

Quadrupole Nutation N.M.R. Reveals the Presence of a New Aluminium Species in Hydrothermally Treated Zeolites

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^{27}Al Quadrupole nutation n.m.r. reveals the presence of four kinds of aluminium in dealuminated zeolite Y; we suggest that distorted framework tetrahedral (DFT) aluminium, which is reported for the first time here, is bonded to hydroxyl groups formed during dealumination.

Quadrupole nutation n.m.r. of nuclei with half-integer spin in powdered samples¹⁻⁷ can distinguish between nuclei of the same chemical element subjected to different quadrupole interactions, the signals of which overlap in conventional spectra. The technique can be usefully applied for the determination of the local environment of Al in zeolitic catalysts, essential for the understanding of their chemistry. Because of strong quadrupole interactions, the amounts of framework and non-framework Al in thermally treated samples determined by ^{27}Al magic-angle-spinning (m.a.s.) n.m.r. disagree with those found by the joint application of ^{29}Si m.a.s. n.m.r. and chemical analysis.⁸⁻¹⁰ We have recently reported an advance towards quantitative determination of aluminium in zeolites by n.m.r.,⁵⁻⁷ showing that *all* the Al can be detected provided certain experimental conditions are met.

^{27}Al N.m.r. spectra were measured at 104.2 MHz using a Bruker MSL-400 spectrometer. To avoid spinning sidebands which often coincide with genuine signals, the spectra were measured without m.a.s. Conventional spectra were obtained using an aluminium-free probehead and 100 mg of sample. The pulse length was $\pi/20$; the recycle delay 0.2 s; spectral width 125 kHz, and instrumental deadtime 12 μs . The nutation spectra⁵⁻⁷ were measured with a high-power static probehead and a 5 mm diameter horizontal solenoidal coil. The amplitude of the r.f. pulse ($\omega_{\text{r.f.}}/2\pi$) was kept constant at 70 ± 5 kHz; the pulse length was increased in 1 μs increments from 2 to 65 μs . The experiments were performed on the same amount of each sample and the same number of transients was accumulated. The free induction decays (f.i.d.s.) were doubly Fourier transformed in the magnitude mode. The projection of a spectrum onto F_1 gives the precession frequencies around the r.f. field in the rotating frame which depend on the ratio of the quadrupolar parameter ω_Q and the r.f. field strength $\omega_{\text{r.f.}}$. When $\omega_Q \ll \omega_{\text{r.f.}}$ a strong peak appears at the nutation frequency $\omega_1 = \omega_{\text{r.f.}}$, while for $\omega_Q \gg \omega_{\text{r.f.}}$ the peak is at $\omega_2 = (I + 1/2) \omega_{\text{r.f.}}$. More complicated line shapes result for stationary samples in the intermediate cases.^{1,11} The strength of the quadrupolar interaction, ω_Q , can be up to several MHz depending on the nucleus and the structure of the solid, while the strength of the r.f. pulse is normally insufficient to allow the quadrupolar interaction to be neglected during irradiation.

Dealuminated samples of zeolite Y were prepared by hydrothermal treatment of 62% ammonium-exchanged NH_4 , Na-Y (sample 1). Samples D-1 and D-2 were made by steaming 20 g portions of sample 1 in a quartz furnace¹² at 525 °C with water being injected by a peristaltic pump with a flow rate of 12 ml/h for 5 and 18 h, respectively. Realuminated samples R-3 and R-4 were prepared by hydrothermal isomorphous substitution^{5,12} by stirring 1 g of sample D-2 in 50 ml of 0.5 M and 2 M KOH at 80 °C for 24 h. All samples were characterized by X-ray diffraction (X.r.d.) and by ^{29}Si and ^{27}Al m.a.s. n.m.r. The unit cell parameters, framework Si/Al ratios, and the numbers of framework Si and Al atoms per unit cell calculated from deconvolution using Gaussian peak shapes are given in Table 1. Samples were fully hydrated over

saturated NH_4Cl for 24 h prior to n.m.r. experiments. Dealuminated samples D-1 and D-2 were highly crystalline to X.r.d. with a reduced unit cell parameter¹³ (Table 1).

