Interaction of water with hydroxyl-groups in h-mordenite - a neutron inelastic-scattering study
Jobic, H.; Czjzek, M.; van Santen, R.A.

Published in:
Journal of Physical Chemistry

DOI:
10.1021/j100183a010

Published: 01/01/1992

Citation for published version (APA):
A neutron inelastic scattering study of water adsorbed in H-mordenite has been recently reported and the spectra show vibrational modes belonging to hydroxonium ions besides the unperturbed OH bands.

One notices that at low water content, the deuterium at O(3) is the first to be perturbed, even though O(1) is considered to be the more acidic one. This can be explained by stabilizing


electric forces in the sodalite cages, where the hydroxonium ion formed can be hydrogen bonded to close framework oxygens or to neighboring water molecules on symmetry equivalent positions in the same sodalite cage. Furthermore, the sites I', II, and II in the sodalite cage have been reported to be the first sites occupied by water, at low water content of the zeolites. The water molecules in a sodalite cage without formation of hydroxonium ions can form small clusters, hydrogen bonded with each other and/or with the framework oxygens.

Acknowledgment. We thank G. Clugnet for helpful advice during the sample preparations. We would also like to thank Prof. H. Fuss from the T.H. Darmstadt for support and encouragement during the course of this work.

Interaction of Water with Hydroxyl Groups in H-Mordenite: A Neutron Inelastic Scattering Study

Hervé Jobic,* Mirjam Czjzek,

Institut de Recherches sur la Catalyse—CNRS Villeurbanne, 2 avenue Albert Einstein, F-69626 Villeurbanne Cedex, France

and Rutger A. van Santen

Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands (Received: October 7, 1991; In Final Form: December 6, 1991)

Neutron inelastic scattering has been used to study the adsorption of water, at low loading, in zeolite H-mordenite. The results are compared to the neutron spectra of the bare zeolite and of ice. For the bare zeolite, the in-plane and out-of-plane bending modes of the bridged hydroxyl groups are measured at 1060 and 320 cm⁻¹, respectively. After water adsorption, the observed vibrational features are assigned to different species: hydroxonium ions, H₂O hydrogen bonded, and free hydroxyl groups.

Introduction

The adsorption of water in cation-containing zeolites has been followed by several spectroscopic methods; however, the influence of water on hydroxyl groups has been less studied.

The formation of hydroxonium ions, H₃O⁺, resulting from the adsorption of small amounts of water on strong Bronsted sites in zeolites has been previously envisaged (e.g., ref 2), but it is only recently that its existence has been proved by experimental and theoretical methods.

Infrared spectra of water adsorbed at various equilibrium pressures on HZSM-5 showed the appearance of bands assigned to H₃O⁺ (at 2885 and 2463 cm⁻¹), while the band at 3610 cm⁻¹ corresponding to the stretching mode of the bridged hydroxyls decreased in intensity. Line-shape simulations of H NMR signals of water adsorbed at various concentrations in HY and HZSM-5 allowed the determination of different species: H₂O⁺, H₂O bonded to bridging OH groups, water, and free hydroxyl groups.

The presence of H₂O⁺ in HY zeolite has also been observed by high-resolution powder neutron diffraction, but the geometry of the hydroxonium ion could not be determined precisely. Therefore, the experimental results on the formation of H₂O⁺ in H-zeolites are still scarce. More information could be obtained by another spectroscopic technique: neutron inelastic scattering (NIS). The vibrational modes involving hydrogen motions can be determined precisely.

* Author for correspondence.

be observed by NIS because of the large incoherent cross section and the low mass of the proton.\(^9\) There are several features which make NIS complementary to the infrared and Raman techniques, e.g., the lack of optical selection rules, and the possibility to compute both the frequencies and the intensities of the normal modes.\(^{10}\) Further, with a neutron reactor equipped with a hot source (the ILL, France) or on a pulsed neutron source (e.g., ISIS, UK), the whole spectral range 1–4000 cm\(^{-1}\) can now be measured. With these sources, spectra are obtained in neutron energy loss, which has the advantage of decreasing the effect of multiphonon features.\(^{11}\)

For cation-containing zeolites (without protons), the NIS spectrum corresponds to the vibrational density of states, weighted by the scattering cross sections and by the atomic displacements. When the zeolite contains hydroxyl groups, the framework vibrations still appear in the NIS spectrum (because the H atoms follow the lattice modes) and on top of these modes one can observe the in-plane and out-of-plane bending modes of the hydroxyl groups.\(^{12,13}\)

Since the existence of hydronium mordenite has been previously reported,\(^2\) we have chosen to study by NIS the adsorption of water in this zeolite. The crystal structure of Na-mordenite has been determined\(^{14}\) and the large pores consist of 12-membered oxygen rings which form straight elliptical cylinders (7.0 \(\times\) 5.8 Å), and along the walls of the main channels side pockets with entrances consisting of 8-membered rings occur at periodic intervals. No convincing evidence for preferential attachment of protons to any particular framework oxygen was found for decationized mordenite.\(^{15}\) Even in HY, the number and localization of the different hydroxyl groups are difficult to determine precisely.\(^7\)

We report in this paper the NIS spectra of H-mordenite and of H\(_2\)O adsorbed on this zeolite. The results are compared to the NIS spectrum of ice and vibrational features assigned to hydroxonium ions are discussed.

