Multiple-quantum ^{27}Al MAS NMR spectroscopy of microporous aluminium methylphosphonate AlMepO-β

Joaõ Rocha,*[a] Zhi Lin,[a] Christian Fernandez[b] and Jean-Paul Amoureux[b]

[a] *Department of Chemistry, University of Aveiro, 3810 Aveiro, Portugal*
[b] *Laboratoire de Dynamique et Structure des Matériaux Moléculaires, CNRS URA 801, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex, France*

Multiple-quantum MAS NMR spectroscopy yields highly resolved ^{27}Al spectra of the unique microporous framework aluminium methylphosphonate (AlMepO-β), confirming the proposed crystal structure.

In the last decade much effort has been devoted to the synthesis of novel microporous aluminophosphates (ALPOs) with zeolite-type structures.[1,2] ALPOs contain Al atoms coordinated to four framework oxygens. In certain structures Al may be five- or six-coordinate but the extra ligands are usually water molecules which reside in the pores and channels of the ALPO, not in the framework. Recently, the synthesis and crystal structure of the first microporous inorganic–organic composite, aluminium methylphosphonate (AlMepO-β) was reported.[3] The skeleton of this remarkable material, built up of fused four-ring chains, forms unidimensional 18-ring channels of *ca.* 5.8 Å cross-section fringed with methyl groups. The asymmetric unit of AlMepO-β contains six crystallographically independent MePO$_3$ tetrahedra which share oxygen atoms at their corners with three adjacent Al atoms. Among the four independent Al atoms, three are four-coordinate and the fourth is six-coordinate, all of which are bound by phosphonates. Six-coordinate Al centres are still present in the framework structure of the dehydrated material.[4] These centres never occur in ALPOs. In view of the rather unusual structure of AlMepO-β we decided to carry out a detailed NMR study. The available ^{31}P MAS NMR results support the proposed structure.[4] The ^{27}Al MAS NMR spectrum (Fig. 1) displays only two peaks at δ 40.5 and -17.8, assigned to four and six-coordinate Al, respectively. Although the observed 3 : 1 intensity ratio of these resonances is expected if the structure of Maeda *et al.* is correct it would be useful to resolve the three resonances which are contained within the δ 40.5 peak. However, this is not a trivial matter since ^{27}Al is a spin 5/2 nucleus and the NMR lines are usually broadened by a second-order quadrupole interaction which is not completely removed by MAS.[5] Recently, multiple-quantum (MQ) MAS NMR spectroscopy has been shown to yield ^{27}Al spectra with unprecedented resolution.[6,7] The peak at δ 40.5 observed in the (single-quantum) 'normal' ^{27}Al MAS NMR spectrum (Fig. 1) is already relatively narrow (FWHM *ca.* 318 Hz) making the resolution of the three resonances contained within a very difficult task. This provides a unique opportunity for testing the power of the multiquantum technique in a real case study.

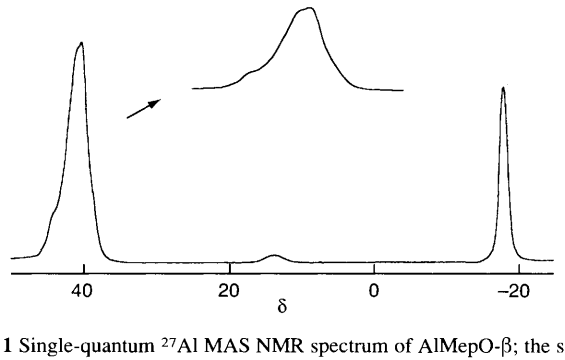

Fig. 1 Single-quantum ^{27}Al MAS NMR spectrum of AlMepO-β; the small peak at δ *ca.* 13 is due to a small amount of an amorphous impurity

The synthesis of AlMepO-β was based on the reported procedure.[4] The samples were characterized by powder X-ray diffraction and ^{13}C, ^{27}Al and ^{31}P solid-state NMR. 3Q and 5Q ^{27}Al MAS NMR spectra were recorded at 104.3 MHz on a Bruker MSL-400P spectrometer. To produce pure absorption lineshapes in the MQ MAS spectra the optimum conditions for excitation and transfer of the (±MQ) coherences using a simple two-pulse sequence were used.[8] The 4 mm rotors were spun at 14 kHz. The recycle delay was 1 s. The radiofrequency magnetic field amplitude was *ca.* 166 kHz. 512 points were acquired in the $t1$ dimension in increments of 13 (3Q) and 5 μs

