Catalysis Letters 11 (1991) 119–128

Comparison of the acidity of dealuminated and non-dealuminated HY zeolite by two ^{1}H-NMR methods: wide line at 4 K and high resolution MAS at 300 K

Patrice Batamack, Claudine Dorémieux-Morin * and Jacques Fraissard

Laboratoire de Chimie des Surfaces associé au CNRS-URA 1428, Université Pierre et Marie Curie,
Tour 55, 4 place Jussieu, 75252 Paris Cedex 05, France

Received 1 September 1991; accepted 2 October 1991

^{1}H-Wide-Line and MAS-NMR at 4 and 300 K, respectively, for HY zeolite samples, non-dealuminated and partially dealuminated with $(NH_4)_2SiF_6$ reveal significant differences.

Keywords: ^{1}H-Wide-Line NMR; ^{1}H-MAS-NMR; HY zeolite; dealuminated HY zeolite; acidity of HY zeolites

1. Introduction

It has already been shown that wide line ^{1}H-NMR at 4 K can be used to determine the hydroxonium ion concentration in partially rehydrated HY zeolite samples containing few defects (denoted ND) (1). This technique has revealed the following steps (2):

$$x\ OH_b + y\ H_2O \rightarrow \inf(x, y)\ H_2O \cdots H_bO + |x - y| OH_b \quad \text{or } H_2O \qquad (1)$$

and

$$\inf(x, y)\ H_2O \cdots H_bO \rightleftarrows z\ H_3O^+ + z\ O^- \qquad (2)$$

where x, y, and z are numerical values and OH_b corresponds to bridging OH groups, SiO(H)Al. Simulation of the wide line spectra of ND zeolite samples allowed us to determine the concentrations of the species involved in these interactions. The mean value of the equilibrium constant of reaction (2) is 2.2 with a standard deviation of 0.9.

Our aim is to compare these results with those obtained with a partially dealuminated HY zeolite (denoted D) and to show once again the interest of the technique proposed.

2. Experimental section and method

The characteristics of the 2 samples are given in table 1. NH_4Y zeolite (Y64 from UOP) gives the ND samples after shallow bed treatment [1] (dehydration under dynamic vacuum before heating at 12 Kh^{-1} to the maximum temperature of 675 K at 10^{-2} Pa, these conditions being maintained for 15 h, the powder layer being less than 5 mm thick). Zeolite D is also prepared from NH_4Y. It is partially dealuminated by Al-Si exchange by means of an aqueous solution of $(NH_4)_2SiF_6$ [3] and shallow bed treated. ^{129}Xe-NMR of adsorbed Xe shows that there are strong adsorption sites in this D zeolite [4]. Water vapour is adsorbed stepwise at 300 K. The amount is determined volumetrically and gravimetrically. Since the water adsorbed in this way is not generally distributed homogeneously the samples are homogenized at 375 K for 4 h. After cooling they are transferred to narrow tubes and sealed. The numbers of OH_b and of adsorbed water molecules per unit cell are denoted $n_i(OH)$ and $n_i(H_2O)$, respectively.

The ^{1}H MAS NMR experiments are performed on a Bruker MSL-400 spectrometer with a special probe. The magnetization turns only through an angle much less than 90° and the time between 2 pulses is either 20–50 s for the anhydrous or slightly hydrated samples or 5 s for the most hydrated. The MAS + echo spectra are recorded using the method recommended by Olejniczak et al. [5] where the time between the echo-pulses is equal to the sample rotation period. The MAS + echo spectra favour mainly immobile species during the rotation period and help with the assignment of the signals. The weak residual signal of the probe is substracted from the total signal. Chemical shifts are expressed with respect to TMS using usual conventions.

The wide line ^{1}H-NMR experiments are performed at 4 K on a home-made continuous wave 60 MHz spectrometer with phase detection and signal accumulation. Although weak, the probe signal is subtracted from each spectrum. The

Table 1
Characteristics of the non-dealuminated HY zeolite (ND) and partially dealuminated HY zeolite

Sample	Preparation	Si/Al (^{29}Si MAS NMR)	Na^+ concentration	Number of OH per unit cell for the anhydrous samples	
				Acidic OH	Silanols
ND	85% Na^+/NH_4^+ exchanged	2.4	15% ion	47.7	0
D	zeolithe ND partially dealuminated by an aqueous solution of $(NH_4)_2SiF_6$	4.4	negligible	35.8	1.5

spectra are absorption derivatives. They are theoretically symmetrical with respect to the centre and, in practice, the two parts of the experimental spectra are averaged; for this reason we present only half of each spectrum.