Experimental Section

A sample of commercial hydrogen mordenite (H-M) was obtained from Norton Co., the composition being Al (6.5%) and Na (0.4%) (by weight). The octahedrally coordinated aluminum in the starting material was found, by \(^{27}\)Al MAS NMR, to be small (≈15%). The dehydration procedure was chosen in order to avoid any further dealumination. The zeolite (initial mass 10 g) was contained in a large glass reactor (diameter 70 mm) to the estimated absolute accuracy is \(\pm 20\) cm\(^{-1}\).

After 3 weeks and then desorbed by heating the zeolite up to 330 K until a vacuum of \(2 \times 10^{-2}\) Pa was obtained. Two different neutron spectra of this sample were recorded. The first was obtained on the INFB spectrometer, at the ILL, the energy range 180–2250 cm\(^{-1}\) being covered with a Cu(220) monochromator. Another NIS spectrum was obtained with the time focused crystal analyzer TFXA, on the ISIS pulsed neutron source, at the Rutherford Appleton Laboratory, UK.\(^{16}\) On TFXA, the energy resolution is better than on INFB, but the signal-to-noise ratio is worse above 700 cm\(^{-1}\). The main advantage of TFXA is to go down to very low frequencies, 15 cm\(^{-1}\), which is useful to collect the translational modes of adsorbed water. The spectrum of an empty container was subtracted for each sample.

The NIS spectra were recorded at very low temperatures, 5–15 K, to sharpen the fundamentals by decreasing the effect of the Debye–Waller factor.\(^{17}\) This is crucial to observe the different species resulting from H\(_2\)O adsorption, but the spectra of bare zeolites can be measured at room temperature because the mean-square amplitude of the H atoms of the hydroxyl groups is lower.

In order to obtain the NIS spectrum of ice, a thin sample of water (0.2 mm) was quenched to 5 K. The sample was contained in a rectangular aluminum cell and the NIS spectrum was recorded on INFB.

Results and Discussion

The NIS spectrum of H-M, obtained at 10 K on INFB, is shown in Figure 1a. The largest bands correspond to the bending modes of the bridged hydroxyl groups, because they involve large displacements for the hydrogen atoms. The peak at 1060 cm\(^{-1}\) is assigned to in-plane (\(\delta\)) bending modes and the peak at 320 cm\(^{-1}\) to out-of-plane (\(\gamma\)) deformations of the bridged OH groups. A value of 1030 cm\(^{-1}\) for the \(\delta\)(OH) vibrations has been measured by diffuse reflectance infrared spectroscopy in Na\(_2\)-M.\(^{17}\)

When water is adsorbed on H-M, the spectra shown in Figures 1b and 3 are obtained. Since the NIS intensities are proportional to the number of hydrogen atoms, it is found from Figure 1b that there is about one H\(_2\)O molecule per OH group. If a comparison is made with the NIS spectrum of ice, shown in Figure 2, it appears that the H\(_2\)O molecules in H-M do not simply form H\(_2\)O clusters, as observed at higher loadings in several zeolites.\(^{20,21}\) In particular, the HOH bending mode \(\delta_2\), measured at 1620 cm\(^{-1}\) in ice, is not observed in Figure 1b. The librating modes of H\(_2\)O, which are measured at 590 and 805 cm\(^{-1}\) in ice are also much changed in the zeolite since maxima are found at 460 and 910 cm\(^{-1}\) in Figure 1b. An intense peak is also observed at 450 cm\(^{-1}\) in Figure 3.
On the basis of the infrared and Raman literature on the vibrational modes of hydroxonium ions, the bands at 1385 and 1670 cm\(^{-1}\) can be tentatively assigned to the symmetric and antisymmetric bending modes of this species. The bands at 460 and 910 cm\(^{-1}\) would then correspond to librational modes.

The shoulders at 600 and 800 cm\(^{-1}\) can be assigned to H\(_2\)O molecules hydrogen bonded to OH groups or bound to extra framework Al or residual cations. Two weaker bands are measured at 340 and 1060 cm\(^{-1}\) in Figure 1b (one of these bands is also observed at 350 cm\(^{-1}\) in Figure 3); they correspond to unperturbed OH bridging groups; the proportion of these OH groups, estimated from the NIS intensities, is ca. 30%.

The low-frequency region, which is shown in Figure 3, is also quite different from the one reported for ice. The bands observed in that energy range correspond to translational motions. The peak at 60 cm\(^{-1}\) is assigned to a translational mode of hydrogen-bonded H\(_2\)O (monodentate), and the peak at 100 cm\(^{-1}\) to a translational mode of H\(_3\)O\(^+\) bidentate coordinated to the zeolite lattice.

Acknowledgment. We thank Dr. H. J. Lauter for his help in performing the neutron experiment on INFB, at the Institut Laue-Langevin, Grenoble, France. We also thank Dr. J. Tomkinson for his assistance during the neutron measurements on TFXA, at ISIS, Rutherford Appleton Laboratory, UK.
