Quantitative Determination of Aluminium in Zeolites by Solid-state ^{27}Al N.m.r. Spectroscopy

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By an appropriate choice of experimental conditions (hydrated samples and very short r.f. pulses) considerable advances can be made towards quantitative determination of aluminium by ^{27}Al n.m.r. spectroscopy in thermally treated (ultrastable) zeolite Y; quadrupole nutation ^{27}Al n.m.r. spectroscopy reveals novel information about the various aluminous species present.

The precise determination of the local environment of Al and Si in zeolitic catalysts is essential for the understanding of their chemistry. One of the difficulties involved is that, as a result of strong quadrupolar interactions, the amounts of framework and non-framework Al in thermally treated samples determined by the joint application of ^{29}Si magic-angle-spinning (m.a.s.) n.m.r. (which monitors *framework* Al) and of chemical analysis (which gives the *total* Al content) are in striking disagreement with the results of ^{27}Al m.a.s. n.m.r.[1–3] The latter technique underestimates the amount of Al, and indirect methods, such as impregnation of the sample with ethanolic acetylacetone[4,5] prior to measurement have been used to observe the 'invisible' aluminium. We report an advance towards quantitative determination of aluminium in zeolite by n.m.r. spectroscopy, and show that all the Al can be detected by n.m.r. in the solid state provided certain experimental conditions are met.

Quantitative n.m.r. determination of the quadrupolar ($I>1/2$) spin populations in powdered samples is difficult because the energy levels of quadrupolar nuclei are shifted by the quadrupolar interaction.[6] For half-integer spins only the central transition ($+1/2 \leftrightarrow -1/2$) is normally *detected* (as opposed to *excited*), which affects the optimal excitation conditions of the spin system by an r.f. pulse. For the selective ($\omega_Q >> \omega_{rf}$) excitation of the central line,[6] maximum line intensity is achieved by pulses the length of which, t_p, fulfils the condition $t_p(I+1/2)\omega_{rf} = \pi/2$. The spectral line intensity and the initial value of the free induction decay $F(t_p)$ in pulsed n.m.r. are proportional to the spin population. For $I = 5/2$ in the case of non-selective (N.S.) excitation ($\omega_Q << \omega_{rf}$), the intensity, F_{NS}, of the central transition is given by equation (1).[7] In the case of selective (S) excitation ($\omega_Q >> \omega_{rf}$), the line intensity, F_S, of the central transition is given by equation (2).

$$F_{NS} = [9\sin(\omega_{rf}t_p)]/2 \qquad (1)$$

$$F_S = [3\sin(3\omega_{rf}t_p)]/2 \qquad (2)$$

^{27}Al N.m.r. spectra were obtained using a Bruker MSL-400 multinuclear spectrometer operating at 104.2 MHz. To avoid spinning sidebands which often coincide with genuine signals, the spectra were measured without m.a.s. Conventional

