

Investigation of the Evolution of Intermediate Phases of AlPO₄-18 Molecular Sieve Synthesis

Yining Huang,* Bryan A. Demko, and Christopher W. Kirby

Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7

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In the present work, we examined the intermediate phases formed during the hydrothermal synthesis of microporous material, AlPO₄-18. The evolution of the long-range ordering of the gel samples as a function of crystallization time was followed by powder X-ray diffraction. The development of the local environments of P and Al atoms was monitored by ³¹P and ²⁷Al magic angle spinning (MAS) NMR. Several representative intermediate phases were further characterized by ²⁷Al multiple quantum MAS and ²⁷Al → ³¹P cross-polarization experiments. Our results show that the formation of AlPO₄-18 undergoes several stages. Mixing phosphorus and aluminum sources together with a template at room temperature yielded a mixture containing an ordered aluminophosphate (AIPO) phase and a phosphate material. These materials were converted to an amorphous AIPO phase under hydrothermal conditions. Continuous heating resulted in the transformation of the amorphous phase into a crystalline microporous material, AlPO₄-5. A further increase in heating time led to the disappearance of AlPO₄-5 and the formation of AlPO₄-18.

Introduction

Microporous materials (often referred to as molecular sieves) are a class of inorganic solids with regular pores and cavities in the size range of 5–20 Å. Zeolites which are aluminosilicates represent the most well-known family of such materials. They are extensively used in industry as ion exchangers, sorbents, and catalysts.¹ Zeolites have been established industrial materials since the 1960s, but in recent years there has been growing interest in a new class of molecular sieves, namely, the aluminophosphates (AlPO₄s).² Some of these materials have the framework topologies of known zeolites, but many have novel structures. These AlPO₄-based materials exhibit distinct molecular sieving characteristics and can be made catalytically active by introducing other elements (such as Si and metal centers) into the frameworks. Due to a wide range of practical applications, the synthesis of new microporous materials is one of the major activities in materials science. However, despite much data having been compiled on the synthesis conditions, the mechanisms of the formation of these materials are still not well understood at a molecular level (for the reviews of microporous material synthesis see ref 3). Similar to zeolites, AlPO₄s are usually prepared by hydrothermal synthesis. The processes involve the formation of intermediate gel phases from which crystalline molecular sieves are produced. But the structural properties of these intermediate phases usually are poorly characterized. Since crystal-

line molecular sieves are eventually produced from the gel phases, obtaining the detailed structural information on the evolution of the intermediate phases will lead to a better understanding of mechanisms underlying molecular sieve crystallization.

In the present work, we have examined the intermediate phases formed at different stages of the crystallization of AlPO₄-18 by using solid-state NMR spectroscopy in conjunction with powder X-ray diffraction (XRD). AlPO₄-18 is a small pore molecular sieve with novel framework topology (AEI).⁴ Its structure consists of layers of tilted double 6-rings that give rise to a three-dimensional 8-ring channel system and a pear-shaped cage.⁵ Although there have been some reports on the synthesis of AlPO₄-18,⁶ none of them involved systematic characterization of the intermediate phases. The crystalline AlPO₄-18 has been examined by several groups using solid-state NMR techniques. But the focus of these studies was on the effect of adsorption of small guest molecules (water, ammonia, and methanol) on the framework structure.⁷

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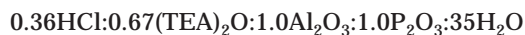
* Corresponding author. E-mail: yhuang@uwo.ca.

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Experimental Section

The hydrothermal synthesis of $\text{AlPO}_4\text{-18}$ was carried out according to the procedure outlined by Simmen et al.⁵ The reagents were pseudo-boehmite, [Catapal-B (Vista, ca. 65 wt % Al_2O_3)], H_3PO_4 (EM Science, ca. 85 wt % H_3PO_4), tetraethylammonium hydroxide (TEAOH) (Aldrich, ca. 35 wt %), and hydrochloric acid (Caledon, concentrated). For the above-mentioned reagents, the remainder of each is water. The crystalline $\text{AlPO}_4\text{-18}$ and corresponding intermediate phases were prepared with initial gel composition:



A typical procedure for the gel preparation was the following: 18.32 g of Catapal-B, 30.82 g of H_3PO_4 , and 16.82 g of water were combined and subjected to vigorous agitation for 15 min. Separately, 4.40 g of HCl was combined with 74.64 g of TEAOH, and this solution was added to the alumina/phosphoric acid mixture. Stirring of the resulting slurry for 2 h produced a white uniform and very viscous gel. For each batch preparation, a small portion of the gel was air-dried and this sample is referred to as initial gel without heating. The rest of the reaction mixture was charged into several Teflon-lined autoclaves and heated in an oven at 150 °C. The autoclaves were quenched after specified lengths of time in cold water and the liquid phase of each autoclave was separated from the solid phase by centrifugation. The solid materials were carefully dried in air at room temperature. All the gel samples were kept in tightly sealed glass vials once dried. They were periodically checked by ^{31}P , ^{27}Al magic angle spinning (MAS) NMR and powder XRD, and there was no change in either the NMR spectra or XRD patterns during the course of the study.

Powder XRD patterns were recorded on a Rigaku diffractometer equipped with a graphite monochromator using $\text{Co K}\alpha$ radiation ($\lambda = 1.7902 \text{ \AA}$).

