Study of the Aluminophosphates AlPO₄-21 and AlPO₄-25 by ²⁷Al Double-Rotation NMR

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Abstract: Aluminum-27 double-rotation NMR in a magnetic field of 11.7 T distinguishes the extremely distorted five-coordinated aluminum sites in the molecular sieve precursor AlPO₄-21. Upon calcination, AlPO₄-21 transforms to AlPO₄-25, which has two tetrahedral aluminum sites with similar isotropic chemical shifts that cannot be resolved in an 11.7 T field. The two tetrahedral environments, however, have different quadrupole coupling constants and are distinguished by double rotation at 4.2 T field. The quadrupole coupling constants obtained for these sites indicate that the tetrahedral aluminum environments are less distorted in the hydrated material.

Introduction

The development of double rotation (DOR) and dynamic angle spinning (DAS) represents a useful advance in the study of quadrupolar nuclei by solid-state NMR.¹⁻⁴ These nuclei, with spin > 1/2, interact not only with magnetic fields but also with electric field gradients. The combination of these interactions produces higher order, orientation-dependent broadening that cannot be removed by magic angle spinning (MAS) or multiple-pulse sequences alone. DOR or DAS, however, average out both the first- and second-order anisotropic interactions. In the DOR experiment the sample is contained inside a rotor, which is itself mounted inside a larger rotor. The big rotor spins about an axis tilted from the magnetic field direction at the conventional "magic angle", 54.74°, the root of the second-rank Legendre polynomial, P₂(cos θ) = 0, while the angle between the two rotors is 30.56°, the root of the fourth-rank Legendre polynomial, P₄(cos θ) = 0. Removal of both the first- and second-order anisotropic broadening in this way permits the environment of quadrupolar sites in solids to be probed by NMR with unprecedented detail.

DOR has recently provided new insights into the structural changes undergone by the porous aluminophosphate VPI-5 during adsorption of water;⁵ well-resolved ³¹P DOR resonances are observed for distinct tetrahedral and octahedral environments. In this paper, we examine the aluminum environments in the aluminophosphate AlPO₄-21, which is particularly interesting as it contains five-coordinate aluminum in the framework. We also investigate the aluminum sites in both hydrated and dehydrated AlPO₄-25, a related molecular sieve.

AlPO₄-21 is one of a range of novel crystalline aluminophosphates first synthesized at Union Carbide Laboratories by hydrothermal treatment of gels containing organic templates.⁶ Calcination to remove the organic species can produce molecular sieves of potential industrial importance. In the case of AlPO₄-21 there is also a structural transition to AlPO₄-25 during the calcination process. The structure of AlPO₄-21 has been determined by single-crystal X-ray diffraction and is shown in idealized form in Figure 1.² There are three distinct crystallographic phosphorus sites, which are all regular P(0)₄ tetrahedra. There are also three distinct aluminum sites: an Al(OP)₄ tetrahedron and two distorted five-coordinate Al(OP)₄(OH) environments. The asymmetric charge distribution at the five-coordinated aluminum sites results in large quadrupolar interactions, which cause severe line broadening, making detection of such species particularly difficult with use of conventional MAS methods. It is interesting to note that AlPO₄-21 contains Al–OH–Al groups, which is unusual for zeolitic structures. As a consequence, AlPO₄-21 comprises three- and five-membered rings as well as the even-numbered rings usually observed in AlPO₄ frameworks. It does not, however, violate the Loewenstein rule⁸ which only forbids linkages between tetrahedral aluminum atoms.

Experimental Section

AlPO₄-21 was synthesized, according to the general procedure described by Wilson et al.,⁴ from a gel containing pyrrolidine as the organic template. The powder XRD pattern obtained for the material verifies the high crystallinity and purity of the AlPO₄-21 product. A portion of the AlPO₄-21 sample was subsequently calcined in dry oxygen gas at 873 K for 24 h (2 K/min heating rate) to form the molecular sieve AlPO₄-25.