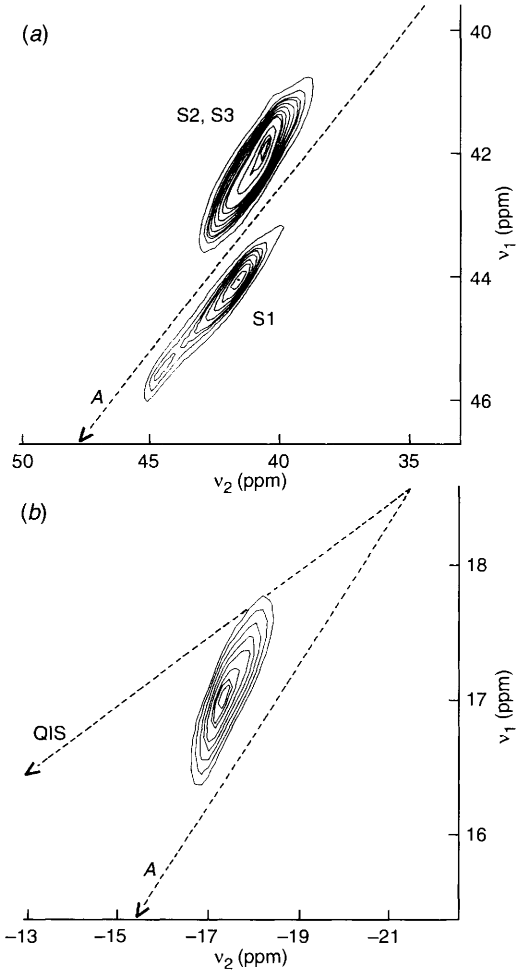

Fig. 2 (*a*) Tetrahedral and (*b*) octahedral regions of the 3Q ^{27}Al MAS NMR spectrum of AlMepO-β

(5Q). Chemical shifts are quoted in ppm relative to $Al(H_2O)_6^{3+}$.

The 3Q spectrum of AlMepO-β [Fig. 2(*a*)] displays two four-coordinate Al peaks while in the same range the 5Q spectrum [Fig. 3(*a*)] clearly contains three resonances. In the six-coordinate Al region both spectra display a single peak [Fig. 2(*b*), 3(*b*)]. The 5Q spectrum resolves all the four crystallographically independent sites expected on the basis of the structure of Maeda *et al.* and therefore validates it. The isotropic chemical shifts (δ_{iso}) and the 'second-order quadrupole effect' parameters (SOQUE) can be easily estimated from the 5Q spectrum:[8,9]

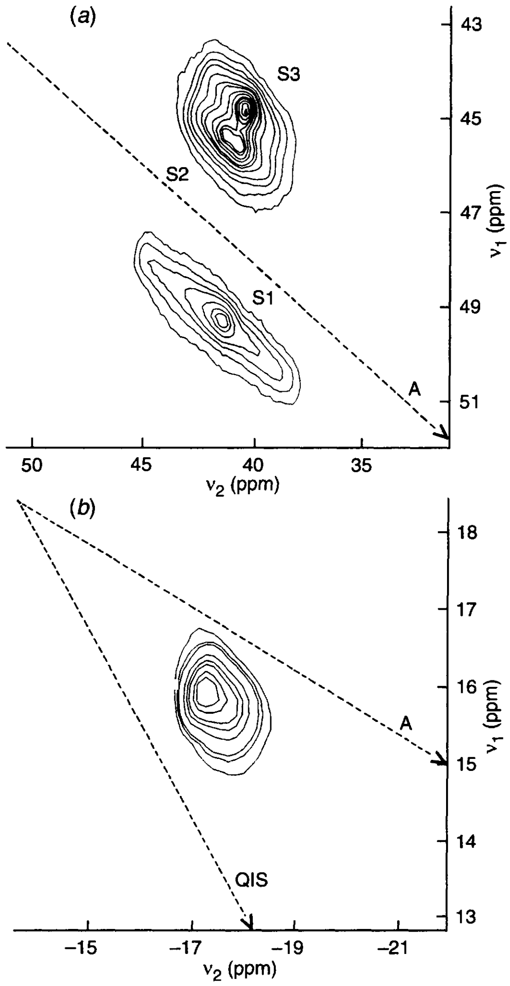

Fig. 3 (*a*) Tetrahedral and (*b*) octahedral regions of the 5Q ^{27}Al MAS NMR spectrum of AlMepO-β

$$\delta_{iso} = 4/9\ \delta_{g1} + 5/9\ \delta_{g2};$$

$$\mathrm{SOQUE}^2/\mathrm{MHz} = C_Q{}^2[1 + (\eta^2/3)] = -\ (\delta_{g2} - \delta_{iso})\ \upsilon_o{}^2/6000$$

where C_Q is the quadrupole coupling constant, η is the asymmetry parameter, υ_o the Larmor frequency and δ_{g1}, δ_{g2} (ppm) are the estimated centres of gravity of the two-dimensional lines. These equations yield for S3, S2 and S1 δ_{iso} of δ 42.3, 42.8 and 45.0, respectively, and C_Q of 1.6 ($\eta = 1$) to 1.9 ($\eta = 0$) MHz for S3, 1.7 to 2.0 for S2 and 2.2 to 2.5 MHz for S1. Thus, the S3 and S2 sites have very similar parameters and this explains why they are not resolved in the 3Q spectrum. The S1 site is clearly different from the two other sites.

Careful consideration of the local distortion of the three Al tetrahedra based on the O–Al–O bond angles derived from the structure of Maeda *et al.* shows that site Al4 is clearly more distorted than sites Al2 and Al3. Hence, we attribute peak S1 to Al4. The assignment of the other peaks is more difficult. We suggest that peak S2 is from Al2, since this site is slightly more distorted than Al3, while S3 is assigned to Al3.

These results illustrate the amazing resolution which can be obtained with 5Q MAS NMR. Consider again Figs. 2 and 3. It is seen that all the four-coordinate Al peaks are located along the anisotropic axes *A* (slopes 19/12 and −25/12 in the 3Q and 5Q spectra, respectively) and therefore correspond to unique undistributed sites. The six-coordinate site is not aligned with axis *A* nor with the 'quadrupole induced shift axis' QIS. This suggests the presence of a small distribution of both chemical shifts and quadrupole constants (average $\delta_{iso} = -16.7$ and SOQUE 1.0 MHz).

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