All NMR experiments were performed on a Varian/Che-magnetics Infinityplus 400 WB spectrometer equipped with three rf channels. At the field strength of 9.4 T, the resonance frequencies are 399.491, 161.968, and 104.293 MHz for ^1H , ^{31}P , and ^{27}Al , respectively. The magic angle was set using the ^{79}Br resonance of KBr. The ^{31}P and ^{27}Al shifts were referenced to 85% H_3PO_4 and 1 M $\text{Al}(\text{NO}_3)_3$ aqueous solution, respectively. Depending on the requirements of the individual experiment, two NMR probes (a Varian/Che-magnetics 7.5-mm triple-tuned T3 MAS probe and a 3.2-mm H/X double-tuned MAS probe) were used.

The standard MAS NMR spectra were obtained by using the 7.5-mm probe with a spinning speed in the range 5–7 kHz. For ^{31}P MAS experiments, a pulse length of 3 μs (30° pulse) was typically used and the recycle delay was 60 s. The rf field strength for ^1H decoupling was about 50 kHz. The ^{27}Al MAS spectra were acquired using a small pulse angle (<15°) and a pulse delay of 200 ms.

The 7.5-mm probe was used for $^{27}\text{Al} \rightarrow ^{31}\text{P}$ cross-polarization (CP) experiments. Because ^{27}Al ($I = 5/2$) is a quadrupolar nucleus, the CP was carried out in the sudden passage regime (weak rf spin-locking field and fast sample spinning).⁸ The modified Hartmann–Hahn matching condition⁸ is

$$\gamma_p B_{1,p} = 3\gamma_{\text{Al}} B_{1,\text{Al}} \pm m\nu_r \quad n = 1 \text{ or } 2$$

The strength of the ^{27}Al spin-locking field is typically 14–16 kHz, corresponding to the ^{27}Al 90° pulse lengths between 18 and 16 μs measured for the central transition. The spinning rate used for experiments ranged from 5 to 7 kHz. The $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP experimental optimization was carried out using crystalline as-made $\text{AlPO}_4\text{-18}$. Although the optimal contact time for $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP was about 3 ms, a shorter contact time of 0.8 or 1 ms was used to ensure that the CP experiments

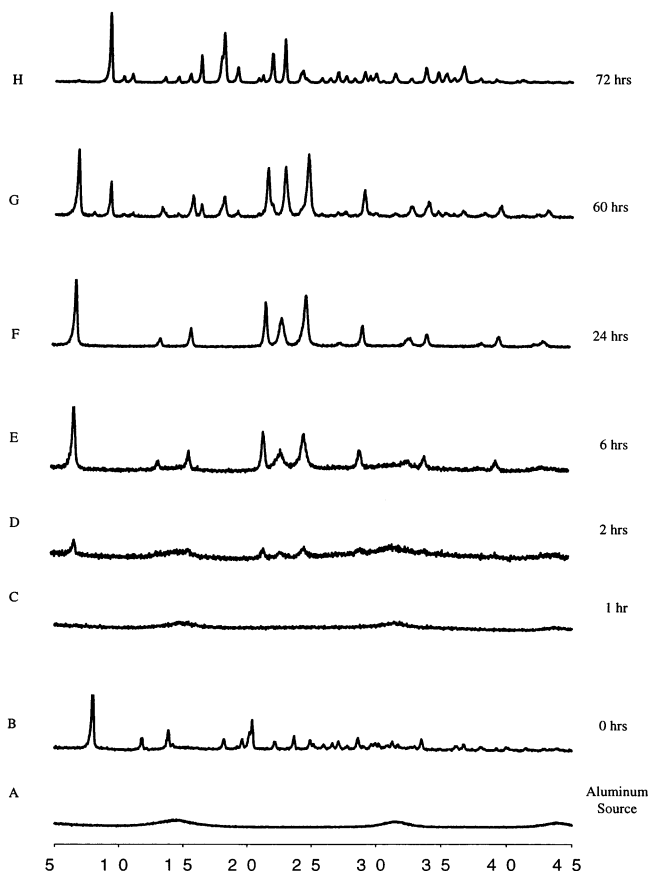


Figure 1. Powder X-ray diffraction patterns of the selected gel samples.

probe direct Al–O–P linkages. The pulse delay was 100 ms. The two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP was performed using the approach described by Fyfe et al.⁹ The TPPI method was used in the 2D data acquisition and processing.

The ^{27}Al triple quantum (3Q) MAS experiments were performed using the 3.2-mm probe capable of producing a rf field of 200 kHz. The 3QMAS spectra were obtained by utilization of a three-pulse, z -filter sequence.¹⁰ The rf strengths of the first two hard pulses and the third soft pulse were individually optimized and the optimized pulse lengths were typically 2.5, 0.85, and 11.5 μs for the three consecutive pulses. The spinning rates were between 20 and 24 kHz.

