^{27}Al Solid-state NMR Spectra of Ultrastable Zeolite Y with Fast Magic-angle Spinning and ^{1}H–^{27}Al Cross-polarization

João Rocha and Jacek Klinowski

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

Fast (>12 kHz) magic-angle-spinning NMR with ^{1}H–^{27}Al cross-polarization quantitatively monitors several aluminous species in dealuminated zeolite Y; the non-framework matter contains 4-, 5- and 6-coordinated Al and the ^{27}Al signal at 30 ppm is an independent resonance probably due to 5-coordinated non-framework Al and not part of a second-order quadrupole lineshape as previously reported.

Since Brønsted acid groups in zeolites are associated with 4-coordinated framework aluminium, their catalytic activity strongly depends on the concentration and location of Al in the structure. Upon hydrothermal treatment of zeolite NH_4-Y, the process known as 'ultrastabilization,'[1,2] part of the aluminium is ejected from the framework into the intracrystalline space, and the framework vacancies are reoccupied by silicon from other parts of the crystal. As a result, thermal stability of the zeolite is greatly increased, so that the product retains crystallinity at temperatures in excess of 1000 °C. Ultrastable faujasitic catalysts, better suited for hydrocracking reactions than the 'as-prepared' zeolites, are a cornerstone of the petroleum industry, and much effort has been devoted to the study of their properties and methods of preparation.

Ultrastable zeolite Y has been extensively examined by ^{29}Si and ^{27}Al solid-state NMR.[3–9] ^{29}Si magic-angle-spinning (MAS) NMR can measure directly the *framework* Si/Al ratio of thermally treated samples, while ^{27}Al MAS NMR shows how 6-coordinated non-framework Al species build up at the expense of the 4-coordinated framework Al as the calcination temperature is increased. However, the precise nature of non-framework aluminium entities, which are amorphous and subject to large second-order quadrupolar interactions, is unknown. It has been shown that special care needs to be taken to obtain quantitatively reliable spectra of non-framework aluminium in zeolites.[5,6] More recently, quadrupole nutation ^{27}Al NMR has provided information about the coordination number of non-framework aluminium, but the actual compounds present in the intracrystalline space have not been identified.[4–7] We demonstrate that very fast MAS combined with ^{1}H–^{27}Al cross-polarization (CP) makes it possible to gain further insights into the chemical status of non-framework Al species.

Our starting material was 80% NH_4-exchanged zeolite Y with Si/Al = 2.41 (sample 1) prepared by three-fold contact of Na-Y with a saturated aqueous solution of NH_4NO_3 at 80 °C followed by washing with water. The zeolite was heated in a tubular quartz furnace at 550 °C for 2 hours under deep-bed conditions with water being slowly injected into the tube by a peristaltic pump so that the partial pressure of H_2O above the zeolite was 1 atm. The product (sample 2) was cooled and re-exchanged with NH_4NO_3. Samples 3, 4, 5 and 6 were prepared by second calcination at 650–750 °C. Sample 7 was steamed at 825 °C for 2 hours, and is the same as sample A7 in ref. 3. The samples were finally hydrated in a desiccator with saturated NH_4NO_3. Powder XRD patterns were collected on a Philips automatic diffractometer fitted with a vertical goniometer using Cu-Kα radiation. Framework $(Si/Al)_{NMR}$ ratios of the samples were calculated from ^{29}Si MAS NMR.[3]

^{27}Al MAS NMR spectra were recorded on a Bruker MSL-400 multinuclear spectrometer at 104.26 MHz (9.4 T) using very short, 0.6 µs (equivalent to $\pi/20$) radiofrequency pulses[5,6] and 0.5 s recycle delays. MAS rotors were spun in air at 12–13 kHz. ^{1}H–^{27}Al CP MAS spectra were measured with a single contact, optimized contact time of 300 µs, ^{1}H $\pi/2$ pulse of 3.5 µs and spinning rates of 7–9 kHz. The Hartmann–Hahn condition was matched in one scan on a sample of high quality kaolinite under similar conditions. Because only the central $(+1/2 \longleftrightarrow -1/2)$ transition is observed, excitation in the ^{1}H–^{27}Al CP MAS experiment is selective and thus the Hartman–Hahn condition is $3\ \gamma_{Al}B_{Al} = \gamma_{H}\ B_{H}$.[6] Chemical shifts are quoted in ppm from external aqueous $Al(NO_3)_3$.

