrations due to the double six-ring are to be found. We attribute these weaker features to proton-coupled framework vibrations.<sup>26-28</sup> The assignments given here differ from the assignments made by Wax et al.<sup>26,27</sup> They assigned the features at  $1089$  and  $1130\text{ cm}^{-1}$  to the out-of-plane and in-plane hydroxyl bend-

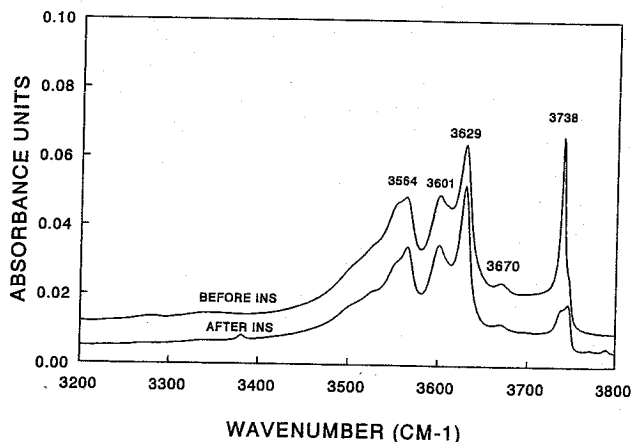
ing vibrations, and a feature at  $360\text{ cm}^{-1}$ , to a proton-coupled framework vibration. Their assignments are based on force-field calculations, but they are not in agreement with results obtained from infrared measurements. Further, the intensity of the peak at  $360\text{ cm}^{-1}$  is too large to correspond to a proton-coupled lattice mode.

The shoulder of the band at  $765\text{ cm}^{-1}$ , centered at approximately  $860\text{ cm}^{-1}$ , can be assigned to the hydroxyl bending vibrations of the terminal Si-OH groups.<sup>21</sup> The appearance of this band indicates that during the heat treatment of the sample a small number of defects is formed.

### Dealuminated HY zeolite

In Figure 4 infrared spectra for the hydroxyl stretching region of sample 4 are presented. The two spectra shown are both obtained after evacuating the sample for 1 h at  $723\text{ K}$  in the infrared cell. The upper spectrum is recorded starting with the fresh  $\text{NH}_4\text{ Y}$  zeolite obtained after ion exchange (sample 4a). The lower spectrum is measured using the HY zeolite resulting after the INS experiment (sample 4b). Both spectra contain the HF and LF hydroxyl groups located, respectively, at  $3629$  and  $3564\text{ cm}^{-1}$  but with a reduced intensity compared to the nondealuminated samples.

Because of the dealumination procedure, the number of terminal hydroxyl groups has increased, as can be seen from the intensity of the peak at  $3738\text{ cm}^{-1}$ . Because of the heating procedure used for the INS experiment, the number of terminal hydroxyl groups has decreased. This observation is in agreement with the calculated Si/Al ratios obtained from  $^{29}\text{Si}$  MAS n.m.r. experiments as presented in Table 1. These ratios are calculated according to the procedure used by Thomas and Klinowski.<sup>11</sup> Here a problem arises when there is a substantial amount of terminal hydroxyl groups present. The chemical shift of  $^{29}\text{Si}$  in such a group is almost equal to the shift of  $^{29}\text{Si}$  with only one aluminum as a next-neighbor. The thus-calculated Si/Al ratio is too low compared to the true Si/Al ratio due to the framework T-atoms. Compared



**Figure 4** Room temperature infrared absorbance spectra in the O-H stretching region for the dealuminated sample 4

**Table 1.** Zeolite properties.

Sample	Si/Al (n.m.r.)	Composition from chemical analysis
1	2.46	Si/Al = 2.1 Na/Al = 0.77
2	2.46	Si/Al = 2.1 Na/Al = 0.002
3	2.76	Si/Al = 2.3 Na/Al = 0.002
4a	15.8 <sup>a</sup>	
4b	29.0 <sup>b</sup>	

<sup>a</sup> Before INS measurement<sup>b</sup> After INS measurement

to the nondealuminated samples, two new vibrations are observed at 3601 and 3670  $\text{cm}^{-1}$ . These vibrations have been attributed to hydroxyl groups on nonframework aluminum species and hydroxyl groups on defect sites.<sup>39-41</sup>

The out-of-plane and in-plane hydroxyl bending modes are characterized in the INS spectrum (Figure 5) by a strong vibration at 395  $\text{cm}^{-1}$ , with shoulders at 298 and at 468  $\text{cm}^{-1}$  and a strong vibration at 1052  $\text{cm}^{-1}$ , including a shoulder at 1169  $\text{cm}^{-1}$ . Analogous to the assignment used for the nondealuminated samples, the strong features at 395 and 1052  $\text{cm}^{-1}$  can be assigned to the out-of-plane and in-plane hydroxyl vibrations, respectively. The values for the hydroxyl bending modes are shifted by approximately 30  $\text{cm}^{-1}$  to lower values compared with the nondealuminated samples.