^{27}Al M.a.s. n.m.r. spectra of samples 1, D-2, and R-3 in the absolute intensity mode are given in Figure 1. As a result of

Table 1. Unit cell parameters and the composition of the samples. Si_F and Al_F denote numbers of Si and Al atoms per unit cell of 192 tetrahedral atoms.

Sample	$a_0/\text{\AA}$	(Si/Al) _{n.m.r.}	Si_F	Al_F
1	24.69	2.56	138	54
D-1	24.58	3.10	145	47
D-2	24.52	4.91	160	33
R-3	24.72	2.59	139	54
R-4	24.98	1.54	116	76

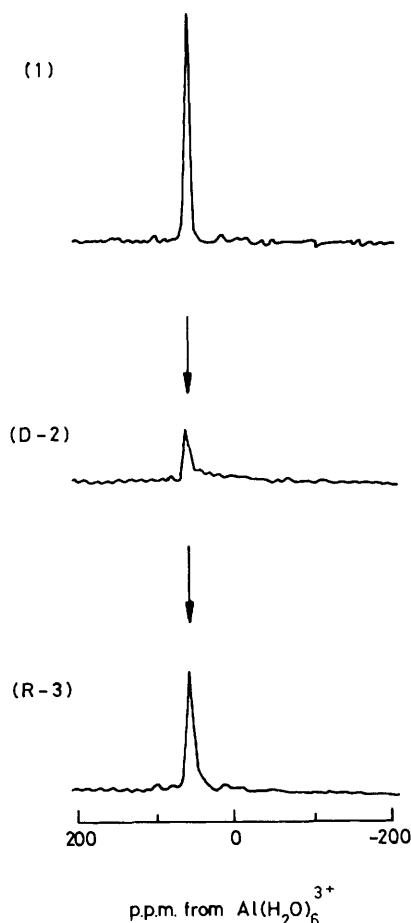


Figure 1. ^{27}Al M.a.s. n.m.r. spectra of samples 1, D-2, and R-3 in the absolute intensity mode.