For recording spectra of dehydrated AlPO₄-25, the sample was heated overnight under vacuum at 623 K and transferred into the rotor in a dry nitrogen atmosphere. Conventional ³¹P and ²⁷Al MAS spectra were recorded in 4.2 and 11.7 T magnetic fields, by using spinning speeds of 5.5–6.5 kHz. The ²⁷Al pulse length was 4 μs, a 90° pulse, while the ²⁷Al data were collected by using 3-μs pulses [90° pulse in solution was 12 μs]. The recycle delay was 3 s. DOR spectra, also recorded at 4.2 and 11.7 T, were obtained by using a home-built probe that is described elsewhere.¹⁰ The inner DOR rotor was spun at around 5 kHz, and the outer rotor at 600–800 Hz. In the DOR experiments, 1000–2000 acquisitions were obtained by using a 1-s delay between 3-μs pulses [solution 90° pulse length was 18 μs]. All spectra were zero-filled to 4K data points, with 100 Hz Gaussian broadening, and referenced to 85% aqueous H₃PO₄ for ³¹P and to an aqueous solution of Al(NO₃)₃ for ²⁷Al.

Results and Discussion

³¹P and ²⁷Al MAS–NMR spectra of AlPO₄-21 are shown in Figure 2. The ³¹P MAS spectrum in Figure 2a shows complete resolution of the three distinct phosphorus sites in a population ratio of approximately 1:1:1. The narrow lines at -13.3, -21.1, and -30.3 ppm confirm the high crystallinity of the sample and cover a range of the frequency regime normally associated with...
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Figure 1. Idealized diagram of $\text{AlPO}_4$ framework. Aluminum atoms are marked by the solid circles, and phosphorus atoms are located at the other vertices. $U$ and $D$ represent upward and downward pointing connections. There is a bridging oxygen in the midpoint of each solid line and a bridging OH group in the middle of the dashed lines which results in two distinct five-coordinate Al sites.

Figure 2. MAS-NMR spectra of $\text{AlPO}_4$ acquired at 11.7 T: (a) $^31\text{P}$ spectrum, spinning speed 6.5 kHz and (b) $^{27}\text{Al}$ spectrum, spinning speed 5.5 kHz.

Figure 3. $^{27}\text{Al}$ DOR spectrum of $\text{AlPO}_4$ acquired at 11.7 T. The outer rotor was spinning at a speed of 790 Hz.

Table 1. Parameters Obtained from DOR Results and Simulation of $^{27}\text{Al}$ MAS Spectra on $\text{AlPO}_4$.

<table>
<thead>
<tr>
<th>site</th>
<th>$\delta_{\text{iso}}$ (ppm)</th>
<th>$\eta$</th>
<th>$C_Q$ (MHz)</th>
<th>$\delta_{\text{iso}}$ (ppm)</th>
<th>$\eta$</th>
<th>$C_Q$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(1) $\text{AlO}_4$</td>
<td>42.2</td>
<td>0.15</td>
<td>3.7</td>
<td>48</td>
<td>0.15</td>
<td>3.7</td>
</tr>
<tr>
<td>Al(2) $\text{AlO}_3^-$</td>
<td>0.4</td>
<td>0.68</td>
<td>5.9</td>
<td>14</td>
<td>0.4</td>
<td>5.1</td>
</tr>
<tr>
<td>Al(3) $\text{AlO}_3^-$</td>
<td>-5.4</td>
<td>0.52</td>
<td>7.4</td>
<td>16</td>
<td>0.65</td>
<td>7.4</td>
</tr>
</tbody>
</table>

*Isotropic chemical shift, $\delta_{\text{iso}}$, asymmetry parameter, $\eta$, and quadrupolar coupling constant, $C_Q$. Our values are compared with those of Alemany et al. [14].

broadened line shape, corresponding to the single tetrahedral aluminum environment, and an additional broad signal at lower frequency associated with the two five-coordinated aluminum sites. [14] These resonance lines are broadened by anisotropic second-order quadrupolar effects which are not removed by MAS even at higher spinning speeds.

