Correct Determination of Aluminium in Y Zeolites by Magic-angle Spinning N.m.r. Spectroscopy

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When Y zeolites are impregnated with ethanolic acetylacetone, the ^{29}Si and ^{27}Al magic-angle spinning n.m.r. spectra can be used to determine the correct Si/Al framework ratios and to quantify the amount of extra-framework aluminiums; evidence suggests that this impregnation does not cause further dealumination of the zeolitic material.

^{29}Si and ^{27}Al magic-angle spinning (m.a.s.) n.m.r. spectroscopy is a unique technique providing direct information on the local environment of these nuclei in zeolite structures.[1] From ^{29}Si n.m.r. studies the Si/Al framework ratio can be quantified and from ^{27}Al n.m.r. data discrimination between tetrahedral framework and octahedral non-framework species is possible (the two species have resonances at *ca.* 60 and 0 p.p.m., respectively).[1] As the tetrahedral Al atoms and the associated hydroxy protons constitute the active sites in many catalytic reactions,[2] careful control and quantitative knowledge of the Al concentration is essential. In hydrothermally dealuminated faujasite the values for non-framework Al, obtained from ^{27}Al spectra are systematically lower than those calculated from the difference between chemical analysis and framework Al measured from ^{29}Si n.m.r. studies.[3] As ^{29}Si m.a.s. n.m.r. spectroscopy seems to be a reliable quantitative method to detect Al in the framework, it follows that a part of the non-framework aluminium is missing in the ^{27}Al spectra. The pulse length, the magic angle setting, or the pulse recycle time do not have any influence on the appearance of the missing Al.[3]

It has been reported that some of this lacking non-framework Al can be made visible after impregnation of the sample with a solution of acetylacetone (acac) in ethanol. This technique, described by Klinowski *et al.*,[3] has been used by Bosacek *et al.*[4] in combination with stationary wide-line ^{27}Al n.m.r. spectroscopy. They reported the existence of an extremely long transient period before the ^{27}Al (6-coordinate) signal showed a constant intensity. This can be easily explained as acetylacetone is able to extract lattice aluminium from NaY zeolites.[5]

We report here that only after short contact times of Y-type zeolites and some of their steamed analogues with acac, can the intensities of the ^{29}Si and ^{27}Al MAS n.m.r. lines be utilized to determine correct Si/Al framework ratios and to quantify exactly the amount of extra-framework Al present.

The Y zeolite samples used were 90% NH_4-exchanged NaY zeolite (sample 1), treated with 1 bar (1×10^5 N m^{-2}) of steam for 1 h at 823 K (sample 2), or at 973 K (sample 3). The three air-dry samples were subjected to two different treatments: saturation with water, or impregnation with acac. The hydration was performed by immersing the powder in water (2 ml water on 1 g zeolite). For the acac impregnation, the air-dry samples were covered with acac in ethanol (38 : 62 v/v), so that the powdered zeolite was fully soaked with the solution (2 ml solution on 1 g powder). After 1 hour, these samples were dried again at room temperature in a stream of dry air. The n.m.r. measurements were performed using a Bruker 400 MSL spectrometer with a magnetic field of 9.4 T. The ^{29}Si and ^{27}Al m.a.s. n.m.r. spectra are shown in Figure 1, and some results are listed in Table 1. The complete hydration or impregnation with acac did not influence the ^{29}Si n.m.r. spectra of sample 1 [$(Si/Al)_{n.m.r.} = 2.43$]. Our treatment with diluted acetylacetone does not cause dealumination of the framework as no octahedral line (0 p.p.m.) in the corresponding ^{27}Al spectrum could be detected, even after storage times of several weeks. Some solutions of acac are known for their Al-extracting properties.[5] (NaY zeolites can be 30% dealuminated this way.)[5] After the steaming process, the ^{29}Si n.m.r. spectrum of sample 2 (A) contained three lines, in contrast with the four lines observed in the spectra after hydration (B), or impregnation with acac (C) (Figure 1). The Si(2Al) line at −96 p.p.m. of sample 2 (A) is broadened and covers a region where the Si(3Al) and Si(4Al) lines are observed in the spectra (B) and (C). This broadening could result from distortions of the T–O–T angles but also from distortions of the tetrahedral Al symmetry in the framework by cations in partially anhydrous material.[6,7] The effect is more pronounced for Si sites with a high degree of Al co-ordination and explains the differences in Si/Al ratio in Table 1. The similarity of the ^{29}Si spectra of (B) and (C) and their identical Si/Al ratios calculated from them confirm the non-dealuminating character of the acac treatment.