Results and Discussion

Powder XRD Patterns. The powder XRD patterns of the gel samples heated for different times were obtained to gain the information about the evolution of the long-range ordering of the intermediate phases as a function of the crystallization time. Selected XRD patterns are shown in Figure 1. The pattern of the initial gel without heating (Figure 1B) exhibits sharp reflection lines, indicating that an ordered phase or phases was formed upon mixing of the Al and P sources in the presence of the template before heating. The pattern does not seem to match any known AlPO_4 -based molecular sieve. The XRD pattern yielded no further information on the nature of this ordered phase, that is, whether it is purely a phosphate phase, or an unknown aluminophosphate phase (no match was found in the database). Observation of an order phase (or

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phases) in the initial gel without heating is interesting, as most studies of AlPO₄-based molecular sieve synthesis have shown that the initial gels without heating are usually amorphous in nature.¹¹ The initial gel samples were prepared by three separate experiments and the results are reproducible. The powder pattern of the gel sample heated under hydrothermal conditions for 1 h is shown in Figure 1C. The pattern is very similar to that of pseudo-boehmite (Figure 1A), the starting material as the aluminum source. All the sharp reflection lines observed in the pattern of the initial gel without heating have disappeared completely, indicating that the ordered material was dissolved under hydrothermal conditions. Careful inspection of the XRD pattern revealed that there is an extremely weak and very broad amorphous peak around a 2θ value of 31° . The results suggest that the solid gel sample heated at 150°C for 1 h is a mixture of the unreacted alumina and an amorphous material. Again, the nature of this amorphous phase is not clear. Heating the gel for 2 h resulted in a powder XRD pattern showing that there are at least three phases in this gel sample (Figure 1D). The very broad reflections at about 15° , 32° , and 44° , representative of the aluminum source, suggest that there was still a significant amount of unreacted pseudo-boehmite in the sample. A very broad diffraction peak between 25° and 40° is indicative of a large amount of an amorphous material present in the sample. In addition, the presence of several sharp reflections signifies that a crystalline phase was beginning to form. These reflections, however, do not correspond to those of AlPO₄-18, implying that a crystalline intermediate was emerging.

Further increasing heating time led to an increase in the intensities of the sharp diffraction peaks seen in Figure 1D at the expense of the peaks due to both the aluminum source and the amorphous phase, as depicted in Figure 1E. After heating the gel for 24 h, a distinct powder pattern (Figure 1F) corresponding to that of molecular sieve AlPO₄-5 with AFI structure was obtained.¹² The fact that no reflections other than those of AlPO₄-5 were observed in the powder pattern implies that heating the initial gel for 24 h resulted in a pure crystalline AlPO₄-5 as an intermediate phase under the reaction conditions. For heating times longer than 24 h, in addition to the peaks due to AlPO₄-5, a new set of reflection lines emerged, indicating that a different crystalline phase started forming. The intensities of these new peaks increased with increasing crystallization time at the expense of those of AlPO₄-5. A typical such powder pattern is shown in Figure 1G corresponding to 60 h of crystallization time. These new peaks correspond to the reflection lines reported for AlPO₄-18.¹² Heating the gel for 72 h or longer resulted in a powder XRD pattern representative of a pure AlPO₄-18 phase (Figure 1H).

³¹P MAS Spectra. To gain the information regarding the development of the local environments of aluminum and phosphorus atoms within the intermediate phases

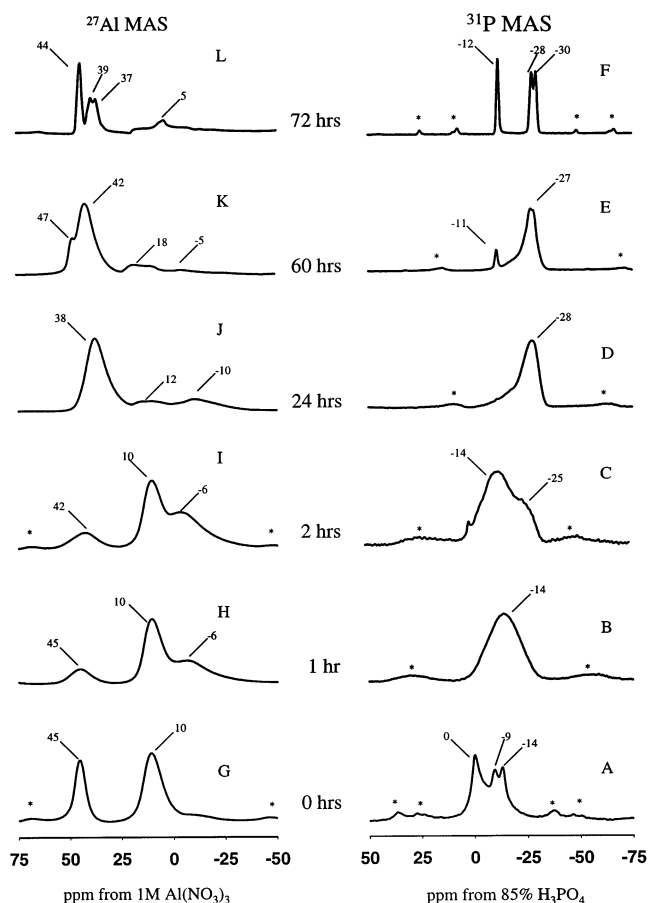


Figure 2. ³¹P and ²⁷Al MAS spectra of the selected gel samples. Asterisks indicate spinning sidebands.

