Infrared Spectroscopic Evidence for the Presence of $H^+(H_2O)_n$ Ions in a Decationated Y-Type Zeolite

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Infrared spectra of adsorbed H_2O and D_2O on an activated HNaY zeolite provide the first experimental evidence for the presence of hydronium ions in Y-type zeolites.

The exceptional ability of protonated and other cationic forms of Y zeolites to catalyse a variety of carbonium ion reactions is usually related to their surface acidity, particularly to hydroxy groups with very acidic hydrogen, whose presence has been well established by infrared spectroscopy.[1] In contrast, evidence for the presence of hydronium ions in such zeolites has not been found,[2–4] although they were expected to be present and to be detectable by i.r. spectroscopy.[5] Carter *et al.*[3] emphasized that if any H_3O^+ ions remain after evacuation at 150 °C, they must be present at low concentrations. In addition, it has been recently proposed[6] that zeolites, in general, may be considered as solids which behave like protonic polyacids in solution. Considering this analogy, one may expect to detect the presence of hydrated protons in Y zeolites when the experimental conditions are favourable. In confirmation, we now report i.r. spectra showing the presence of the hydrated proton $H^+(H_2O)_n$ on an activated decationated Y zeolite (HNaY) treated with small amounts of water. These results show the high mobility of the protons in zeolites and the presence of some highly acidic sites which exist as $H^+(H_2O)_n$ entities, as in the case of acid solutions,[7] zeolites Rho,[8] mordenite and zeolite L,[9] and other solids.[10,11]

A purified sample of NaY, obtained by repeated exchange of an NaY zeolite (SK-40, Union Carbide) with aqueous sodium acetate, and an 81% NH_4^+-exchanged NaY zeolite, in the form of thin wafers (5 mg cm^{-2}) were degassed (10^{-5} Torr) in a conventional i.r. cell (400 °C, 18 h), and then either H_2O or D_2O (4 mmol g^{-1} zeolite) was introduced into the cell at room temperature. I.r. spectra were recorded on a Perkin-Elmer 5808 spectrophotometer equipped with a Data Station.

