

Infrared Evidence of Three Distinct Acidic Hydroxyls in Defect-Free HY Faujasite

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Trimethylamine (TMA) and ammonia (NH_3) were coadsorbed over a free extraframework aluminum (EFAL) HY zeolite, which allowed us to distinguish at least three different acidic hydroxyls in the faujasite structure.

1. Introduction

Zeolites are crystalline microporous aluminosilicates where both silicon and aluminum (denoted as T atoms) are present in the framework in a tetrahedral coordination. Each TO_4 tetrahedron shares its corners with its neighbors to form many different crystalline structures characterized by a cages and/or pores system of molecular dimensions.¹ The presence of tetracoordinated aluminum atoms generates an excess of negative charge over the framework oxygen atoms, which is compensated by extraframework cations. Among all the known zeolite structures, the faujasite is surely the most studied and the most present in industrial applications as molecular sieves and because of its acidic properties. Figure 1 shows its framework and porous system. The first structural resolution was done in the late 60s starting from XRD data obtained for natural faujasites in the alkaline form.² More recently, the acidic form obtained after cationic exchange with ammonium and thermal NH_4^+ decomposition was characterized by neutron powder diffraction to directly locate the protons.³ Both studies agree with the presence of four distinct crystallographic positions for the oxygen atoms of the framework (labeled from 1 to 4 in Figure 1).

For Si/Al ratio higher than 2.3 (linde Y faujasite type) alkaline cations were shown to occupy three distinct extraframework crystallographic sites: I and I' inside the hexagonal prisms and the sodalite cages, respectively, and sites II inside the supercages α .⁴ When alkaline cations are substituted by protons inside the zeolite, the formation of acidic hydroxyls (with a rather high covalent character) takes place. From the four candidates, only the first three (O_1 to O_3) are told to be proton holders.³ For the former hydroxyl, the O_1H bond lies approximately in a plane of a 12-membered ring connecting supercages of the structure whereas the O_2H groups are in the plane of the six-membered ring of the sodalite units. Finally, the O_3H groups point inside the hexagonal prisms connecting the sodalite blocks.⁵ Adsorption of basic probe molecules followed by infrared spectroscopy has been widely used to study the Y faujasite acidity^{6–8} but even if theoretical deconvolutions were attempted, to our knowledge, no direct experimental evidence of the three distinct previously proposed hydroxyls was given for defect-free faujasite with low Si/Al ratio.

2. Results and Discussion

To avoid a possible perturbation of acidic hydroxyls by the presence of extraframework alkaline cations or aluminum

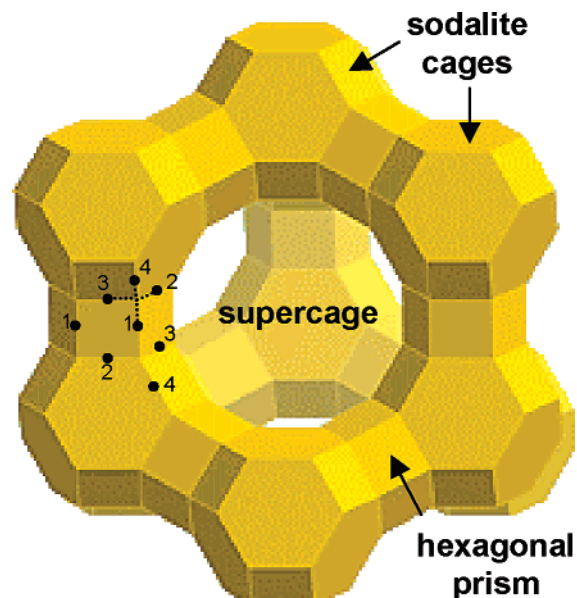


Figure 1. Schematic representation of the faujasite framework illustrating the four different crystallographic locations for oxygen atoms.

species,⁹ we started our study from a mother NH_4Y sample (Si/Al = 2.7 in the whole ammonium form), provided by the Institut Français du Pétrole, that was in situ transformed to its proton form by gentle thermal treatment (0.3 K/min till 723 K) to preserve the structure from any dealumination. Chemical analysis confirmed the absence of residual alkaline cations, whereas ^{27}Al MAS NMR analysis excluded the presence of extraframework aluminum. The infrared spectrum **a** on Figure 2 corresponds to the acidic HY sample obtained. The classically reported high-frequency hydroxyls (OH_{HF}) and low-frequency hydroxyls (OH_{LF}) are more clearly observed on Figure 3 (spectrum **a**) at wavenumbers equals to 3637 and 3548 cm^{-1} , respectively. The (OH_{HF}) is already known to be easily accessible because the corresponding high-frequency infrared vibration disappears when pyridine is adsorbed over HY samples.⁶ For steric hindrance reasons, the OH_{HF} should then be located inside the supercages to allow this interaction and the best candidate for this is the O_1H group. Concerning the (OH_{LF}) hydroxyls, the adsorption of carbon monoxide (CO) at low temperature affects very little the corresponding low-frequency component;⁷ nevertheless, the adsorption of another small but stronger base (NH_3) leads to the complete disappearance of both OH_{HF} and OH_{LF} , indicating the proton-transfer generating ammonium cations.⁸ CO appears thus to be a too