as a function of crystallization time, the ²⁷Al and ³¹P MAS spectra of the gel samples were also obtained. The selected ²⁷Al and ³¹P MAS spectra are illustrated in Figure 2. In the ³¹P spectrum of the initial gel without heating (Figure 2A), there are three relatively sharp resonances at 0, -9, and -14 ppm. The appearance of three sharp peaks suggests that there are three well-defined P chemical environments. This is consistent with the corresponding XRD pattern, which suggests the presence of at least one ordered phase (Figure 1B). However, the assignments of these peaks are not straightforward. In previous studies of the AlPO₄-based molecular sieve synthesis, the broad ³¹P resonance signals were often seen in the region -10 to -20 ppm in the initial gels without heating and assigned to the phosphorus sites in the amorphous aluminophosphate (AlPO) materials.^{11,13} Thus, the chemical shifts indicate that the -9 and -14 ppm peaks might be due to tetrahedral environments of phosphorus sites in aluminophosphate materials and that the P atoms are not fully condensed.¹⁴ However, in addition to aluminophosphates, some mono-, di-, and polyphosphate species can

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also exhibit resonances in the same region.¹⁵ The assignment of the 0 ppm peak is also ambiguous as many protonated phosphate species have peaks near 0 ppm,¹⁵ but recent work has shown that mesostructured aluminophosphates can also have resonances with chemical shifts near 0 ppm.¹⁶ Further, it is unclear from the MAS spectrum if the three phosphorus sites belong to a single ordered phase or a mixture of an aluminophosphate and a phosphate phase.

The ³¹P MAS spectrum (Figure 2B) of the gel sample heated for 1 h contains a single resonance at -14 ppm. The fact that the peak is extremely broad ($\Delta\nu_{1/2} = 2.7$ kHz) is indicative of a large distribution of chemical shift, suggesting that the gel sample is amorphous in nature. This is consistent with the disappearance of an ordered phase observed in the corresponding XRD pattern (Figure 1C).

Upon heating the gel for 2 h, a new ³¹P resonance started appearing at about -25 ppm as a broad shoulder alongside the -14 ppm main peak (Figure 2C). In the literature, most of the reported ³¹P chemical shifts of AlPO₄-based molecular sieves fall within the range -19 to -31 ppm.¹⁷ It is generally accepted that the peaks in this region are due to tetrahedral phosphorus bound to four aluminums via bridging oxygen atoms, P(OAl)₄.¹⁷ Thus, this new peak at -25 ppm can be assigned to tetrahedral phosphorus environments, P(OAl)₄, in a microporous aluminophosphate material. The emergence of the -25 ppm peak indicates the development of a new AIPO phase in the gel sample. This agrees well with the corresponding XRD pattern (Figure 1D), which showed the appearance of an ordered phase. On the basis of the XRD results discussed earlier, we can further conclude that the -25 ppm shoulder corresponds to the crystalline AIPO₄-5 phase emerging from the amorphous phase. Treating the gel sample at 150 °C for 24 h resulted in a ³¹P MAS spectrum (Figure 2D), exhibiting a single asymmetric peak at -28 ppm. Both the line shape and the position of this peak are consistent with those reported for AIPO₄-5.¹⁸ The broad resonance at -14 ppm seen in the spectrum of the 2-h gel sample (Figure 2C) has disappeared. Together with the XRD pattern, the ³¹P MAS spectrum provides convincing evidence that a pure AIPO₄-5 phase is present in the sample.

Increasing the crystallization time more than 24 h led to the appearance of a new phosphorus resonance at -11 ppm in the MAS spectrum, suggesting that a new phosphorus site different from those of the pure AIPO₄-5 started forming. This -11 ppm peak corresponds to one of the three ³¹P peaks belonging to AIPO₄-18^{7a} (the other

two peaks at -28 and -30 ppm are buried underneath the strong resonance due to AIPO₄-5). The intensity of the -11 ppm peak increased with increasing crystallization time. A typical ³¹P spectrum (of a gel sample heated for 60 h) is shown in Figure 2E. The MAS spectrum is consistent with the corresponding XRD pattern (Figure 1G), which also shows the emergence of new reflection lines due to AIPO₄-18.

After heating the gel for 72 h, three sharp resonances at -12, -28, and -30 ppm were observed in the MAS spectrum (Figure 2F). The asymmetric line shape of the -28 ppm peak associated with AIPO₄-5 (Figure 2D) has disappeared. The resulting ³¹P MAS spectrum of the 72-h sample matches exactly that reported for pure crystalline AIPO₄-18.^{7a} The three phosphorus resonances are due to three crystallographically nonequivalent sites of AIPO₄-18.⁵ As mentioned earlier, the ³¹P chemical shifts of the most AlPO₄-based molecular sieves representing P(OAl)₄ environments fall in the region -19 to -31 ppm. AIPO₄-18 is one of the few exceptions with one phosphorus peak being outside the range at -12 ppm.^{7a} The appearance of this peak at low field has been related to the rather small P-O-Al angle associated with this site.^{7a}

²⁷Al MAS Spectra. The ²⁷Al MAS spectrum of the initial gel without heating is shown in Figure 2G. It exhibits two peaks at 45 and 10 ppm. The 45 ppm peak falls within the reported range (35–48 ppm) for tetrahedral aluminum environments, Al(OP)₄, in microporous aluminophosphate materials.¹⁷ However, there is, from the spectrum, no direct proof that this tetrahedral aluminum site is actually connected to any of the phosphorus peaks observed in the corresponding ³¹P MAS spectrum. Since the ²⁷Al MAS spectrum of the aluminum source, pseudo-boehmite, contains a single resonance at 10 ppm (not shown), the 10 ppm aluminum peak may be assigned to unreacted aluminum source. However, the pentacoordinated Al atoms in an AIPO material may also have peaks in this region.