The simulated spectra correspond to the weighted sum of the contributions of the various species for which the following magnetic configurations have been calculated [1,2]: (i) H_2O, a r distant 2-spin configuration; (ii) H_3O^+, a magnetic configuration with three r distant spins at the vertices of an equilateral triangle; (iii) $H_2O \cdots HO$ or deformed H_3O^+: a magnetic configuration with 3 spins at the vertices of an isoceles triangle, where r is the base and r' the equal sides; (iv) OH, a 2-spin configuration or a pure Gaussian function and/or a pure Lorentzian function. Each of the corresponding functions (except the Gaussian and the Lorentzian) is convoluted by a Gaussian which allows for the interactions between the protons of the configuration and those belonging to neighboring configurations and also those of the other nuclei with non-zero spin in the environment (^{27}Al in the present case). When the effect of the Al nuclei is small the parameter of each Gaussian is related to a distance X which is close to the shortest distance between a proton of the configuration considered and a proton outside it. The calculations are referenced to a crystallographic unit cell by means of a numerical base which takes into account the total number of protons in the sample, equal to the number of OH groups plus twice the number of water molecules introduced. Moreover, since the number of independent parameters for each simulation is high we impose the condition that the concentrations obtained be in agreement with the number of OH groups and the number of water molecules introduced. Finally, the distances r found must lie in the range corresponding to the various oxygen-proton groups identified and, for each configuration, the value of X must be greater than (or at least equal to) that of r and r'.

3. Results and interpretation

1. ^1H MAS NMR

1.1. Non-dealuminated HY zeolite (ND)

The spectrum of the anhydrous sample consists of 2 poorly resolved Gaussian signals at 4.3 and 5.3 ppm, with large spinning sidebands, characteristic of the two types of OH_b oriented towards the centre of the supercages and that of the sodalite cavities, respectively [6]. A weak signal at 2.3 ppm indicates the presence of traces of silanol groups SiOH. When the value of $n_i(H_2O)$ is increased, but remains less than $n_i(OH)$, the above signals are replaced or masked by a new signal which broadens progressively and becomes Lorentzian, bearing weak side bands. The chemical shift of this signal increases slowly from 5 to 5.7 ppm. When $n_i(H_2O) = n_i(OH)$ the spectrum consists of two signals: the first, Lorentzian, is at 5.8 ppm and is 3 ppm wide; the second, small and Gaussian, is at 2.3 ppm and corresponds to newly visible silanol groups; although clear, this signal represents only 2–3% of the total number of H atoms. For $n_i(H_2O) = 106.5$, there is only the Lorentzian signal at 5.4 ppm, still broad (4–5 ppm) with spinning sidebands stronger than for $n_i(H_2O) = 48.5$. For $n_i(H_2O) = 129$ the Lorentzian signal is almost unchanged but a new very weak signal appears at about 10 ppm. This signal, although it is always weak, is easy to see for $n_i(H_2O) = 142$ because the width of the Lorentzian part at 5.3 ppm is reduced to 2.5–3 ppm.

All the MAS + echo spectra for the hydrated samples contain a signal at about 2.3 ppm and another between 5 and 6 ppm. For $n_i(H_2O) = 129$ a signal at about 10 ppm appears and this persists to higher water concentrations. The 5 ppm signal is very weak compared to that of the MAS spectra without echo.