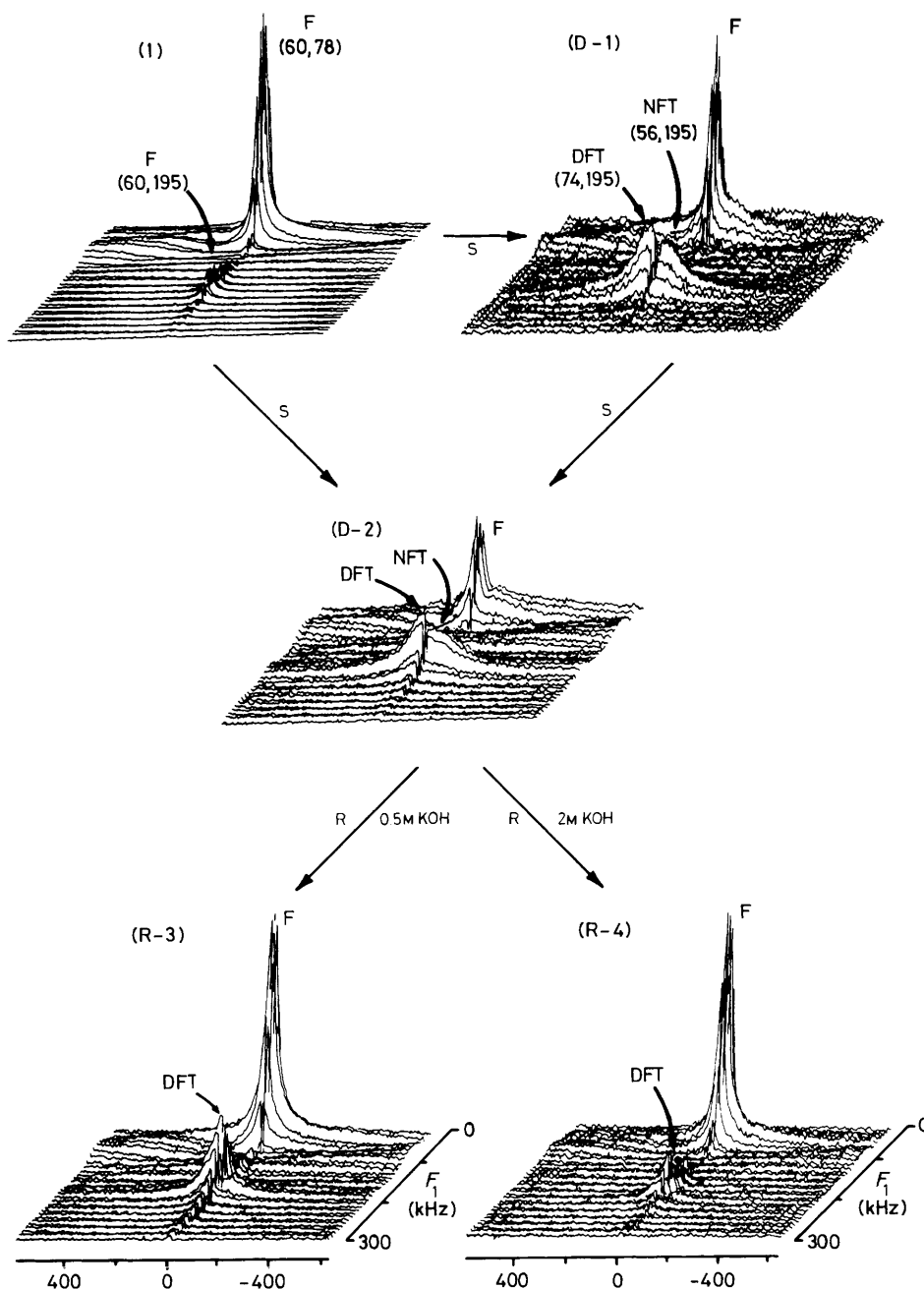


Figure 2. ^{27}Al Quadrupole nutation spectra.

dealumination, the intensity of the framework aluminium (F) signal at *ca.* 60 p.p.m. in sample D-2 is much lower than in sample 1. The absence of spectral features at 0 p.p.m. shows that aluminium extracted from the framework is in tetrahedral co-ordination, but the broadening of the ^{27}Al signal indicates that there is a wider range of quadrupole interactions than before thermal treatment.

The nutation spectrum of sample 1 (Figure 2) consists of two signals [at (60 p.p.m., 78 kHz) and (60, 195)], both with the

same linewidth of 855 Hz and both corresponding to framework (F) aluminium. The presence of *two* signals is due to the fact that the quadrupole interaction characteristic of framework ^{27}Al is of the same order of magnitude as the strength of the r.f. pulse ($\omega_{\text{r.f.}} = 440$ kHz). Since the latter is insufficient to overcome the quadrupole interaction entirely, the excitation is not fully non-selective.⁷ We shall demonstrate that, in general, dealumination of sample 1 for various periods leads to spectra composed of up to *four* signals (Table 2).

Table 2. Signals following dealumination of sample 1.

	Signal	Assignment
1	60 p.p.m., 78 kHz;	(F)
2	-2 p.p.m., 78 kHz;	(NFO)
3	56 p.p.m., 195 kHz;	(NFT)
4	74 p.p.m., 195 kHz;	(DFT, see below)

Signals 1–3 have been assigned^{4,11} to tetrahedral framework (F), non-framework octahedral (NFO), and non-framework tetrahedral (NFT) aluminium, respectively. The projection of the spectra of samples D-1 and D-2 in Figure 2 onto F_2 gives a very broad signal at 60 p.p.m., while the projection onto F_1 clearly reveals *three* component signals.^{1,4,11} No NFO aluminium is found in this highly crystalline sample.