Heating the gel for 1 h resulted in significant line broadening of the 45 ppm resonance and a decrease in its relative intensity (Figure 2H). The 10 ppm resonance presumably due to the aluminum starting material remained as the most intense peak in the spectrum. A new peak appeared at around -6 ppm. The shift of this new peak implies that this resonance may be due to the octahedral aluminum site in an AIPO species.¹⁷ However, since the -6 ppm is partially overlapped with the strong peak at 10 ppm, it might also be possible that the environment of the octahedral Al in pseudo-boehmite becomes much less symmetric upon heating, leading to a large second-order quadrupolar interaction, therefore, an asymmetric line shape. After 2 h of heating, Figure 2I shows the slight shift of the tetrahedral Al site from 45 ppm in the 1-h gel to 42 ppm. An increase in the relative intensity of the -6 ppm peak with respect to the 10 ppm main peak was also observed.

The ²⁷Al MAS spectrum of the gel sample heated for 24 h is shown in Figure 2J. The tetrahedral Al continued shifting to 38 ppm. This peak now becomes the strongest peak in the spectrum. An additional weak peak at -10 ppm was also observed. The -6 ppm peak representative of the octahedral Al in the amorphous AIPO

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material has disappeared. The intensity of the peak at around 10 ppm representing the aluminum source has become extremely weak, suggesting that the aluminum source has been consumed almost completely. Similar to the XRD pattern and the ³¹P MAS spectrum for the 24-h sample, the ²⁷Al MAS spectrum is in good agreement with that reported for AlPO₄-5.¹⁸

Heating the gel for more than 24 h yielded an ²⁷Al MAS spectrum, which is distinctly different from that of AlPO₄-5. A representative spectrum of the sample heated for 60 h is shown in Figure 2K. It contains a strong peak at 42 ppm as well as a well-resolved downfield shoulder at about 47 ppm. Although one of the tetrahedral Al peaks of as-made AlPO₄-18 is at 44 ppm,^{7a} it is difficult to judge from the MAS spectrum alone if the two maxima at 47 and 42 ppm are due to two separate resonance signals or a single peak with line shape. Several broad, weak overlapping peaks were also observed in the region of 18 to -5 ppm. The spectrum of the gel heated for 72 h (Figure 2L) looked identical to that of as-made AlPO₄-18 reported in the literature.^{7a}

²⁷Al 3QMAS Spectra. Although, based on the approximate chemical shift ranges known to be typical of different aluminum coordinations, the ²⁷Al MAS spectra can be partially assigned, the structural information obtained from straightforward ²⁷Al MAS is limited by the incomplete MAS averaging of the second-order quadrupolar interaction that causes broadening and shifting of the resonance signals. For instance, the crystallographic data indicate that there are only three nonequivalent aluminum sites for as-made AlPO₄-18.⁵ The ²⁷Al MAS spectrum corresponding to the pure crystalline AlPO₄-18 phase (Figure 2L) exhibits four resolved maxima at 44, 39, 37, and 5 ppm. It is not apparent from the MAS spectrum if the two maxima at 39 and 37 are due to different Al sites or just a single resonance with distinct line shape. The problem of this type can be solved by using the recently developed multiple quantum magic angle spinning (MQMAS) technique.¹⁹ This two-dimensional technique can effectively eliminate the second-order quadrupolar interaction experienced by half-integer quadrupolar nuclei and therefore narrow asymmetric line shapes considerably. The triple quantum MAS (3QMAS) spectrum of as-made AlPO₄-18 is shown in Figure 3. The isotropic (F1) dimension displays unambiguously only three sharp peaks at 47, 44, and 27 ppm. In particular, the two maxima at 39 and 37 ppm in the MAS (F2) dimension now appears as a single narrow resonance in the high-resolution dimension, indicating clearly that the two maxima are due to the asymmetric line shape of a distorted tetrahedral Al. This example illustrates the improvement in resolution by MQMAS NMR.

In the ²⁷Al MAS spectra of the gel samples heated for 1 and 2 h, there is a strong peak centered at 10 ppm overlapping with a broad signal positioned at -6 ppm. It is not clear whether these two overlapping maxima at 10 and -6 ppm originate from two separate Al sites or just a single resonance with a quadrupolar powder pattern. To clarify the situation, we have carried out ²⁷Al 3QMAS experiment on these samples. The 3QMAS

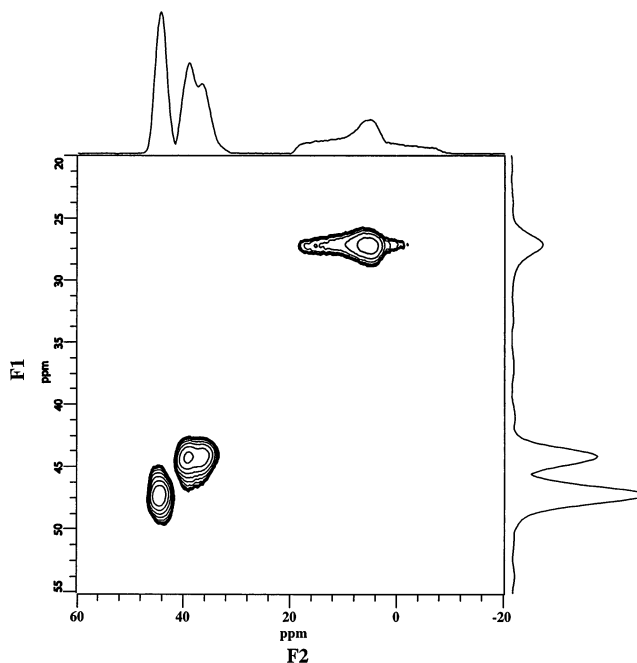


Figure 3. ²⁷Al 3QMAS spectra (9.4 T) of as-made AlPO₄-18. The spectrum was obtained using a spinning rate of 24 kHz; a t_1 increment of 41.7 μ s and a total of 256 t_1 increments. 240 scans were acquired with a repetition delay of 0.5 s.

