

## A $^{27}\text{Al}$ NMR Study of the Interaction of Water with $\text{AlPO}_4\text{-11}$

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Spectral simulations of  $^{27}\text{Al}$  MAS and double rotation (DOR) NMR spectra measured at 7.0 T prove the preferential hydration of one tetrahedral Al site in  $\text{AlPO}_4\text{-11}$ , transforming this site reversibly into octahedral aluminium.

$\text{AlPO}_4\text{-11}$  is built of alternating  $\text{AlO}_4^-$  and  $\text{PO}_4^+$  tetrahedra linked together *via* joined oxygen atoms to form a microporous three-dimensional network with a uni-dimensional pore system of  $4.4 \times 6.7 \text{ \AA}$ . In recent literature, some discrepancies arose concerning the nature of water adsorption by this important molecular sieve. Meinhold and Tapp<sup>1</sup> observed that  $\text{AlPO}_4\text{-11}$  reversibly adsorbs water. X-Ray diffraction measurements indicated that upon hydration the crystal symmetry changes from body-centred orthorhombic

( $a = 13.54, b = 18.51, c = 8.37 \text{ \AA}$ ) to primitive orthorhombic ( $a = 13.54, b = 18.02, c = 8.12 \text{ \AA}$ ) within two hours. With  $^{27}\text{Al}$  MAS NMR significant differences were noticed between the dry and the wet samples, however, no octahedral aluminium was reported. IR measurements indicated the presence of physisorbed water only.

Barrie *et al.*<sup>2</sup> studied hydrated  $\text{AlPO}_4\text{-11}$  using  $^{27}\text{Al}$  MAS and DOR NMR at 9.4 and 11.7 T. The MAS spectrum at 9.4 T of the hydrated sample (five crystallographically different