Better resolution is obtained in the $^{27}\text{Al}$ spectrum of $\text{AlPO}_4$ by using double rotation NMR. Figure 3 shows the $^{27}\text{Al}$ DOR spectrum obtained at 11.7 T. DOR averages the second-order quadrupolar interaction to its isotropic component, thus substantially narrowing the peaks. The spectrum shows a single symmetric peak at 42.2 ppm, while two resonances, at 0.4 and -5.4 ppm, due to the five-coordinate sites can be distinguished from the spinning sidebands by varying the spinning speed of the outer rotor. The sideband manifold remains relatively broad, however, making it difficult to quantify the relative amounts of aluminum in each site. The centerband peaks appear at their respective isotropic shifts, incorporating contributions from both the isotropic chemical shift, $\delta_{\text{iso}}$, and the isotropic second-order quadrupolar shift, $\delta_{Q,\text{iso}}$, as given by

$$\delta_{\text{iso}} = \delta_{\text{cs}} + \delta_{Q,\text{iso}}$$  \hspace{1cm} (1)

The isotropic quadrupolar shift $\delta_{Q,\text{iso}}$ is related to the asymmetry parameter $\eta$, and the quadrupolar coupling constant $C_Q$ by the equation

$$\delta_{Q,\text{iso}} (\text{ppm}) = \frac{3[(I + 1) - \eta^2]}{40f^2(2I - 1)^2} \left(1 + \frac{\eta^2}{3}\right) \frac{C_Q}{\nu_b^6} \times 10^6$$  \hspace{1cm} (2)

where $I$ is the nuclear spin and $\omega_0$ is the resonance frequency. The DOR results and spectral simulations of the MAS data [Figure 4] yield the quadrupolar parameters for the three sites shown in Table I. It should be pointed out that the parameters obtained by Alemany et al. upon fast spinning MAS, do not produce a good fit to our experimental data [Figure 4c], although they give a good fit to their experimental spectrum. In particular, our parameters for the five-coordinated site $\text{Al}(2)$ are significantly different from those reported previously, though there is good agreement for the other sites. This discrepancy may indicate greater sensitivity of one of the five-coordinate aluminum sites to the method of sample preparation. Our spectral simulation of the centerbands required an intensity ratio of 1:0.3:0.5 for $\text{Al}(1)$, $\text{Al}(2)$, and $\text{Al}(3)$, respectively, which is different from the theoretical 1:1:1 ratio. This difference occurs because of the relatively slow spinning speed—resulting in a significant fraction of the signal from the five-coordinate aluminum to be contained in spinning sidebands. It is possible too that the 3-µs pulse was not short enough for quantitative analysis of this system, in which the aluminuous sites possess substantially different quadrupolar parameters.

The transformation of AlPO$_4$-21 into AlPO$_4$-25 is achieved upon removal of the organic template during calcination. The structure of dehydrated AlPO$_4$-25 above 530 K has been solved recently by Rietveld refinement of neutron time-of-flight data and is shown schematically in Figure 5. This high-temperature form of AlPO$_4$-25 contains the same type of two-dimensional net as depicted in Figure 1 for AlPO$_4$-21 but with an up-down-up-down chain of tetrahedra rather than the up-up-down-down arrangement. This produces two aluminum sites and two phosphorus positions, both of which occur in population ratios of 2:1. At temperatures below 530 K, dehydrated AlPO$_4$-25 appears to adopt a lower symmetry structure. The Rietveld structural refinement showed all aluminum and phosphorus atoms to be tetrahedrally coordinated but was unable to distinguish between them.

Figure 6 shows the $^{31}$P and $^{27}$Al MAS–NMR spectra of dehydrated AlPO$_4$-25. The $^{31}$P spectrum in Figure 6 acquired at 11.7 T contains a single broad peak at -30.7 ppm, suggesting a range of similar P(OAl)$_4$ environments. The $^{27}$Al MAS spectra, obtained at 11.7 and 4.2 T [Figure 6 (parts b and c, respectively)], are broadened primarily by second-order quadrupolar effects. The two expected aluminum sites are not resolved in the $^{27}$Al DOR spectrum of dehydrated AlPO$_4$-25 recorded in an 11.7 T field [Figure 7a]. They are clearly resolved, however, at 21.9 and 33.6 ppm in the DOR spectrum at 4.2 T shown in Figure 7b. The two sites correspond to tetrahedral aluminum and have an intensity ratio of 2:1 as anticipated. The peaks overlap in the higher magnetic field as they have similar isotropic chemical shifts, and their isotropic quadrupolar shifts are comparatively small. Thus, use of lower magnetic fields, for which greater isotropic quad-