The appearance of the ^{27}Al n.m.r. spectra of sample 2 (Figure 1) depends strongly on the treatment following the steam process. No octahedral signal is observed, and the tetrahedral Al signal (61 p.p.m.) of sample 2 (A) is at least five times weaker than the corresponding line in (B) or (C) (the small peak at −30 p.p.m. is due to a background ^{27}Al signal of the n.m.r. probehead). The weakness of this signal is easily explained by the very strong quadrupole interactions between the tetrahedral Al sites and cations in the partially dehydrated sample. The intensity of the tetrahedral signal in sample 2 (B) and (C) is exactly the same, the line of (C) being somewhat broader than that of (B). The intensity of the octahedral peak is quite different; the acac treatment is clearly more efficient, permitting quantification of formerly invisible non-framework aluminium.

Qualitatively the same results are obtained in the case of sample 3 (Figure 1) except for the appearance of supplementary small lines in the ^{27}Al n.m.r. spectrum of the acac-treated powder in the octahedral region at −7.5 and −12.5 p.p.m. Knowing the original ratio of silicon to total aluminium (Si/Al) of the starting material (sample 1) from ^{29}Si n.m.r. data, the share of non-framework aluminium (Al^{NF}) in the steamed samples (samples 2 and 3) can be calculated from equation (1):[8] where Si/Al^{F} is determined from the ^{29}Si spectrum of the

$$Al^{NF} = 1 - (Si/Al)/(Si/Al^{F}) \qquad (1)$$

steamed sample and Al^{F} represents the framework Al. The total aluminium content (Al) is equal to $Al^{NF} + Al^{F}$, and Si/Al can be determined directly from chemical analysis of the steamed samples.

The amount of non-framework aluminium, determined by both ^{29}Si and ^{27}Al n.m.r., is listed in Table 1.

It is clear from these results that only the samples treated with dilute acetylacetone solution give ^{27}Al m.a.s. n.m.r. spectra which can be reliably used for quantitative interpretation, and consequently give values for Al^{NF} which are close to those obtained from ^{29}Si n.m.r. spectra. It is important to note that the full intensity of the octahedral ^{27}Al line in the acac-treated sample is only reached 3 hours after the impregnation after which time it stabilises. This suggests that the acac needs some time to form Al complexes within the pore structure of the zeolite. Bosacek *et al.*[4] used stationary wide-line ^{27}Al n.m.r. studies for their acac-treated samples and found a long-term change (3 months) in the intensity of