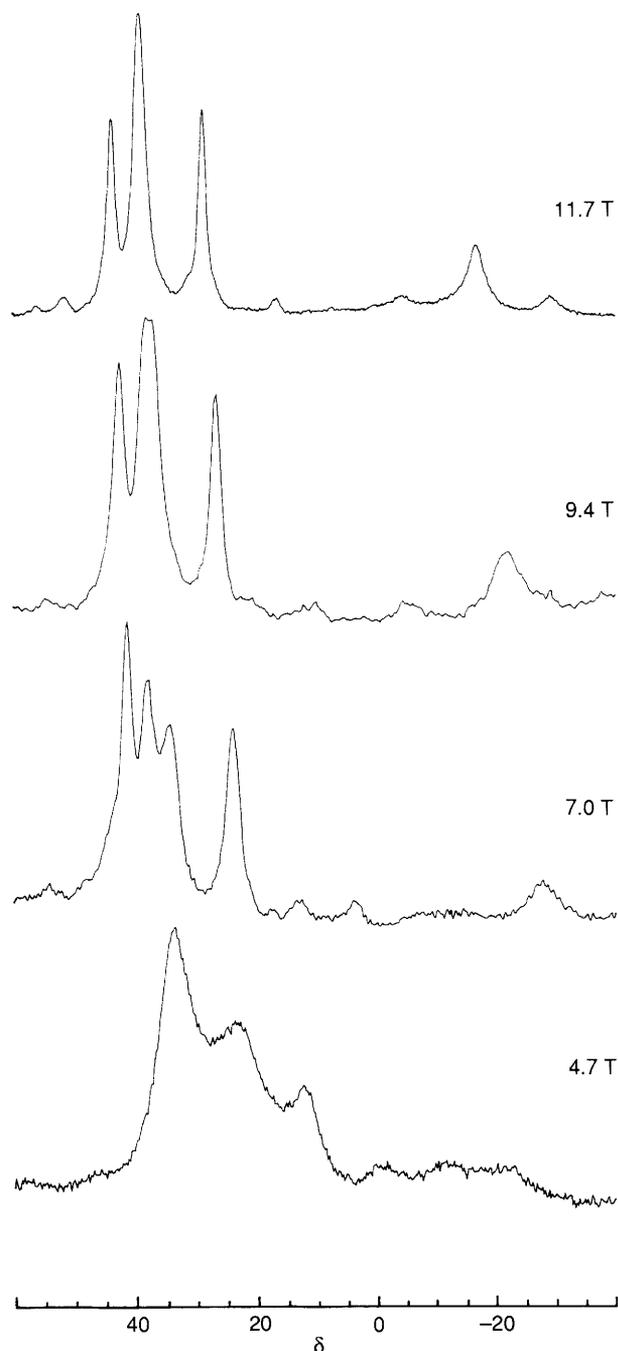


Fig. 1  $^{27}\text{Al}$  DOR NMR spectra at different magnetic fields

T-sites) showed three peaks in the tetrahedral region with intensity ratios of 21.3 : 60.2 : 18.5, together with an octahedral signal (approximately 20% of the total area). To simulate the tetrahedral region of the MAS spectra at 9.4 T, five signals were needed. DOR NMR resulted in a significant decrease of the linewidths of two resolved peaks in the tetrahedral region while the linewidth of the octahedral signal did not decrease. This led to the conclusion that all five aluminium sites are hydrated to about the same extent.

Recently Prasad *et al.*<sup>3</sup> reported the preferential adsorption of water on the  $\text{T}_3$  site (located at the junction of 6-, 6-, 10-membered rings) according to MNDO calculations. On the basis of these calculations both the  $^{27}\text{Al}$  and  $^{31}\text{P}$  MAS NMR spectra were interpreted.

Here we report  $^{27}\text{Al}$  DOR NMR experiments of wet  $\text{AlPO}_4\text{-11}$  at 4.7, 7.0, 9.4 and 11.7 T as well as  $^{27}\text{Al}$  MAS NMR

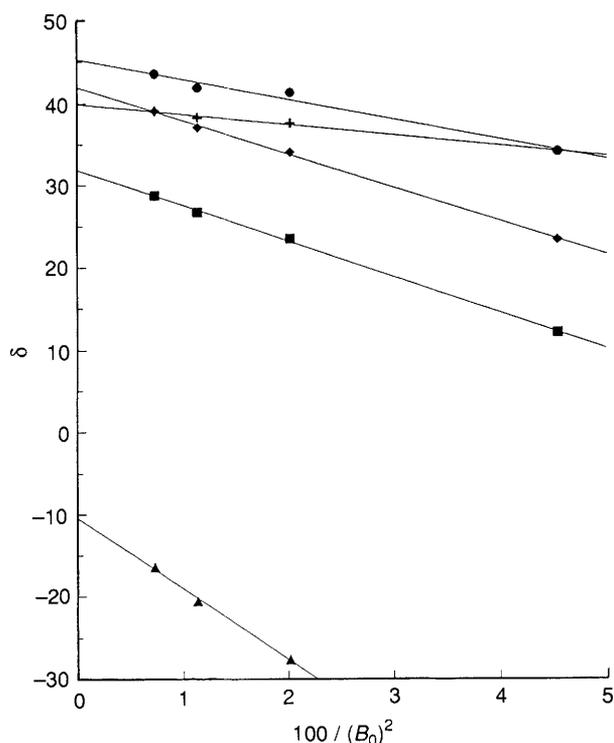


Fig. 2  $^{27}\text{Al}$  NMR peak positions as a function of  $1/(B_0)^2$ . No octahedral signal could be observed at 4.7 T.