spectrum of the 1-h gel (Figure 4A) shows clearly that there are three separate Al resonance signals, indicating that two overlapping maxima at 10 and -6 ppm seen in the simple ²⁷Al MAS spectrum are indeed due to two different aluminum environments. However, the resonance signals appearing in the high-resolution dimension remain very broad. The relatively broad peaks are apparently due to the distribution of chemical shift and/or quadrupole-induced shift. This is consistent with the disordered nature of this amorphous material as indicated by its powder XRD pattern (Figure 1C). While higher resolution was indeed achieved by 3QMAS, the question regarding the exact nature of the 10 ppm peak still exists. Is this peak due to unreacted alumina or a pentacoordinated aluminum site in an amorphous AlPO material? This question will be addressed momentarily.

For the sample heated for 60 h, a similar question of spectral resolution arises from the ²⁷Al MAS spectrum shown in Figure 2K. From the MAS spectrum alone, it is unclear whether the maxima at 47 and 42 ppm correspond to two distinct aluminum environments or they are the result of asymmetric line shape of a single aluminum site. Also, there seem to be several overlapping resonances in the range 20 to -5 ppm and it is not immediately apparent how many sites are in this region. Figure 4B displays the 3QMAS spectrum of the sample. Four distinct Al sites can be distinguished in the 2D contour plot. The isotropic shift of the narrow resonance labeled as A1 is at 47 ppm. This tetrahedral peak is assigned to AlPO₄-18 co-existing with AlPO₄-5 since the shift of this peak coincides with that of pure as-made AlPO₄-18. The second tetrahedral signal, A2, is rather broad along both isotropic and MAS dimensions, indicating the dispersion of the chemical shift and quadrupolar coupling constant. This signal likely has contributions from tetrahedral aluminum sites of both AlPO₄-18 and AlPO₄-5 (both have peaks in this region).

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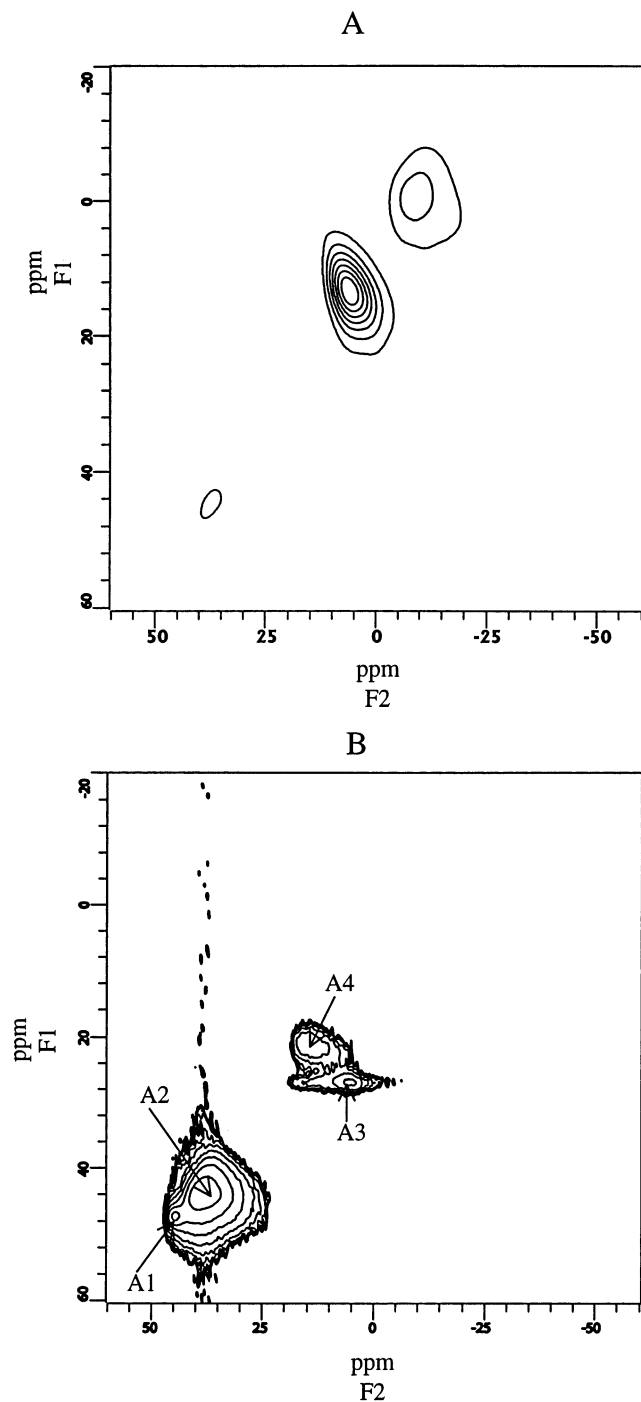


Figure 4. ^{27}Al 3QMAS spectra (9.4 T) of (A) the 1-h gel and (B) the 60-h gel. The spectra were obtained using a spinning rate of 20 and 24 kHz; a t_1 increment of 25 and 41.7 μs and a total of 64 and 128 t_1 increments for (A) and (B), respectively. 480 and 240 scans were acquired for (A) and (B), respectively, with a repetition delay of 0.5 s.