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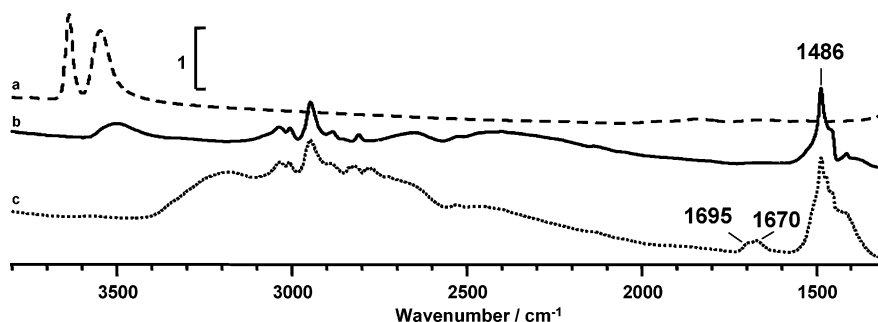


Figure 2. Infrared spectra in the 3800–1400 cm^{-1} range of the HY sample (a) after thermal treatment at 723 K under a vacuum, (b) after adsorption of 1 Torr of TMA at equilibrium followed by evacuation at room temperature, and (c) after coadsorption of 1 Torr of NH_3 at equilibrium.

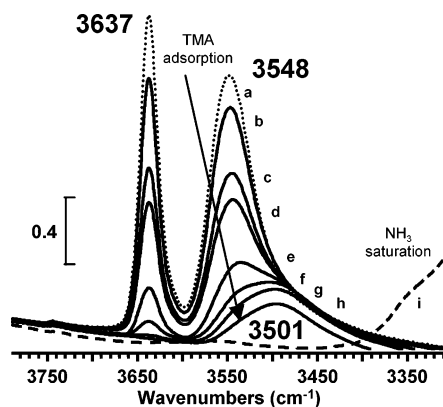


Figure 3. Infrared spectra in the 3800–3300 cm^{-1} range of the HY sample (a) after activation at 723 K under a vacuum and adsorption of (b) 402 μmol , (c) 804 μmol , (d) 1006 μmol , (e) 1608 μmol , (f) 2010 μmol , and (g) 2408 μmol of TMA per gram of solid, (h) after saturation with 1 Torr of TMA at equilibrium, and (i) after evacuation at room temperature followed by subsequent introduction of 1 Torr of NH_3 at equilibrium.

weak basic molecule to involve hydrogen bonding with the OH_{LF} hydroxyls, whereas pyridine seems to be too bulky to access these OH_{LF} . The combination of pyridine and ammonia adsorption is not very informative, because pyridine is partially replaced by the smaller but more basic NH_3 molecule.

Therefore, to clarify the nature of the hydroxyls giving rise to the OH_{LF} vibrations, we decided to adsorb TMA: a basic molecule stronger than pyridine (and ammonia) but almost as big as pyridine. The spectrum **b** of Figure 2 shows the general feature observed after saturation of HY with TMA and evacuation at room temperature. The OH_{HF} completely disappears but only a part of the OH_{LF} is affected, leaving a remaining wide and very low-frequency component. Considering the adsorbed species vibrational modes, we observe the methyl group $\nu(\text{CH})$ stretches between 2800 and 3100 cm^{-1} : the fine peaks around 3035 cm^{-1} being certainly typical of the trimethylammonium cations^{10,11} as their formation inside the faujasite supercages was first proposed from an NMR study.¹² Another characteristic vibration is also present in the bending mode region around 1486 cm^{-1} . To confirm that the remaining very low frequency $\nu(\text{OH})$ component corresponds to acidic hydroxyls inaccessible to TMA, we undertook the consecutive adsorption of the smaller and weaker basic ammonia molecule. The spectrum **c** of Figure 2 effectively confirms that NH_3 coadsorption after TMA saturation leads to the complete consumption of OH_{LF} . The enlargement in the $\delta_a(\text{NH})$ bending vibration region around 1450 cm^{-1} traduces the formation of NH_4^+ species whose corresponding $\delta_s(\text{NH})$ bending mode appears around 1670 cm^{-1} . The 1695 cm^{-1} component is probably due to coordinated ammonia. Finally, the broad band

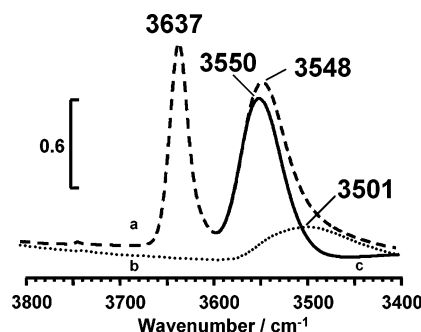


Figure 4. Infrared spectra in the 3800–3400 cm^{-1} range of the HY sample (a) after thermal treatment at 723 K under a vacuum, (b) after adsorption of 1 Torr of TMA at equilibrium followed by evacuation at room temperature, and (c) (a) minus (b).

between 3400 and 2600 cm^{-1} illustrates the formation of hydrogen bonding between the so formed ammonium cations and the framework oxygen atoms.