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Due to incomplete overlapping of the two tetrahedral sites as well as water per material that is shown in Figure 6a. *Al DOR spectra of the hydrated material are shown in Figure 8. At 11.7 T, the spectrum contains a main peak at 40.8 ppm. The extremely broad resonance between zero and -50 ppm, observed at 4.2 T for the hydrated sample, is assigned primarily to octahedrally coordinated framework aluminum and a range of distorted environments. It is difficult to determine population ratios of the various aluminum sites in hydrated AIPO₄-25 owing to the broad line widths. It seems, however, that both tetrahedral aluminum environments in the framework are hydrated to approximately the same extent; the change of the isotropic quadrupolar shifts in the hydrated and dehydrated materials and their isotropic quadrupolar contributions are shown in Table II. We have also estimated the magnitude of the quadrupolar coupling constant by taking the value of \( \eta \) to be 0.67, which ensures that \( C_Q \) will be correct within 13% from eq 2. The quadrupolar shifts are smaller for the hydrated sample than the dehydrated material, showing that hydration confers a more symmetric environment to the tetrahedral sites. This result reflects as well the greater strain in the aluminophosphate framework of the dehydrated form.

### Table II. Isotropic Quadrupolar Shifts, \( \delta_{Q,i} \), and Chemical Shifts, \( \delta_a \), Calculated for the Two Tetrahedral Aluminum Sites in Dehydrated and Hydrated AIPO₄-25*  

<table>
<thead>
<tr>
<th></th>
<th>dehydrated AIPO₄-25</th>
<th>hydrated AIPO₄-25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site A</td>
<td>( \delta_a ) = 39.2 ppm</td>
<td>( \delta_a ) = 40.8 ppm</td>
</tr>
<tr>
<td></td>
<td>( \delta_{Q,i} = -2.2 ) ppm</td>
<td>( \delta_{Q,i} = -1.5 ) ppm</td>
</tr>
<tr>
<td>11.7 T</td>
<td>( \delta_{Q,i} = -17.3 ) ppm</td>
<td>( \delta_{Q,i} = -11.7 ) ppm</td>
</tr>
<tr>
<td></td>
<td>( C_Q = 2.3 ) MHz</td>
<td>( C_Q = 1.9 ) MHz</td>
</tr>
<tr>
<td>Site B</td>
<td>( \delta_a ) = 37.5 ppm</td>
<td>( \delta_a ) = 39.5 ppm</td>
</tr>
<tr>
<td>11.7 T</td>
<td>( \delta_{Q,i} = -0.5 ) ppm</td>
<td>( \delta_{Q,i} = -0.3 ) ppm</td>
</tr>
<tr>
<td>4.2 T</td>
<td>( \delta_{Q,i} = -3.9 ) ppm</td>
<td>( \delta_{Q,i} = -2.3 ) ppm</td>
</tr>
<tr>
<td></td>
<td>( C_Q = 1.1 ) MHz</td>
<td>( C_Q = 0.8 ) MHz</td>
</tr>
</tbody>
</table>

*The estimates of \( C_Q \) take the value of \( \eta \) to be 0.67, ensuring an accuracy of \( \pm 13\% \). Measurements were made at two field strengths: 4.2 and 11.7 T. 

High-resolution NMR data of quadrupolar nuclei. DOR spectra of AIPO₄-21, isotropic shifts are obtained for aluminum in one tetrahedral and two five-coordinated aluminum species in AIPO₄-21 is possible only at field strengths approaching 11.7 T. Upon hydration, AIPO₄-25 adsorbs approximately 0.145 g of water per 1 g of dehydrated sample. The ³¹P MAS spectrum of hydrated AIPO₄-25 was almost identical with the dehydrated material that is shown in Figure 6a. ²⁷Al DOR spectra of the hydrated material are shown in Figure 8. At 11.7 T, [Figure 8a], the spectrum contains a main peak at 39.5 ppm, typical of tetrahedral Al(OP)₆ species. This tetrahedral peak is broader than the corresponding resonance in dehydrated AIPO₄-25 [Figure 7a] due to incomplete overlapping of the two tetrahedral sites as well as embedded spinning sidebands. The broad smaller peak near -16 ppm reflects the existence of octahedrally coordinated framework aluminum bound to adsorbed water. There is a broad resonance at about 10 ppm which indicates the presence of distorted aluminum environments and perhaps extra-framework species. This has also been observed in related aluminophosphates, including VPI-5.5. Integration of the peak areas indicates that approximately 25% of the framework aluminum sites acquire octahedral coordination upon hydration.