These assignments are consistent with the corresponding XRD pattern and ^{31}P MAS spectrum, which showed that the 60-h sample is a mixture of $\text{AlPO}_4\text{-18}$ and $\text{AlPO}_4\text{-5}$. The third signal, A3, apparently has a larger second-order quadrupolar coupling constant. This resonance appears as a sharp line at 26 ppm in isotropic dimension and can be assigned to the pentacoordinate Al in $\text{AlPO}_4\text{-18}$. The last resonance, A4, appears as a rather broad peak in F1 dimension. The shape and shift value suggest that this peak probably originates from a small amount of unreacted alumina.

$^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP Spectra. From the above discussion, it is apparent that although ^{31}P and ^{27}Al MAS NMR provided much crucial information regarding the local environments of P and Al atoms in the gel samples, uncertainties do exist in spectral assignments as well as the nature of the intermediate phases. As mentioned earlier, powder XRD pattern indicates that there is, at least, one ordered phase in the sample of the initial gel without heating, but XRD cannot provide further insight into the nature of the ordered phase, that is, whether this is a phosphate or an aluminophosphate phase. The corresponding ^{31}P MAS spectrum exhibits three sharp lines, indicating that these P environments are well-defined. This is consistent with the existence of ordered materials. However, as explained earlier, the ambiguities arise from the fact that the chemical shifts of these peaks can be due to either phosphate or aluminophosphate species. Both species have been found to exist in the gels formed during the synthesis of AlPO_4 -based materials.^{11,13,16} To clarify the situation, we have performed $^{27}\text{Al} \rightarrow ^{31}\text{P}$ cross-polarization experiments. Cross polarization (CP) is mediated by the heteronuclear dipolar interaction.²⁰ Since dipolar coupling strongly depends on the internuclear distance, CP experiments can provide information on the connectivity between two unlike spins. In $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP experiments, only those phosphorus nuclei that are within close proximity to an aluminum nucleus will be detected. Thus, this approach can be used to select Al–O–P linkages in AlPO_4 -based materials. Fyfe and co-workers have first demonstrated that $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP is a very useful method for characterization of the structure of crystalline AlPO_4 molecular sieves.⁹ Recently, we have been able to show that $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP can be utilized to map out the Al–O–P connectivity in the gel phases formed during the molecular sieve synthesis.²¹ Figure 5B illustrates the $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP spectrum of the initial gel without heating. Interestingly, the peak at 0 ppm observed in the ^{31}P MAS spectrum (Figure 5A) does not appear in the CP spectrum, suggesting that this phosphorus site is not connected to any aluminum and is thus likely due to a phosphate species. In the CP spectrum, two weak signals were observed at –9 and –14 ppm, whose positions coincide with those seen in the corresponding ^{31}P MAS spectrum (Figure 5A). Observation of the CP signals at –9 and –14 ppm indicates that these two phosphorus sites are connected to Al atoms. Therefore, our $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP result shows unambiguously that, in addition to the phosphate species, there must be an aluminophosphate phase coexisting with phosphate species as well. The ^{27}Al MAS spectrum (Figure 2G) of this sample shows two peaks at 45 and 10 ppm. The one-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP experiment does not indicate which of the Al sites is the source for ^{27}Al magnetization transfer. Normally, the two-dimensional CP or HETCOR (heteronuclear chemical shift correlation spectroscopy) could be used to obtain a correlation map between various phosphorus and aluminum sites. However, $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP signals of this particular sample were extremely weak. Practically, it would be too difficult to perform a two-dimensional experiment. Since

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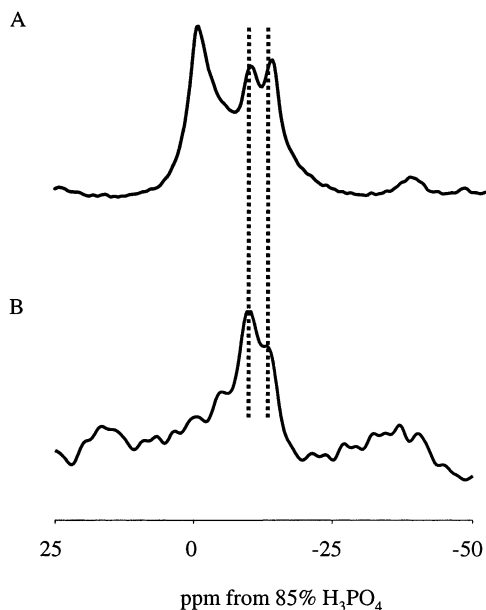


Figure 5. (A) ^{31}P MAS spectrum of the initial gel without heating. (B) $^{27}\text{Al} \rightarrow ^{31}\text{P}$ one-dimensional CP spectrum of the initial gel without heating. Contact time was 0.8 ms, and 750000 scans were acquired with a recycle delay of 0.1 s, resulting in a total experimental time of 21 h. Line broadening of 100 Hz was applied.

we know unambiguously that the 10 ppm peak in the MAS spectrum is due to unreacted pseudo-boehmite (see the discussion in the next paragraph) and thus not connected to any P atoms, it can be safely concluded that the tetrahedral aluminum at 45 ppm is the source of coherence transfer and therefore connected to both phosphorus sites. Our CP results suggest that the initial gel without heating contains, at least, three phases. An ordered aluminophosphate phase with two phosphorus sites at -9 and -14 ppm (both are connected to the tetrahedral aluminum site at 45 ppm), a phosphate species represented by the phosphorus peak at 0 ppm in the MAS spectrum, and unreacted pseudo-boehmite.