Our aim is to assign signal 4. Figure 2 shows that, as dealumination progresses, there is a change in relative intensities of the F and NFT signals and of the signal we wish to assign. The last two peaks first appear in sample D-1 and become more intense in comparison to the F signal in the more highly dealuminated sample D-2. Signal 4 cannot be part of either the F or the NFT peak since it occurs at a lower field: its projection onto F_2 is at 74 p.p.m. and has a larger linewidth than signal F. A simple calculation based on the ²⁹Si m.a.s. n.m.r. spectra and the fact that the *total* amount of Al in the sample remains constant upon heat treatment, shows that 16% of the total aluminium in sample D-2 is part of the framework. Deconvolution of the ²⁷Al spectrum in Figure 1 based on the (incorrect) assumption that the linewidth of the ²⁷Al signal remains constant upon hydrothermal treatment always gives much lower amounts of framework Al than calculated from ²⁹Si m.a.s. n.m.r. and X.r.d.^{9,10,14} Since it has been demonstrated that *hydrated* zeolite samples contain no 'invisible' Al,^{5–7} signal 4 at 195 kHz in F_1 in Figure 2 must represent framework Al in sites distorted as a result of the hydrothermal treatment (DFT). Since it occurs at a higher nutation frequency than the 'ordinary' (F) aluminium, such Al is affected by stronger quadrupole effects. It has been shown¹⁵ that almost all non-framework aluminium dissolves in ethanolic acetylacetone but that no framework aluminium does so unless the treatment is continued for extended periods. The nutation spectrum of sample D-2 treated with acetylacetone (not shown) indicates that a considerable amount of NFT aluminium has been removed, but that the F and DFT signals remain virtually unaffected. This confirms that framework aluminium is not complexed, and that signal 4 comes from Al in the framework, but subjected to stronger quadrupole interactions than in untreated samples.

The nutation spectra (Figure 2) clearly show that the aluminium does re-enter the framework. As realumination progresses, the F signal at (60, 78) increases. By comparing nutation spectra of many realuminated samples containing different amounts of framework aluminium as a result of treatment with KOH solutions of different concentrations we have found that *both* the NFT and (whenever present in the ultrastable precursors) the NFO species are affected. Upon treatment with 0.5 M KOH (sample R-3) the NFT signal disappears faster than the DFT signal, indicating that the initial stage of the reaction involves primarily a conversion of NFT aluminium into F aluminium. The intensity of the DFT signal falls significantly only after most NFT aluminium has

gone back into the framework (as in sample R-4 which has been treated with a more concentrated base). The F signal in the realuminated sample R-4 is narrower than in sample D-2 from which it was prepared, which indicates that the F aluminium in sample R-4 is experiencing a narrower range of quadrupolar interactions. This effect is not sufficiently large for the chemical shifts and/or quadrupole interactions to be manifested as a change in the F_1 frequency.

To demonstrate that our samples contain only crystalline aluminosilicate and that the possibility of tetrahedral Al from any amorphous material interfering with our conclusions may be discussed, we have acquired nutation spectra of samples which have deliberately been made amorphous.¹⁶ Both 4- and 6-co-ordinated Al was present in the amorphous samples; the broad ²⁷Al m.a.s. n.m.r. spectra indicated that many kinds of non-equivalent environments for aluminium were simultaneously present. Upon treatment with KOH *all* these are converted into tetrahedral co-ordination. However, the nutation signals in F_1 were broader and occurred at a higher field (56 p.p.m.) in F_2 which corresponds to NFT aluminium. Large quadrupolar effects and low concentration of the latter species make the small difference in F and NFT peak positions unobservable by conventional ²⁷Al m.a.s. n.m.r. The increase in ²⁷Al linewidth observed upon dealumination of zeolites is due to a superposition of these two signals.

²⁹Si M.a.s. n.m.r. signals from base-treated amorphous samples were at more negative chemical shifts than in the crystalline materials which rules out the possibility of interference from the amorphous phase. Our assignment of signal 4 as due to DFT aluminium is therefore confirmed, and the reinsertion of Al into the zeolitic framework quantitatively demonstrated.

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