The ²⁷Al DOR spectrum at 4.2 T [Figure 8b] reveals the splitting between the two tetrahedral sites as well as a broad resonance at lower frequency. The positions of the two tetrahedral resonances in the hydrated and dehydrated materials and their isotropic quadrupolar contributions are shown in Table II. We also find that different coupling constants exist for the two tetrahedral sites. In Table II, site A corresponds to aluminum at the nodes sharing 6,8- and 8-rings of the framework [see Figure 5]. It is not possible for both the 6- and 8-rings to be regular in the AIPO₄-25 structure, and thus the tetrahedron at site A is expected to be quite distorted, accounting for its high quadrupolar coupling constant. Site B corresponds to aluminum sharing 4,6- and 8-rings and will have a more symmetric environment.

The extremely broad resonance between zero and -50 ppm, observed at 4.2 T for the hydrated sample, is assigned primarily to octahedrally coordinated framework aluminum and a range of distorted environments. It is difficult to determine population ratios of the various aluminum sites in hydrated AIPO₄-25 owing to the broad line widths. It seems, however, that both tetrahedral aluminum environments in the framework are hydrated to approximately the same extent; the change of the isotropic quadrupolar and chemical shift contributions upon hydration is almost identical for both sites.

### Conclusions

This work demonstrates the use of double rotation in obtaining high-resolution NMR data of quadrupolar nuclei. DOR spectra of ²⁷Al species in AIPO₄-21 and AIPO₄-25 display substantially narrower peaks compared with the second-order quadrupolar broadened line shapes present under MAS conditions. For AIPO₄-21, isotropic shifts are obtained for aluminum in one tetrahedral and two five-coordinated environments. The enhanced resolution provided by DOR, combined with MAS spectral simulations, yield quadrupolar parameters for the three sites. During calcination AIPO₄-21 is structurally transformed to AIPO₄-25, which contains two different tetrahedral aluminum sites that are resolved by DOR at 4.2 T. The tetrahedral aluminum environments conform to higher symmetry upon hydration, relieving the strain present in the framework of the dehydrated material. The water molecules adsorbed produce octahedral aluminum configurations and

Solution Structure and Dynamics of a Mixed Tetramer of Lithium 3,5-Dimethylphenolate and Lithium Perchlorate in Diethyl Ether and Some Related Systems

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Abstract: Lithium 3,5-dimethylphenolate forms a mixed tetramer Li₄R₂Br₂(Et₂O)₄ (R = n-Bu, iPr) in diethyl ether and this species may be important in reactions with ketones. The first-order rate constants for the intramolecular exchange of Li₄R₂Br₂(Et₂O)₄ and intermolecular exchange between Li₄R₂Br₂(Et₂O)₄ and free LiCIO₄ have been determined. These rate constants are of the order of 1 s⁻¹. The rates of exchange between free and bound CIO₄⁻ and iodide ions are also of this order.

We have reported¹ that the regiochemistry of the methylation of the tetrameric lithium enolate of isobutyrophenone by methyl p-toluenesulfonate (methyl tosylate) in the weakly polar, aprotic solvent dioxolane is profoundly affected by both lithium tosylate, to form tetramers in weakly polar solvents, form mixed tetramers with LiBr and LiI. Thus Brown has demonstrated the nature of this species was at the time indicated an interaction between the salts and the tetrameric lithium phenolate and we suggested that the resulting phenolate under the same conditions suffers a second-order exchange of Li⁺ and Li⁺ and the intermolecular exchange between Li⁺ and free LiCIO₄ has been determined. These rate constants are of the order of 1 s⁻¹. The rates of exchange between free and bound CIO₄⁻ and iodide ions are also of this order.

The rates of exchange between free and bound CIO₄⁻ and iodide ions are also of this order.