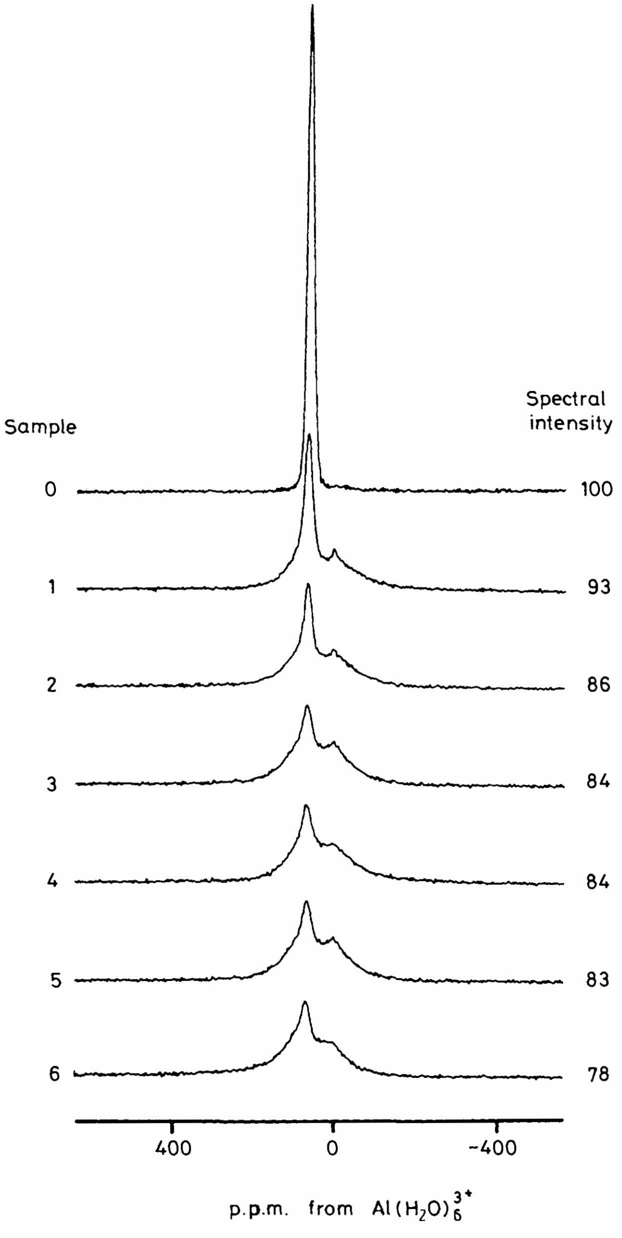

Figure 1. Static ^{27}Al n.m.r. spectra on the absolute intensity scale of the starting material (sample 0) and of dealuminated samples 1—6 acquired with $\pi/20$ pulses. Numbers refer to the relative intensity of each spectrum corrected for water content. Chemical shifts are given in p.p.m. from Al(H$_2$O)$_6^{3+}$.

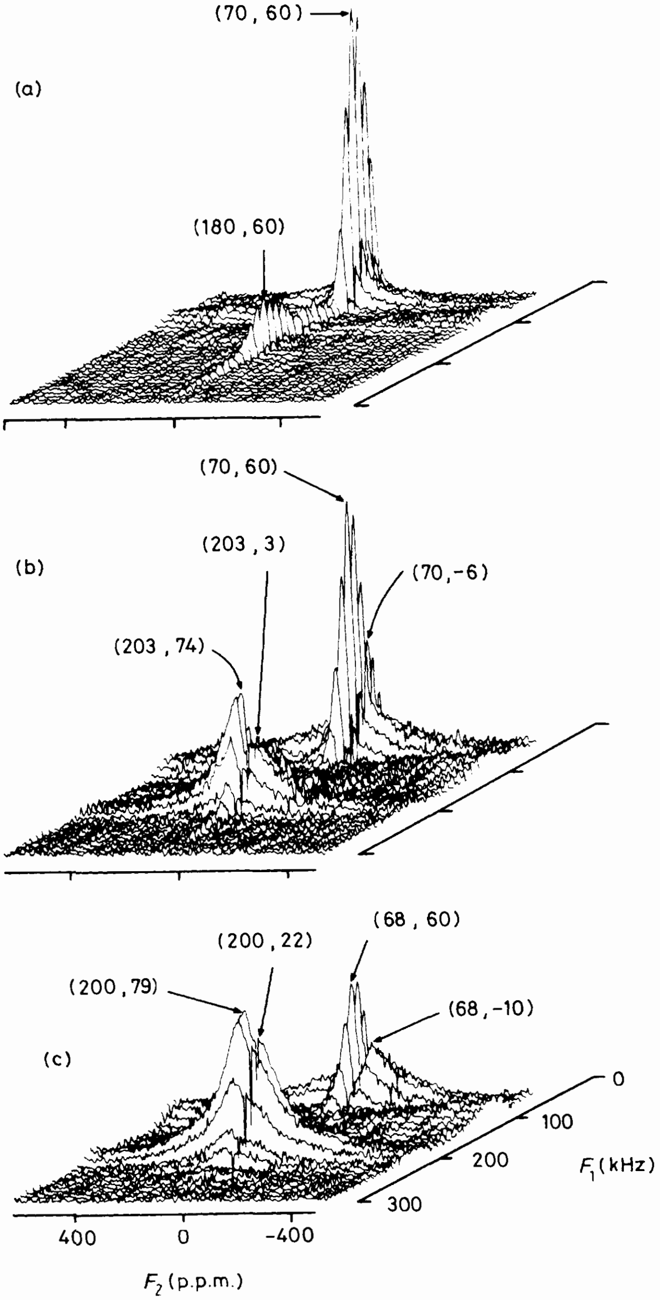

Figure 2. Static ^{27}Al quadrupole nutation spectra of (a) the starting material (sample 0); (b) sample 1; and (c) sample 6. Numbers in parentheses have units of kHz (for F_1) and p.p.m. (for F_2), respectively.