1.2. Partially dealuminated HY zeolite (D)

The MAS spectrum of the anhydrous sample is qualitatively identical with the corresponding spectrum of zeolite ND. However, the signal at 2.3 ppm, attributed to silanol groups, is greater in sample D than in ND and corresponds to 3–4% of the H atoms. When the spectra of weakly hydrated zeolites ($n_i(H_2O) \leqslant n_i(OH)$) are compared the fundamental difference is the presence of a distinct signal at 7 ppm in the spectra of D (fig. 1). For this sample when $n_i(H_2O) = 36$ (approximately equal to $n_i(OH)$), the spectrum consists of only 2 signals: one at 7.2 ppm, 4 ppm wide, and the silanol signal at 2.5 ppm: the wide signal probably masks the Gaussian signal present at 7 ppm for lower water concentrations. An additional shoulder appears at 9.5–10 ppm on the side of the Lorentzian signal then centered at 6.9 ppm, for $n_i(H_2O) = 72$. For $n_i(H_2O) = 130$ the width of the Lorentzian signal is reduced to 2–2.5 ppm and the spinning sidebands are weakened; the Gaussian signal at 9.8 ppm, although weak, is well resolved with easily identifiable spinning sidebands. The situation remains qualitatively the same for higher water concentrations, except that the width of the Lorentzian signal decreases further and that the number of protons resonating at 9.2 ppm does not appear to increase beyond $n_i(H_2O) = 130$.

The MAS + echo spectra of zeolite D are qualitatively similar to those of MAS for high water content. However, at low water concentrations ($n_i(H_2O) = 4$ and 9 as example) (fig. 1), the MAS + echo spectra are better resolved because the width (1.5–2 ppm) and the size of the signal at about 5 ppm are smaller than in the MAS spectra.

1.3. Interpretation

There is only one obvious difference between the spectra of the anhydrous samples: D has more silanol defects than ND. After water adsorption, when the Lorentzian signal allows it to be observed, the signal of the SiOH groups is always present, showing that they do not interact with water. The Lorentzian