We have also examined the gel heated for 1 h. The reason this gel sample needed to be better characterized is that as stated earlier, it is not apparent whether the 10 ppm peak observed in the ^{27}Al MAS and 3QMAS spectra originates from unreacted alumina or a penta-coordinated Al site. If the former is the case, this peak should have no correlation with phosphorus. If the latter were true, the connectivity between the 10 ppm resonance and phosphorus would be observed. Further, although the broad peak at -14 ppm in the ^{31}P MAS spectrum (Figure 2B) might be assigned to a P site in an amorphous AIPO material based on its chemical shift, there is no direct proof that this P site is actually connected to any Al sites. To address these questions, we carried out two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP experiment and the result is shown in Figure 6. Observed on the phosphorus projection is a single resonance at -14 ppm corresponding to the only phosphorus site seen in the ^{31}P MAS spectrum. This undoubtedly confirms that this phosphorus is indeed connected to aluminum. On the aluminum projection, however, only two of the three resonances observed in the ^{27}Al MAS (Figure 2H) were detected. The aluminum sites at 45 and -6 ppm correlate with the phosphorus peak, indicating that both tetrahedral and octahedral aluminum sites are present

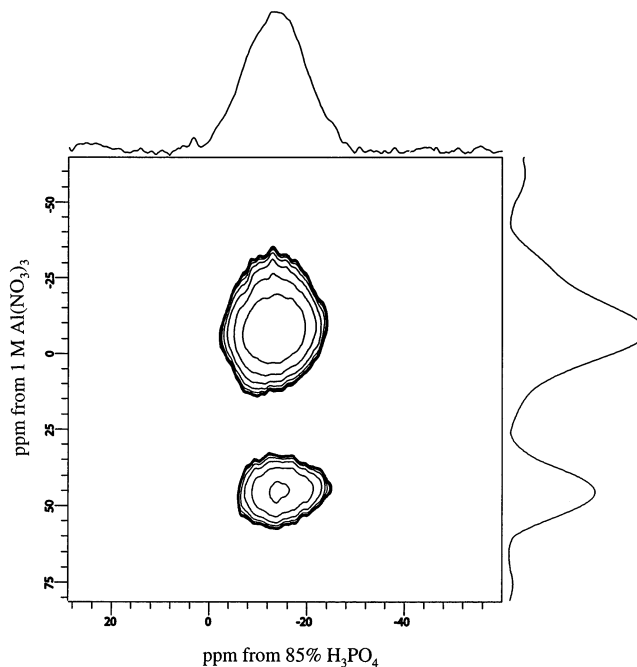


Figure 6. Two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP spectrum of the 1-h gel with a contact time of 0.8 ms. 18000 scans were acquired for each of 32 experiments in t_1 . The recycle delay of 0.1 s resulted in a total experimental time of 17 h.

in the amorphous AIPO materials and both connected to the phosphorus site. Interestingly, the strongest aluminum peak at 10 ppm observed in the ^{27}Al spectrum does not appear in the ^{27}Al projection, indicating that this Al site is not connected to phosphorus. Thus, the CP spectrum shows unambiguously that the 10 ppm peak is definitely not due to a penta-coordinated Al in an AIPO species and must result from the unreacted starting aluminum source, which is not expected to be connected to phosphorus. Our CP results have directly confirmed that the amorphous material is aluminophosphate in nature, containing both tetrahedral and octahedral aluminum sites.

Summary

In the present work, we have examined the intermediate phases formed during hydrothermal synthesis of molecular sieve AlPO₄-18 by using several solid-state NMR techniques in combination with powder XRD. The results clearly show that the formation of AlPO₄-18 includes at least four different stages: (1) upon mixing Al and P sources in the presence of the template, an ordered aluminophosphate material together with a phosphate phase was formed immediately at ambient conditions. The AIPO phase contains a tetrahedral Al site only. (2) After the initial gel was treated at 150 °C under hydrothermal conditions for about 1 h, these ordered materials were “dissolved” and an amorphous material was formed. The amorphous phase is aluminophosphate in nature and contains both tetrahedral and octahedral aluminum sites and both sites are connected to phosphorus via Al–O–P linkages. (3) The amorphous AIPO material began to transform to microporous AlPO₄-5 after heating the gel for 2 h. After 24 h, a pure phase of AlPO₄-5 was obtained. (4) Treating the gel sample for more than 24 h resulted in the disappearance of AlPO₄-5 and the formation of AlPO₄-18. The crystallization of AlPO₄-18 was complete after

a total heating time of 72 h. The results seem to imply that $\text{AlPO}_4\text{-5}$ is an intermediate, which directly transforms to $\text{AlPO}_4\text{-18}$. However, since our study was not in situ, the possibility of $\text{AlPO}_4\text{-5}$ being a competing phase cannot be ruled out.

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