^{27}Al MAS NMR spectra of zeolite Na-Y and steamed samples 2–6 with increasing degrees of dealumination are shown in Fig. 1. The spectrum of zeolite Na-Y (sample 1) consists of a single sharp signal at *ca.* 60 ppm due to 4-coordinated Al in the zeolitic framework (Al^{F}). Hydrothermally treated samples give two further signals at *ca.* 0 and 30 ppm, associated with non-framework Al species (Al^{NF}). The intensity of Al^{NF} signals, particularly that at 30 ppm, increases with increasing degree of dealumination, while the intensity of the Al^{F} signal decreases. In addition, a very broad peak, extending from *ca.* 200 to *ca.* −180 ppm and responsible for the raised spectral baseline, grows with the degree of dealumination. At moderate spinning rates (<8 kHz) the broad signal is more prominent, while the intensities of both

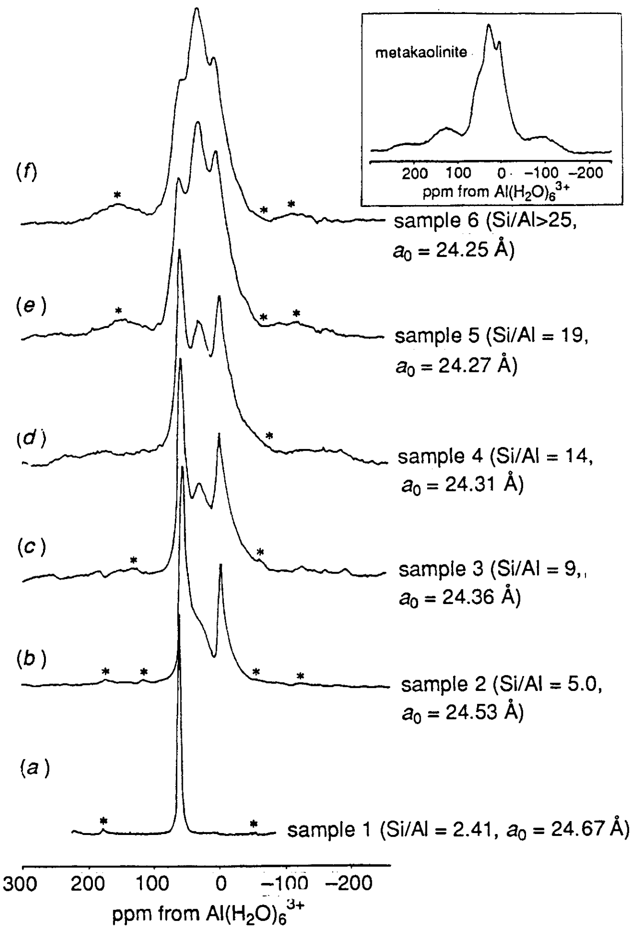

Fig. 1 ^{27}Al MAS NMR spectra of (*a*) zeolite NaY and (*b*)–(*f*) increasingly dealuminated zeolite HY recorded at spinning rates of 12–13 kHz. The Si/Al ratios calculated from ^{29}Si MAS NMR spectra and the unit cell parameters, a_0, are indicated. For comparison with (*e*) and (*f*), the inset shows the spectrum of metakaolinite, prepared by calcining the clay mineral kaolinite at 600 °C. Asterisks denote spinning sidebands.

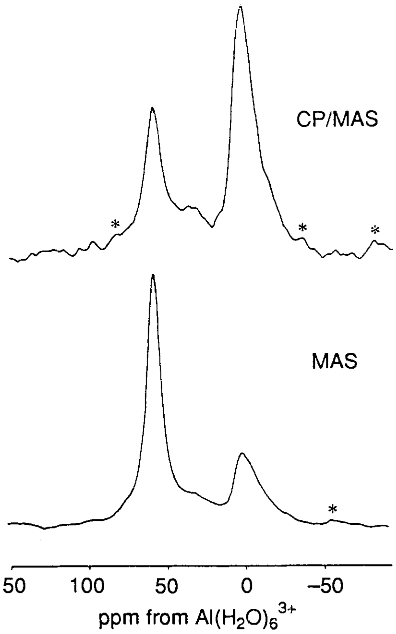

Fig. 2 ^{27}Al MAS and ^{1}H–^{27}Al CP MAS NMR spectra of sample 7 with $(\mathrm{Si/Al})_{\mathrm{NMR}} = 4.8$ and $a_0 = 24.50$ Å. The spectrum was recorded with a contact time of 30 μs, recycle delay of 1 s and at a spinning rate of 9 kHz.