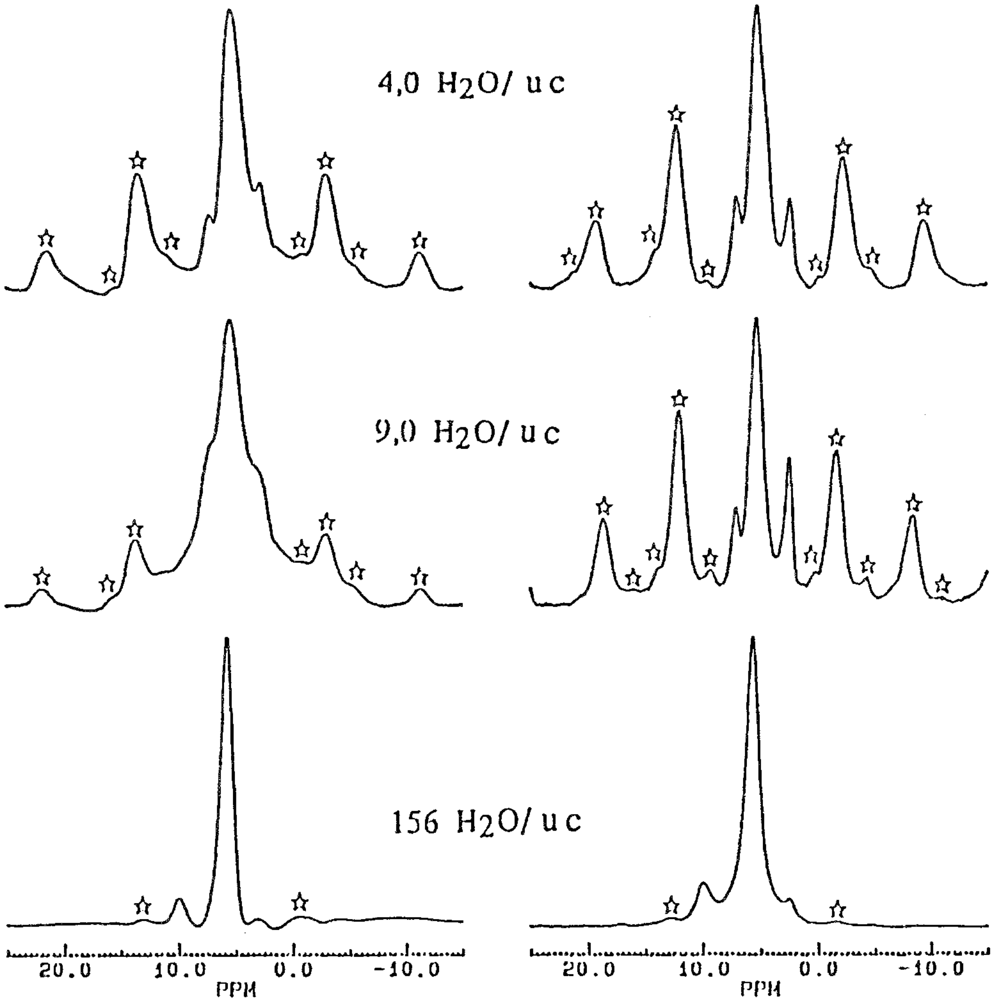

Fig. 1. ^1H MAS NMR spectra (left) and ^1H MAS + echo (right) of dealuminated HY zeolite (D) after adsorption of the numbers of water molecules indicated. The asterisks indicate spinning sidebands.

signal observed in the presence of water is characteristic of protons rapidly exchanging between OH_b groups, water molecules and H_3O^+ ions [7]. For ND, its chemical shift reflects the composition of the exchanging medium and the numerous hydrogen bonds which the various species make [7]. The chemical shift of this signal can be greater for D (7.2 ppm) than for ND (5.8 ppm). This does not mean that D contains more H_3O^+ than ND ($n_i(H_2O) = n_i(OH)$ in both cases): as we have already indicated, it is likely that the independent signal at 7 ppm in the spectra of D at lower water concentrations is still present.

The most probable assignment of the Gaussian signal at about 7 ppm, found in the spectra of D but not in those of ND, has been given by Hunger et al. [8]: it corresponds to water molecules interacting with Lewis sites which are not extra-framework Al atoms. Such groups therefore occur in sample D; they could be the polarizing sites revealed by adsorbed Xe NMR.

The signals at about 9–10 ppm, present on the spectra of both zeolites at higher values of $n_i(H_2O)$ characterize $Al(H_2O)_6^{3+}$ species [9].

2. WIDE LINE ^{1}H NMR AT 4 K

2.1. *Non-dealuminated HY zeolite (ND)*

The results for non-dealuminated HY zeolite are in press [2] and have been summarized in the introduction to this article. The concentrations are given in fig. 2A.

2.2. *Partially dealuminated HY zeolite (D)*

The ^{1}H MAS NMR results indicate that there is no interaction between the silanol groups and water molecules. These results are in agreement with those of previous studies on HZSM5 samples, carried out by the two ^{1}H NMR methods, wide line and MAS [7]. Consequently, in order to improve the precision of the simulation of the wide line spectra of D we have introduced an additional constraint which consists of the presence of a small number of relatively isolated OH groups in the samples (3–4% of the OH groups in the anhydrous sample), at least when $n_i(H_2O)$ is not very high.

Some examples of experimental and simulated spectra are presented in fig. 3 with the partial contributions of the various spin configurations. All the spectra of the zeolite D can be simulated without any problem in the entire water concentration range (not those of ND (2)). The concentrations of various oxygen-proton species are given in table 2. Fig. 2B shows that the hydroxonium ions concentration increases for $n_i(H_2O) < n_i(OH)$ and levels off in the region where $n_i(OH) \leqslant n_i(H_2O) < 2\ n_i(OH)$. The number of H_3O^+ again increases markedly with $n_i(H_2O) > 2\ n_i(OH)$. In the horizontal section about 20% of the initial Brönsted acidities are found as hydroxonium ions. This value is very similar to that obtained for sample ND (1). The results would represent the 300 K equilibrium [7,1,2].