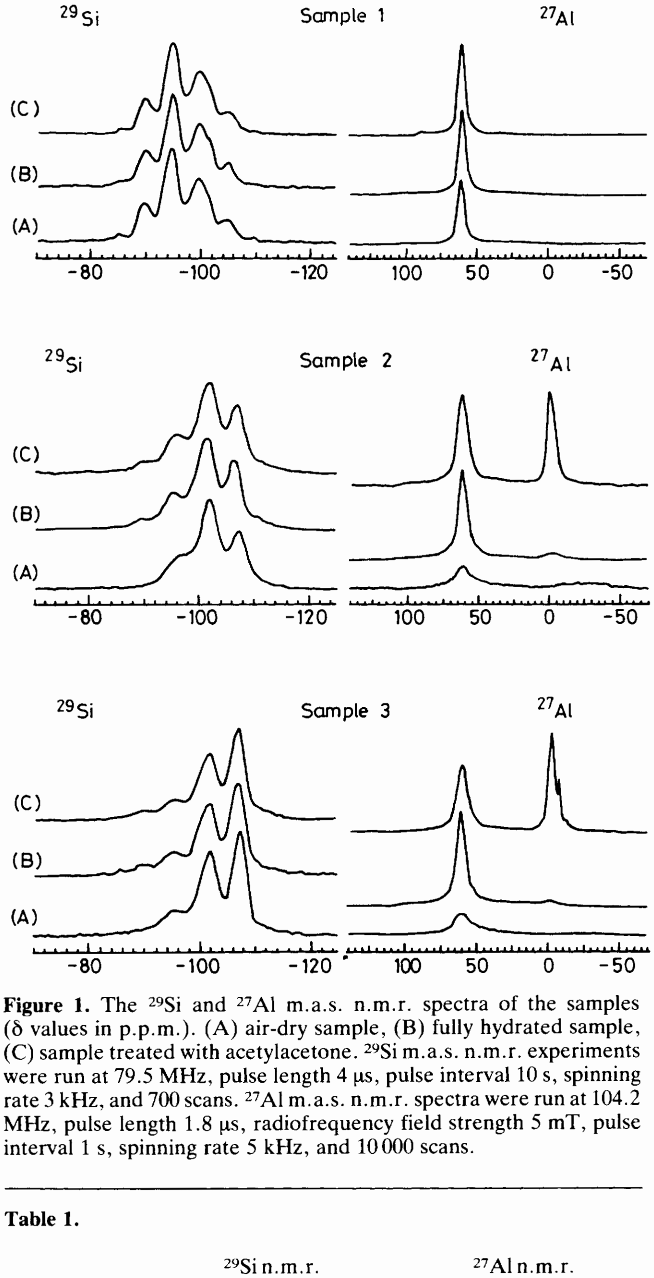

Figure 1. The ^{29}Si and ^{27}Al m.a.s. n.m.r. spectra of the samples (δ values in p.p.m.). (A) air-dry sample, (B) fully hydrated sample, (C) sample treated with acetylacetone. ^{29}Si m.a.s. n.m.r. experiments were run at 79.5 MHz, pulse length 4 μs, pulse interval 10 s, spinning rate 3 kHz, and 700 scans. ^{27}Al m.a.s. n.m.r. spectra were run at 104.2 MHz, pulse length 1.8 μs, radiofrequency field strength 5 mT, pulse interval 1 s, spinning rate 5 kHz, and 10 000 scans.

Table 1.

	^{29}Si n.m.r.		^{27}Al n.m.r.	
	Si/Al^{F}	% Al^{NF}	% Al^{F}	% Al^{NF}
Sample 1	2.43			
Sample 2				
A	4.4	45	100	0
B	4.0	39	87	13
C	4.0	39	58	42
Sample 3				
A	5.8	58	100	0
B	4.8	49	97	3
C	4.8	49	52	48

the octahedral ^{27}Al line. As they left the acac solution in contact with their samples we suppose that in their case a rapid appearance of the formerly invisible non-framework ^{27}Al line occurred followed by a slower increase of the same line due to further dealumination of the framework. This explains the two time-dependent processes which they observed.[4]

One can speculate on the possible status of the 'invisible' aluminium. It cannot be attributed to non-framework Al cations; in that case the full intensity of the octahedral line should appear on hydrating the sample. Perhaps this n.m.r.-invisible aluminium has to be associated with aluminium in polymeric species with large quadrupole interactions, as suggested by Klinowski *et al.*;[2] these species are converted into visible Al complexes by acac impregnation. Indeed, sample 3 (C) shows several peaks in the octahedral region which might be indicative of the presence of some $Al(acac)_3$.

Our impregnation method with acetylacetone proves to be a a useful method of quantifying the ratio of all aluminium species in the ^{27}Al m.a.s. n.m.r. spectra in hydrothermally dealuminated Y zeolites. It solves the problem of observed discrepancies between ^{29}Si and ^{27}Al m.a.s. n.m.r. measurements. Recently we have applied this acac-impregnation method to very strongly hydrothermally dealuminated Y zeolites as well as other dealuminated zeolites (cf. refs. 8 and 9). We believe that our method should be generally applicable to zeolites.

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References

1 J. Klinowski, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1984, **16**, 237.

2 W. O. Haag, R. M. Lago, and P. B. Weisz, *Nature (London)*, 1984, **309**, 589.

3 J. Klinowski, C. A. Fyfe, and G. C. Gobbi, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 3003.

4 V. Bosacek, D. Freude, T. Fröhlich, H. Pfeifer, and H. Schmiedel, *J. Colloid Interface Sci.*, 1982, **85**, 502.

5 R. Beaumont and D. Barthomeuf, *J. Catal.*, 1972, **27**, 45.

6 P. J. Grobet, W. J. Mortier, and K. Van Genechten, *Chem. Phys. Lett.*, 1985, **119**, 361.

7 A. J. Vega and Z. Luz, *J. Phys. Chem.*, 1987, **91**, 365.

8 A. Samoson, E. Lippmaa, G. Engelhardt, U. Lohse, and H.-G. Jerschkewitz, *Chem. Phys. Lett.*, 1987, **134**, 589.

9 J.-P. Gilson, G. C. Edwards, A. W. Peters, K. Rajagopalan, R. F. Wormsbecher, T. G. Roberie, and M. P. Shatlock, *J. Chem. Soc., Chem. Commun.*, 1987, 91.