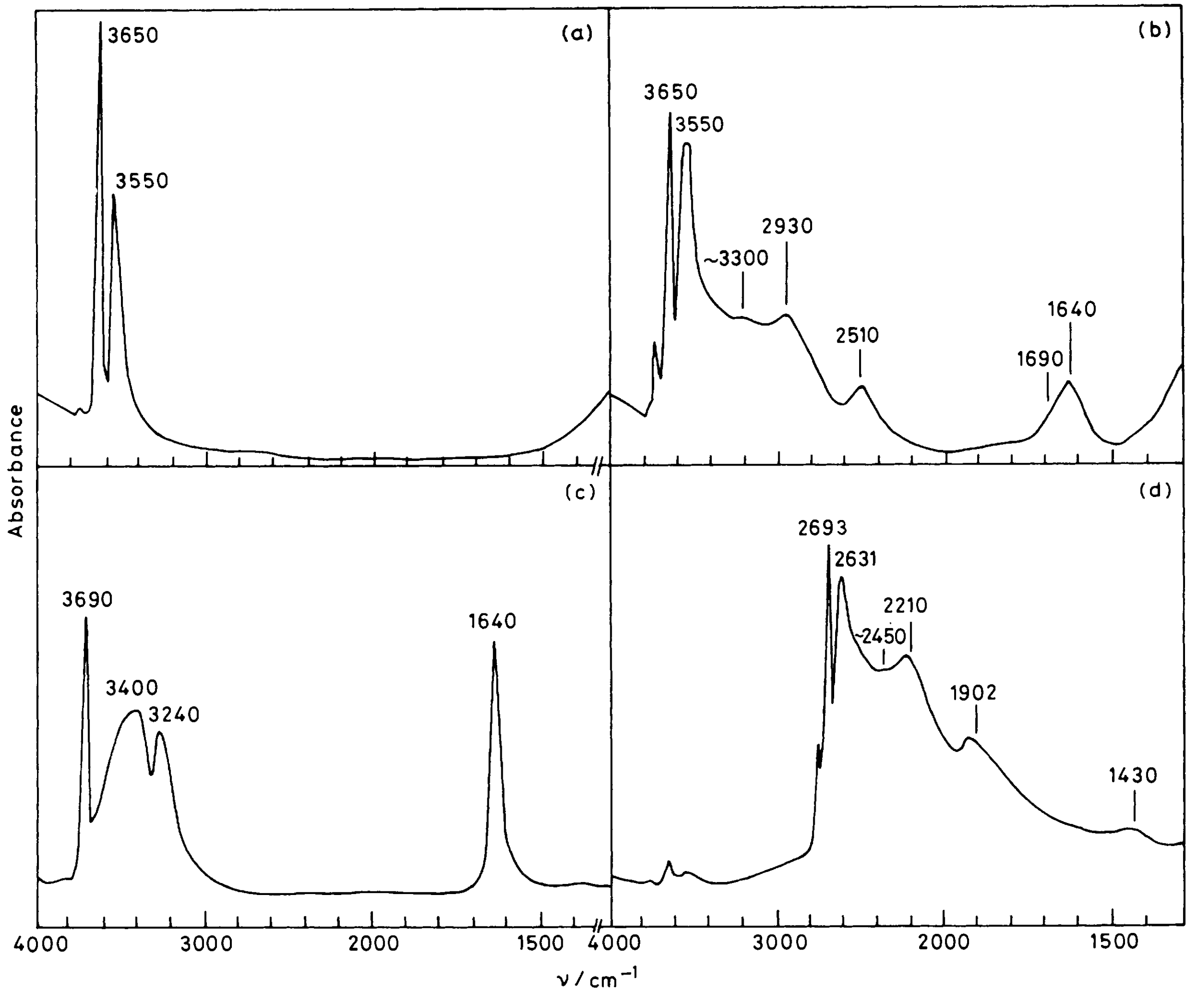

Figure 1. I.r. spectra of NaY and a HNaY (81% exchanged) zeolite after different treatments. (a) HNaY (81% NH_4^+ exchanged) degassed at 400 °C, 10^{-5} Torr, 18 h. (b) (a) + 4 mmol H_2O g^{-1} zeolite. (c) NaY degassed at 400 °C, 10^{-5} Torr, 18 h + 4 mmol H_2O g^{-1}. (d) (a) + 4 mmol D_2O g^{-1}.

The spectrum of the preactivated HNaY zeolite shows no bands due to NH_4^+ (near 3200 and 1400 cm^{-1}) [Figure (1a)], while acidic hydroxy groups (bands at 3650 and 3550 cm^{-1}) are clearly present. Upon addition of water, besides the bands characteristic of adsorbed water (3300 and 1640 cm^{-1}) and acidic hydroxy groups in zeolites,[1,4] two broad bands at 2930 and 2510 cm^{-1}, and a shoulder near 1690 cm^{-1} could be observed, spectrum (b). It is interesting that the three bands did not appear in the non-acidic NaY sample treated with H_2O (4 mmol), spectrum (c). The broad bands at 2930 and 2510 cm^{-1} of the rehydrated HNaY zeolite are in similar positions to those reported by Colomban *et al.*[10] for an asymmetric dioxonium ion, $H_3O^+{\cdot}H_2O$, detected on a treated β-alumina. Accordingly, we assigned the 2930 cm^{-1} band to the terminal OH groups of the H_3O^+ ion, and the 2510 cm^{-1} band to the hydrogen bond bridging the oxonium ion with the oxygen atom of a water molecule (Figure 2). This assignment seems to be reasonable considering the differences in the structure of β-alumina and Y zeolite.

The shoulder near 1690 cm^{-1} [Figure 1(b)] may be due to the antisymmetric bending vibration ν_4 of the H_3O^+ ion[12] which appears in minerals at higher frequency generally than that corresponding to the ν_2 of water. A small band at 1685 cm^{-1} observed in an evacuated NH_4-Rho zeolite was similarly assigned.[8]

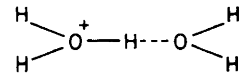

Figure 2

When D_2O was introduced into the cell, instead of H_2O, the OH groups of the zeolite were deuteriated and then OD and $D_5O_2^+$ species were produced, giving rise to bands at 2693, 2631, 2210, and 1902 cm^{-1}, Figure 1(d). The isotopic ratios were 1.355, 1.349, 1.326, and 1.32, respectively. The ν_{OH}/ν_{OD} ratio decreased with the OH stretching frequency in the expected way.[13] Absorption due to the bending mode ν_4 of D_3O^+ ions could not be detected in our experiments since the band would have appeared at about 1250 cm^{-1} which would be overlapped by the SiO stretching vibrations of the silicate lattice.

It is of interest that other authors[2–4] did not find any trace of hydronium ion bands even when small amounts of water were added to activated (anhydrous) zeolites. This apparent discrepancy seems to be due to differences in the procedure. For instance, in ref. 4 the water was added after chemisorption of NH_3 which might lead to a marked broadening in the region 1640—1700 cm^{-1} by partial overlapping of the NH_4^+, NH_3, H_2O, and H_3O^+ bands. However, the absence of the characteristic bands of the oxonium ion in the NaY sample is in agreement with the results reported by Bertsch and Habgood[2] and Carter *et al.*[3] who also used activated forms of alkaline-metal zeolites.

In conclusion, our results indicate that oxonium and dioxonium ions are present in a decationated Y zeolite suggesting the presence of strong Brönsted sites on the surface of Y zeolites.

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