spectra were obtained using an aluminium-free probehead and 100 mg of sample. 20 000 and 5000 scans were accumulated for the pulse lengths of $\pi/20$ and $\pi/6$ respectively, with a recycle delay of 0.2 s and spectral width of 125 kHz. Instrumental deadtime was 12 µs. The duration of $\pi/2$ pulse (9 µs) and the chemical shifts were determined with an aqueous solution of $Al(NO_3)_3$.

We have also used ^{27}Al quadrupole nutation n.m.r.[8,9,15] to monitor the status of Al during thermal treatment of the sample. In this technique, a series of free induction decays during the interval t_2 is acquired using powerful resonant radiofrequency pulses while monotonically increasing the length, t_p, of the pulse. Double Fourier transformation in t_2 and t_p gives a two-dimensional (2D) n.m.r. spectrum (in the magnitude mode) with the axes F_2 (containing combined chemical shift and the second-order quadrupole effects) and F_1 (containing quadrupolar information only). The technique permits ^{27}Al sites with different quadrupole coupling constants to be resolved along F_1. Quadrupole nutation spectra were acquired using a high-power static probehead with a 5 mm diameter horizontal solenoidal coil. The r.f. pulse length was increased in 1 µs increments from 1 to 64 µs, with a recycle delay of 0.2 s. The strength of the pulse was $\omega_{rf}/2\pi = 70$ kHz.

The starting material was 80% NH_4-exchanged zeolite Y (Si/Al = 2.53). 5 g portions of the zeolite were heated in a tubular quartz furnace as follows. Sample 1 was brought from room temperature to 525 °C in the space of 30 min, whereupon the furnace was turned off; samples 2, 3, 4, 5, and 6 were kept at 525 °C for 0.25, 1, 2, 17 and 19 h, respectively, before being cooled down. Water was injected into the tube by a peristaltic pump so that the partial pressure of H_2O above the sample was 1 atmosphere.[10] The samples were finally hydrated over saturated NH_4NO_3, which is necessary for well developed n.m.r. signals to be observed.[11—13] During rehydration the protons of bridging hydroxy units co-ordinate to water and to non-framework Al to produce H_3O^+ and $Al(H_2O)_6{}^{3+}$ complexes, respectively, thus restoring symmetry to the Al.

Unit cell parameters, a_0, of the samples are listed in Table 1. It is clear that the framework shrinks during the treatment, while ^{29}Si m.a.s. n.m.r. indicates that the framework Si/Al ratio increases. The number of framework aluminium atoms per unit cell, Al_F, was determined using the relationship (3) between a_0 (in Å) and Al_F determined from ^{29}Si m.a.s. n.m.r.[14]

$$Al_F = 170.1\,(a_0 - 24.238) \qquad (3)$$

Static ^{27}Al n.m.r. spectra acquired with $\pi/20$ pulses are given in Figure 1 in the absolute intensity mode. Their integrated intensities in the range from 500 to −400 p.p.m. and relative to sample 0 refer to the same dry weight of each sample, and thus to the same number of Al atoms. For $\omega_{rf}t_p = \pi/20$, equations (1) and (2) give $F_{NS}/F_S = 1.03$, which means that the intensity from samples 1—6 (for which the excitation is selective, because of much larger quadrupolar interactions) should be only 3% lower than from sample 0 (where the excitation is non-selective). In practice, the intensity in sample 1 is 7% below that of sample 0, and there is some further loss of intensity in more strongly dealuminated samples. The reason is the experimental deadtime, which is more critical for broad n.m.r. signals. This effect can be minimized by a careful probe design and by using m.a.s. n.m.r., provided that samples are spun fast enough to narrow the very broad (18 kHz) lineshape. Such spinning speeds have recently become available. On the other hand, when spectra were acquired using $\pi/6$ r.f. pulses (not shown), there was a 40% loss of intensity between samples 0 and 1, and an even more dramatic loss for samples 2—6. Results from samples treated at 700 °C instead of 525 °C were very similar.