4. Conclusion

The results obtained for non-dealuminated (ND) and partially dealuminated (D) HY zeolite reveal some characteristic differences. The D samples show additional effects compared to ND. Firstly, the MAS spectra of the weakly rehydrated samples contain a signal which can be attributed to water molecules interacting with Lewis acid sites. Secondly, the wide line spectra of the very rehydrated D samples correspond to an increase in the hydroxonium ion concentration. These observations appear to be related, though they do not

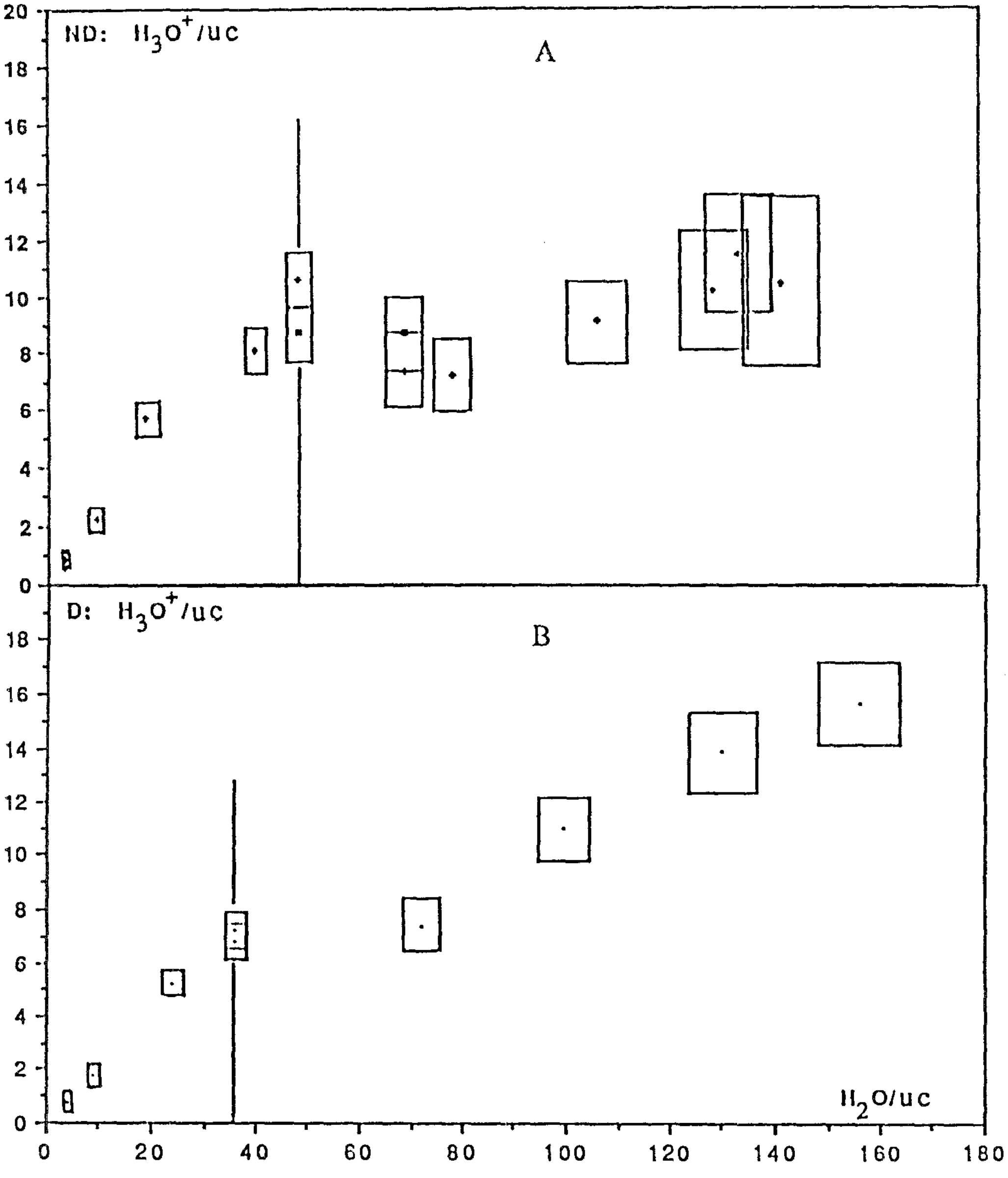

Fig. 2. H_3O^+ variation with H_2O. A: non-dealuminated HY zeolite samples (ND); B: dealuminated HY zeolite samples (D). The vertical line corresponds to $n_i(H_2O)$ (number of water molecules introduced) = $n_i(OH)$ (number of initial acidic OH groups).