$\mathrm{Al^{NF}}$ signals decrease relatively to the intensity of the $\mathrm{Al^F}$ signal. This indicates that the broad signal is associated with $\mathrm{Al^{NF}}$ and that a quantitative treatment of the ^{27}Al MAS NMR spectra of dealumianted zeolite Y requires fast (>12 kHz) MAS. We were struck by the similarity between the ^{27}Al MAS NMR spectrum of metakaolinite[10] (see inset in Fig. 1), the dehydroxylate of the clay mineral kaolinite, $\mathrm{Si_2O_5(OH)_4Al_2}$, and the spectrum of highly dealuminated zeolite Y (sample 6).

^{27}Al quadrupole nutation NMR[4] suggests that the $\mathrm{Al^{NF}}$ signal at *ca.* 30 ppm has a large quadrupolar coupling constant (>6 MHz) for dealuminated samples with $(\mathrm{Si/Al})_{\mathrm{NMR}}$ ratios between 5.2 and 20. Samoson *et al.*[4] concluded that it is not an independent resonance but the low-frequency component of a second-order quadrupolar lineshape, the high-frequency counterpart of which overlaps with the $\mathrm{Al^F}$ signal at *ca.* 60 ppm. However, others[8–10] assigned resonances in the range 27–30 ppm in aluminosilicates to 5-coordinated Al. In order to elucidate the nature of $\mathrm{Al^{NF}}$ we have recorded ^{1}H–^{27}Al CP MAS NMR spectra of samples of the dealuminated samples. Fig. 2 clearly shows that the intensity of the signals at 0 and 30 ppm increases relative to the signal at 60 ppm. This indicates that the 30 ppm signal is a separate ^{27}Al resonance, possibly due to 5-coordinated Al. Furthermore, the position of NMR signals in ^{27}Al MAS NMR spectra reported in ref. 4, recorded at the higher field of 11.7 T (as opposed to 9.4 T in the present study), is the same at 0, 30 and 60 ppm. Computer simulations indicate that increasing B_0 should decrease the distance between the two components of a second-order quadrupolar lineshape. Since the distance between peaks is unchanged, we conclude that they correspond to independent resonances.

The CP spectrum of zeolite Na-Y (not shown) contains two very faint signals at 61 and 9 ppm, presumably due to a small amount of impurity. These signals are an order of magnitude weaker than the signals in the spectrum of dealuminated Y shown in Fig. 2. A signal at *ca.* 60 ppm is clearly seen in the ^{1}H–^{27}Al CP MAS spectrum of dealuminated zeolite Y, probably associated with 4-coordinated non-framework Al. The possibility that two (or more) ^{27}Al resonances overlap at *ca.* 60 ppm must therefore be considered. In fact, quadrupole nutation studies have previously given some support for the presence of 4-coordinated $\mathrm{Al^{NF}}$ in dealuminated zeolite Y.[4–7] We are using quadrupole nutation NMR with fast MAS and very strong radiofrequency fields in tandem with ^{1}H–^{27}Al CP MAS NMR to clarify this problem.

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References

1 C. V. McDaniel and P. K. Maher, in *Molecular Sieves*, Society of Chemical Industry, London, 1968, p. 186; in *Zeolite Chemistry and Catalysis*, ACS Monograph 171, 1976, p. 285.

2 D. W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry and Use*, Wiley, London, 1974.

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

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

5 P. P. Man and J. Klinowski, *Chem. Phys. Lett.*, 1988, **147**, 581; *J. Chem. Soc., Chem. Commun.*, 1988, 1291.

6 P. P. Man, J. Klinowski, A. Trokiner, H. Zanni and P. Papon, *Chem. Phys. Lett.*, 1988, **151**, 143.

7 H. Hamdan and J. Klinowski, *J. Chem. Soc., Chem. Commun.*, 1989, 240.

8 J. 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.

9 L. B. Alemany and G. W. Kirker, *J. Am. Chem. Soc.*, 1986, **108**, 6158.

10 J. Rocha and J. Klinowski, *Phys. Chem. Min.*, 1990, **17**, 179.