We must now assign the various spectral features to aluminium in different chemical environments in the sample. The position of the signals in 2D spectra is described using the axes F_1 (labelled in kHz) and F_2 (in p.p.m.). The spectrum of sample 0 [Figure 2(a)], which contains only one kind of Al site, is composed of two signals at (70 kHz, 60 p.p.m.) and (180, 60), both with the same linewidth in the F_2 dimension. The presence of the second signal in the sample containing only *one* kind of Al is due to the fact that the quadrupole interaction characteristic of the framework Al and the strength of the r.f. pulse are of the same order of magnitude.[15] On the other hand, the spectrum of sample 1 [Figure 2(b)] consists of *four* peaks: at (70 kHz, 60 p.p.m.), (70, −6), (203, 74), and (203, 3). As in Figure 2(a), the first signal corresponds to framework Al, and the second to mobile Al species in an octahedral environment. The positions of the other two signals (one relatively sharp and one very broad) clearly indicate that the associated Al is in a strongly asymmetric environment: their frequency along F_1 is almost exactly three times that for the first signal ($\zeta = 3$, and theory shows that there should be a three-fold difference in peak displacement for the two kinds of excitation). The spectrum of sample 6 [Figure 2(c)] also consists of four signals: at (68 kHz, 60 p.p.m), (68, −10), (200, 79), and (200, 22). The signal corresponding to framework Al peak has decreased in intensity in comparison with Figure 2(b), because sample 6 is more highly dealuminated than sample 1. The sharp peak of the mobile Al has disappeared, but a broad NF octahedral peak remains. The third signal has also decreased in intensity in comparison with the fourth. The fourth signal must therefore correspond to NF aluminium.

The spectra cannot be rationalized by assuming that the lineshape and linewidth of n.m.r. signals from framework Al in samples 1—6 is the same as in the starting material.

Table 1. Preparation and properties of dealuminated samples. % Al_{NF} (apparent) is the fraction of non-framework Al calculated from ^{27}Al spectra assuming that the lineshape and linewidth of the line from the *framework* is the same as in sample 0.

		X.r.d.		^{29}Si M.a.s. n.m.r.			^{27}Al N.m.r.
Sample	Heated for t/h	a_0/Å	Al_F	Si/Al	Al_F	% Al_{NF}	% Al_{NF} (apparent)
0	—	24.71	51	2.53	54	0	0
1	0	24.60	39	4.00	38	30	80
2	0.25	24.59	38	3.91	39	28	84
3	1	24.60	39	4.43	35	35	91
4	2	24.51	29	5.33	30	44	93
5	17	24.47	25	6.02	27	50	92
6	19	24.45	23	6.19	27	50	93

Deconvolution of the ^{27}Al spectra would then give the *apparent* relative amounts of NF aluminium, $\mathrm{Al_{NF}}$, listed in the last column of Table 1. These are incompatible with the reliable information from ^{29}Si n.m.r. and *X*-ray powder diffraction (x.r.d), both of which indicate the presence of much less NF aluminium. It is also shown in Figure 2(c) that the intensity of the signal at (68 kHz, 60 p.p.m.) is insufficient to account for all the framework aluminium, which amounts to 50% of that in the parent sample, and we have shown that all the aluminium is observable. The conclusion is that one of the two peaks located at 200 kHz along F_1 in Figures 2(b) and 2(c) represents Al *tetrahedra* which are distorted following the hydrothermal treatment. This is in agreement with the report[16] that while ^{29}Si n.m.r. and x.r.d. show that substantial dealumination of the zeolite framework has taken place, ^{27}Al m.a.s. n.m.r. does not detect any decrease in the amount of tetrahedral aluminium. This is because signals corresponding to the same nuclear species in environments of different electric field gradient often overlap in conventional n.m.r. spectra as a result of the shifting of line position by the second-order quadrupole interaction.

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