concern the same range of water concentrations. The method of preparing zeolite D should not, in principle, give a compound with extra-framework Al atoms. Nor should the Lewis acid sites be identified with extra-framework Al. However, ^{129}Xe-NMR of xenon adsorbed on the anhydrous samples reveals the

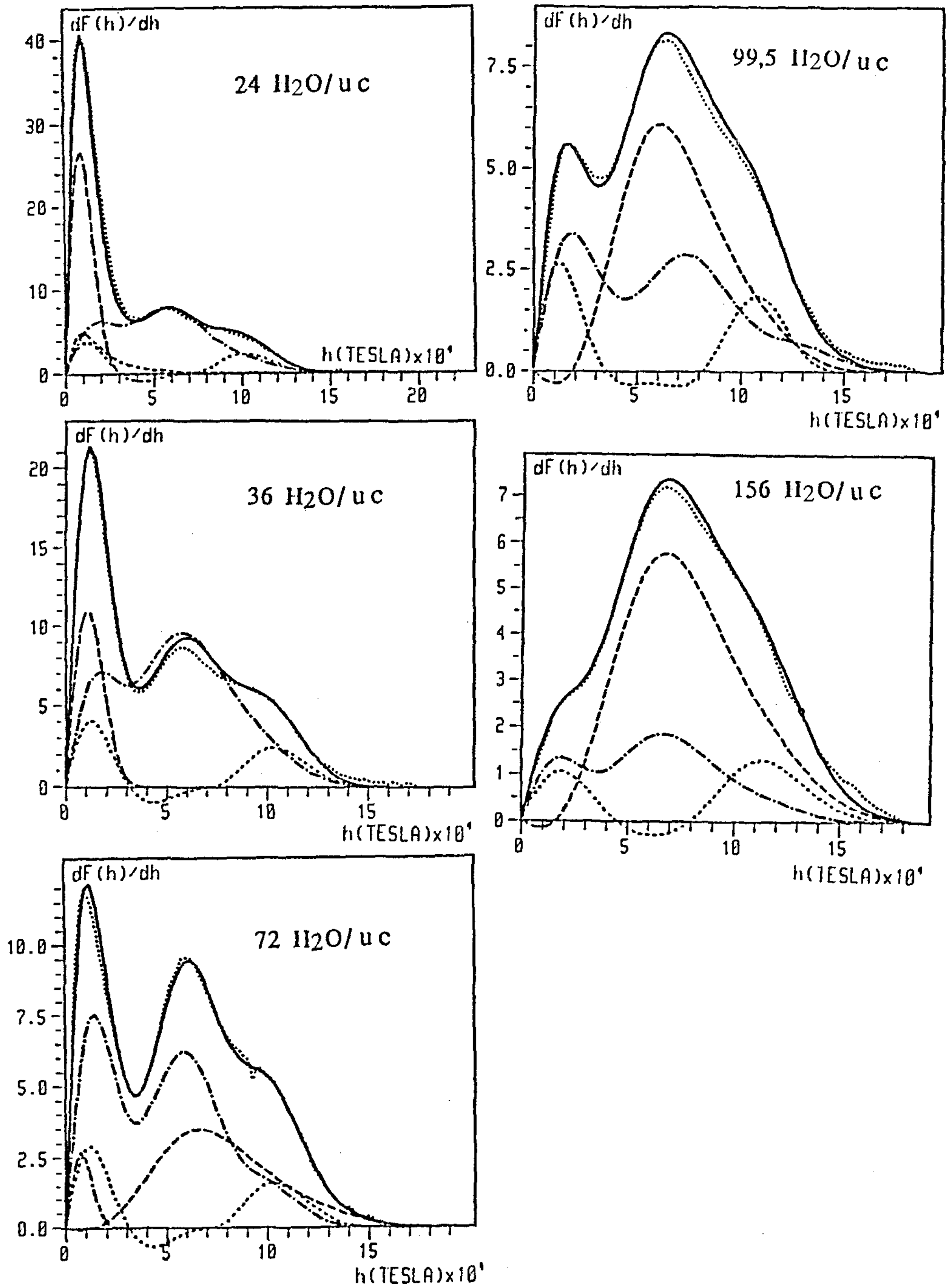

Fig. 3. ······ Half derivative of the experimental absorption spectrum of HY zeolite samples (D) after adsorption of the numbers of water molecules indicated. ———: simulated spectrum; ------: weighted contribution of the H_3O^+ ions; ·—·—·: weighted contribution of the $H_2O\cdots HO$ groups; — — —: weighted contribution of the H_2O groups; -—-—-: weighted contribution of the OH groups.