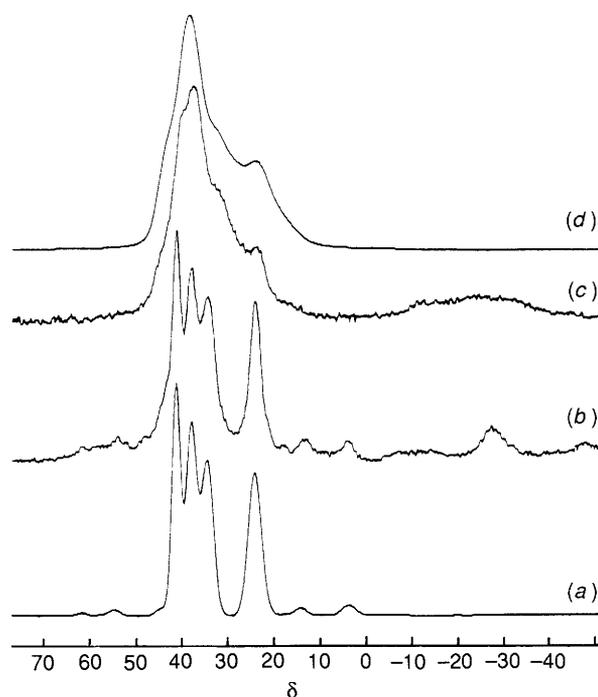


Fig. 3  $^{27}\text{Al}$  NMR spectra of wet  $\text{AlPO}_4\text{-11}$  at 7.0 T: DOR simulation (a), DOR spectrum (b), MAS spectrum (c) and MAS simulation (d)

at 7.0 T. We reinterpret the  $^{27}\text{Al}$  NMR spectra based on spectral simulations of both  $^{27}\text{Al}$  MAS and DOR NMR spectra. The results can be reconciled with the calculations of Prasad *et al.*<sup>3</sup>

The  $^{27}\text{Al}$  DOR NMR spectra of fully hydrated  $\text{AlPO}_4\text{-11}$  at various magnetic fields are given in Fig. 1. The peak positions shift with changes in the external magnetic field. The DOR spectrum measured at 7.0 T yields the best line separation. Here, four distinct peaks in the tetrahedral region are observed together with an octahedral signal. The observed shifts of the  $^{27}\text{Al}$  DOR NMR lines are inversely proportional

**Table 1** Quadrupolar parameters used for the simulation

| Isotropic chemical shift, $\delta$ ( $\pm 0.15$ ) | Relative area (%) ( $\pm 1.5$ ) | $e^2qQ/h$ (MHz) ( $\pm 0.02$ ) | $\eta$ ( $\pm 0.05$ ) |
|---|---------------------------------|--------------------------------|-----------------------|
| 46.1  | 25                              | 2.23                           | 0                     |
| 42.1  | 25                              | 2.69                           | 0.5                   |
| 40.8  | 25                              | 1.63                           | 0.5                   |
| 32.6  | 25                              | 2.63                           | 0.95                  |

to  $(B_0)^2$ ,<sup>4</sup> see Fig. 2. Extrapolation of the chemical shifts to infinite magnetic field yields the isotropic chemical shifts at  $\delta$  32.6, 40.8, 42.1 and 46.1.

The DOR and MAS NMR spectra at 7.0 T were simulated with the program QNMR.<sup>5</sup> Centres of gravity were taken from the DOR spectrum at 7.0 T. Combination of the centres of gravity and the isotropic shifts yield information regarding the quadrupolar interaction parameters  $e^2qQ/h$  and  $\eta$ . Simulation of the MAS spectra allows the determination of the two parameters separately. MAS and DOR spectral simulations were performed using four peaks with equal areas in the tetrahedral region. The results of the DOR and MAS NMR simulations are shown in Fig. 3. The octahedral aluminium site caused a signal with an equal area. The parameters used for the simulations are listed in Table 1.

On the basis of these experiments we feel that we have presented unambiguous proof of the preferential hydration of one of the aluminium sites, transforming this site into octahedrally coordinated aluminium. More details will follow after the assignments of the isotropic  $^{27}\text{Al}$  NMR shifts and/or quadrupolar parameters to the five specific lattice positions in hydrated AlPO-11.

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