Figure 3 details the evolution of the $\nu(\text{OH})$ bands with increasing amounts of adsorbed basic molecules. From spectra **b** to **g**, well-known quantities of TMA were adsorbed, leading to the disappearance of both the $\nu(\text{OH})_{\text{HF}}$ and the high wavenumber component of the $\nu(\text{OH})_{\text{LF}}$ massif. The “bi-component composition” of the $\nu(\text{OH})_{\text{LF}}$ is particularly clear on spectrum **e** and is confirmed by the remaining very low wavenumber component at 3501 cm^{-1} when a 1 Torr TMA equilibrium pressure is introduced in the cell (spectrum **h**). This last spectrum changes very little upon desorption at room temperature (not shown), but it is evident from spectrum **i** that the subsequent introduction of ammonia leads to the total disappearance of the less accessible but acidic hydroxyls at 3501 cm^{-1} . Subtracting spectrum **h** from spectrum **a** (Figure 4), it is possible to isolate the $\nu(\text{OH})_{\text{LF}}$ component characteristic of hydroxyls able to interact with TMA (found at 3550 cm^{-1}).

The nature of the interaction between TMA and OH_{HF} or accessible OH_{LF} seems to be different, but this will be developed in a following paper.

Summarizing our results, the OH_{HF} vibration at 3637 cm^{-1} is attributed to O_1H groups pointing inside the supercages. The OH_{LF} massif can be experimentally separated into two distinct components: a very low wavenumber one at 3501 cm^{-1} and another at 3550 cm^{-1} . In the absence of “nonideal” species (spurious elements or extraframework aluminum), the 3550 cm^{-1} component affected by TMA adsorption should be attributed to O_2H groups pointing inside the sodalite units. On the other hand, the very low wavenumber component hydroxyls at 3501 cm^{-1} , being inaccessible to TMA (too far away from this bulky basic molecule for a proton transfer or H-bonding to occur) can be suggested to correspond to the O_3H groups pointing inside the hexagonal prisms.

3. Conclusions

As a conclusion, we report the first experimental decomposition of the infrared $\nu(\text{OH})$ stretching vibration low-frequency component of a non-dealuminated defect-free HY zeolite using the adsorption of a rather unusual probe molecule. Considering previous studies relative to the protons location inside the structure together with accessibility limitations, we propose for each O_1H , O_2H , and O_3H an assignment for the corresponding $\nu(\text{OH})$ wavenumbers.

References and Notes

- (1) Meier, W. M.; Olson, D. H. *Atlas of zeolite structure types*, 3rd revised ed.; Butterworth-Heinemann: London, 1992.
- (2) Olson, D. H.; Dempsey, E. J. *J. Catal.* **1969**, *13*, 221.
- (3) Csizsek, M.; Jobic, H.; Fitch, A. N.; Vogt, T. *J. Phys. Chem.* **1992**, *96*, 1535.
- (4) Mortier, W. J. *Compilation of Extraframework Sites in Zeolites*; Butterworth Scientific Ltd.: Guildford, Surrey, U.K., 1982.
- (5) Smirnov, K. S. *J. Phys. Chem.* **2001**, *105*, 7405.
- (6) Parker, L. M.; Bibby, D. M.; Burns, G. R. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3319.
- (7) Cairon, O.; Chevreau, T. *J. Chem. Soc., Faraday Trans.* **1998**, *94* (2), 323.
- (8) Zecchina, A.; Marchese, L.; Bordiga, S.; Pazè, C.; Gianotti, E. *J. Phys. Chem. B* **1997**, *101*, 10128.
- (9) Fritz, P. O.; Lunsford, J. H. *J. Catal.* **1989**, *118*, 85.
- (10) Ouasri, A.; Rhandour, A.; Dhamelincourt, M. C.; Dhamelincourt, P.; Mazzah, A. *Spectrochim. Acta A* **2003**, *59*, 851.
- (11) Harmon, K. M.; Gennick, I.; Madeira, S. L. *J. Phys. Chem.* **1974**, *78* (25), 2585.
- (12) Earl, W. L.; Fritz, P. O.; Gibson, A. A. V.; Lunsford, J. *J. Phys. Chem.* **1987**, *91*, 2091.