Table 2

Number of experimentally water molecules	Number of H_3O^+	Number of $H_2O\cdots HO_b$	Number of OH_b	Number of SiOH	Number of H_2O
4.0±0.5	0.8±0.35 *	1.9±0.4	Total number of OH: 37.2±1.1		0
9.0±1.1	1.8±0.4 *	7.2±0.4	Total number of OH: 28.2±1.4		0
24.0±1.9	5.2±0.5 * 5.1±0.5 **	19.0±0.5 18.5±0.5	Total number of OH: 14.5±2.5		0
36.0±2.0	7.2±0.7 *	27.7±0.7	0	5.9±1.0	0
	6.8±0.7 **	27.8±0.7	0	5.4±1.0	0
72.0±3.5	7.4±1.0 *	28.3±0.7	0	1.1±1.0	36.6±1.5
	7.4±1.0 **	28.3±0.7	0	1.1±1.0	36.6±1.5
99.5±5.0	11.0±1.2 *	25.5±0.6	0	0.0±1.0	62.6±2.0
	11.0±1.3 **	26.0±0.6	0	1.4±1.0	62.6±2.0
130.0±6.5	13.9±1.5 *	24.5±0.6	0	0.9±1.0	90.7±3.0
	13.9±1.5 **	24.5±0.6	0	0.9±1.0	90.7±3.0
156.0±8.0	15.7±1.5 *	21.5±0.5	0	0.0±1.0	120.2±8.0
	15.7±1.5 **	21.5±0.5	0	0.0±1.0	120.2±8.0

Number of the different symbol groups per unit cell of HY zeolite partly dealuminated calculated from the fits. The initial number of OH_b species is 35.8±2.0 (from ^{29}Si MAS NMR), and that of SiOH groups 1.5±0.7 (from ^{1}H MAS NMR); * hydroxonium ions assumed with equilateral symmetry of protons; ** hydroxonium ions with isosceles symmetry of protons.

presence of strongly polarized sites which could be the Lewis acid sites indicated by MAS NMR. The nature of these sites remains to be determined.

It appears to be impossible to perform studies such as those described in this article without dealuminating the samples slightly. Simply hydrating the anhydrous samples probably induces the beginning of a dealumination process, at least when the water concentration is greater than that of the acidic OH groups. Moreover, the fact of heating the rehydrated samples slightly in order to homogenize them enhances this dealumination. This evolution could be the cause of the relatively poor definition of the horizontal section in the hydroxonium ion concentration variation for ND zeolite at high water concentrations.

Finally, this comparative study again demonstrates the interest of the proposed technique for studying the acid strength of solids.

References

[1] P. Batamack, C. Dorémieux-Morin and J. Fraissard, Chem. Phys. Lett. 180 (1991) 545, and references therein.

[2] P. Batamack, C. Dorémieux-Morin and J. Fraissard, J. Chim. phys., Physico-chim. biol., in press.

[3] Q. Chen, M.-A. Springuel-Huet and J. Fraissard, unpublished results.

[4] G.W. Skeels and D. Breck, *Proc. Sixth Int. Zeolite Conf.*, Reno (1984) 87.

[5] E.T. Olejniczak, S. Vega and R.G. Griffin, J. Chem. Phys. 81 (1984) 4804.

[6] D. Freude, Stud. Surf. Sci. Catal. 52 (1989) 169, and references therein.

[7] P. Batamack, C. Dorémieux-Morin, J. Fraissard and D. Freude, J. Phys. Chem. 95 (1991) 3790.

[8] M. Hunger, D. Freude and H. Pfeifer, J. Chem. Soc., Faraday Trans. 87 (1991) 657.

[9] J.W. Akitt, J.M. Elders and X.L.R. Fontaine, J. Chem. Soc., Chem. Commun. (1986) 1047.