The peak at 766  $\text{cm}^{-1}$  and the shoulders at 298, 468 and 1169  $\text{cm}^{-1}$  are due to proton-coupled lattice modes. The positions for the symmetrical stretching mode at 766  $\text{cm}^{-1}$  and the O-T-O bending mode at 468  $\text{cm}^{-1}$  are not affected by dealumination. Because of dealumination, the pore-opening mode around 300  $\text{cm}^{-1}$  is shifted to lower frequencies and the asymmetrical stretching mode around 1130  $\text{cm}^{-1}$  is shifted to higher frequencies. Additionally, a broad band is found at 627  $\text{cm}^{-1}$ , which can be attributed to a proton-coupled framework vibration. For the nondealuminated samples, the corresponding bands could be observed at 565  $\text{cm}^{-1}$ .

The small shoulder located at 833  $\text{cm}^{-1}$  can be attributed to the Si-OH bending mode of the terminal hydroxyl groups, which is in good agreement with a value of 830  $\text{cm}^{-1}$  as calculated by Sauer.<sup>37</sup>

## CONCLUSION

Using a combination of FTi.r. and INS spectroscopy and results from quantum chemical cluster calculations, two types of zeolitic vibrations could be assigned for the HY zeolites studied.

The bending vibrations for the acidic sites in the nondealuminated HY zeolites are observed around 419  $\text{cm}^{-1}$  for the out-of-plane modes and around 1089  $\text{cm}^{-1}$  for the in-plane modes. The in-plane modes could be resolved into modes belonging to the LF hydroxyl groups and modes belonging to the HF hydroxyl groups. The in-plane bending mode frequency for the HF hydroxyl groups is found to be approximately 35  $\text{cm}^{-1}$  lower than that for the LF

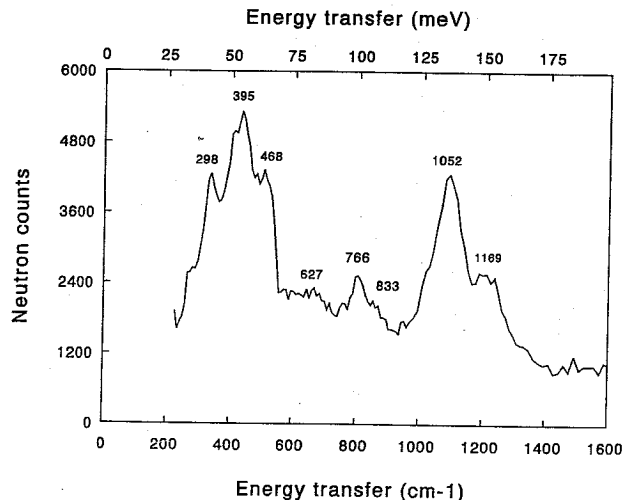
hydroxyl groups when neglecting anharmonicity effects. From theoretical calculations, the effects of anharmonicity are known to be small for the hydroxyl bending vibrations. No influence of the level of exchange on the positions of the hydroxyl bending modes could be found for the samples studied. Upon dealumination, both the out-of-plane and the in-plane hydroxyl bending modes are shifted to lower frequencies by approximately 30  $\text{cm}^{-1}$ . Also, the shoulders of the observed bands become more pronounced upon dealumination.

The second type of vibrations is assigned to proton-coupled framework vibrations. The feature at 765  $\text{cm}^{-1}$  is assigned to the symmetric T-O stretching modes and the feature at 1130  $\text{cm}^{-1}$  is assigned to the asymmetric T-O stretching modes of the zeolitic framework. The band found at 565  $\text{cm}^{-1}$  is ascribed to vibrations of the double six-ring. The shoulders observed at 319 and 470  $\text{cm}^{-1}$  are attributed to, respectively, pore-opening modes and O-T-O bending modes. These lattice modes are not influenced upon dealumination except for the pore-opening mode at 319  $\text{cm}^{-1}$ , which is shifted to lower frequencies (298  $\text{cm}^{-1}$ ). The band at 565  $\text{cm}^{-1}$  and the shoulder at 1130  $\text{cm}^{-1}$  are shifted to higher frequencies (627 and 1169  $\text{cm}^{-1}$ , respectively).

In this paper, the assignment of the different vibrational modes is divided into two classes: hydroxyl vibrations and proton-coupled lattice vibrations. The bands observed in the INS spectra are generally a superposition of modes belonging to both of these classes. It should be noted that these two classes can be discriminated by deuterium-exchange experiments. This kind of experiment will be subject to investigation in order to give further justification for our assignments.

## ACKNOWLEDGEMENTS

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**Figure 5** Inelastic neutron scattering spectrum for the dealuminated sample 4 at 20 K

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