

Solid-State Nuclear Magnetic Resonance Study of the Microporous Aluminophosphate AIPO₄-41

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Highly crystalline aluminophosphate molecular sieve AIPO₄-41 has been synthesized using dipropylamine as the templating molecule. Materials in the as-made, calcined never rehydrated, and calcined rehydrated forms have been characterized by solid-state NMR spectroscopy using ²⁷Al and ³¹P magic angle spinning (MAS), two-dimensional ²⁷Al 5Q-MAS, and ²⁷Al → ³¹P CP/MAS techniques. Both ³¹P MAS and ²⁷Al 5Q-MAS spectra of the as-synthesized AIPO₄-41 exhibit several resonances, all of them being assigned to framework atoms. Spectra are drastically modified after calcination. While the ³¹P MAS spectrum of the calcined never rehydrated solid is composed of a single broad resonance at ca. −30.5 ppm, five signals can be observed after rehydration. Rehydration slightly modifies the unit cell parameters, particularly the *b* axis and γ angle, but it is a completely reversible process. ²⁷Al NMR spectroscopy shows that water preferentially coordinates one of the five nonequivalent aluminum sites of the structure and transforms it into a six-coordinated species. The position of this site in the structure has been unambiguously determined from P–O–Al framework connectivities and confirmed by ¹H → ³¹P CP/MAS experiments. The location of the amine in the pores of the as-synthesized AIPO₄-41 was also estimated, suggesting that a specific interaction with one framework oxygen could account for the special shape of the channels (monoclinic space group *P*112₁).

Introduction

AIPO₄-41 is a synthetic microporous aluminophosphate molecular sieve (IZA structure code AFO)¹ whose framework contains monodimensional 10-ring channels. It was first synthesized as a mixed-phase product by Lesch and Wilson in 1988.² Later, Clark et al.³ reported on the possibility to obtain AIPO₄-41 as a pure phase using a mixed solvent alcohol/water system. However, the synthesis procedure required numerous steps and a relatively long crystallization time. Actually, pure AIPO₄-41 can also be prepared within a very short period provided that the synthesis gel containing aluminum, phosphorus, and dipropylamine (Pr₂NH) as the templating molecule is seeded with a small amount of AIPO₄-41 crystals previously synthesized.² Under such conditions, highly crystalline materials are obtained after a few hours (typically 7–15 h) at 200 °C. The organic molecules occluded in the channels can be easily removed by calcination of the as-made product in air at high temperatures, without degradation of the microporous structure.

The X-ray powder diffraction pattern of the calcined never rehydrated material is very similar to that of the as-synthesized molecular sieve. This indicates that the framework topology of AIPO₄-41 is preserved upon removal of the template provided that the calcined solid is maintained in an inert atmosphere. In contrast, drastic changes are immediately observed upon contacting calcined AIPO₄-41 with air at room temperature.^{3,4} Nevertheless, the transformation is completely reversible and

the original X-ray pattern is restored after evacuation of the hydrated solid in a vacuum at moderate temperature. Such reversible transformations, commonly observed in the family of microporous aluminophosphates, result from the ability of framework aluminum species to modify their coordination in the presence of water molecules.

The structure of the calcined never rehydrated material was originally described in the orthorhombic symmetry (space group *Cmc*2₁, *a* = 9.7169(1) Å, *b* = 25.8193(1) Å, *c* = 8.3484(1) Å) (Figure 1), assuming strictly elliptical channels with pore openings of ca. 7 Å × 4.3 Å.⁴ In space group *Cmc*2₁, the unit cell contains 20 Al and 20 P atoms with 4 non equivalent *T* sites. More recently, Kirchner and Bennett⁴ have shown that a monoclinic symmetry better describes the topology of calcined dehydrated AIPO₄-41 (space group *P*112₁, *a* = 9.7179(1) Å, *b* = 13.7915(1) Å, *c* = 8.3591(1) Å, γ = 110.6(1)°). The channels become slightly nonelliptical, which leads to a unit cell containing five nonequivalent *T* sites (Figure 1). Even though the Rietveld refinement in space group *P*112₁ gave a better fit between the experimental and calculated profiles for some of the reflections, the bond lengths and angles calculated in the two space groups were not significantly different. The main difference appeared in the mean P–O–Al angle value, which was 157(12)° in space group *Cmc*2₁ and 147(13)° in space group *P*112₁.

Attempts to elucidate the framework structure of AIPO₄-41 by solid-state nuclear magnetic resonance (NMR) were not successful. Indeed, the ³¹P magic angle spinning (MAS) NMR spectrum of the calcined never rehydrated AIPO₄-41 is composed of a unique line at ca. −31 ppm consistent with either

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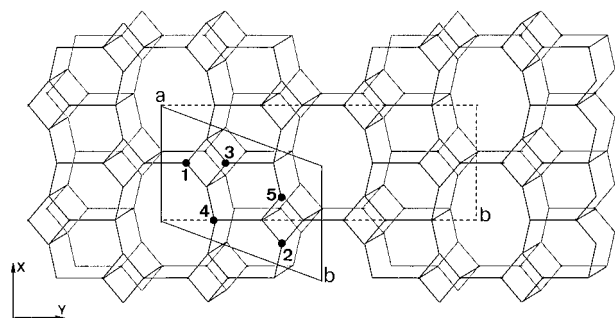


Figure 1. Framework topology of calcined never rehydrated $\text{AlPO}_4\text{-41}$ showing both the orthorhombic (dashed line) and monoclinic (full line) unit cells. In the orthorhombic symmetry, sites 2 and 5 are equivalent.

symmetry.^{3,5} The resolution of the ^{27}Al MAS NMR spectrum is also not good enough to distinguish the different sites in the structure. This contrasts with the ^{31}P NMR spectrum of as-synthesized $\text{AlPO}_4\text{-41}$, which shows several well-defined peaks in the region between -10 and -40 ppm. Hartmann et al.⁵ tentatively assigned these peaks to the various crystallographic sites of the structure. However, the resolution of the ^{31}P NMR spectrum was quite poor, thus leading to incorrect intensities and assignments of the various signals. Furthermore, the assignment was made assuming that the space group of as-synthesized $\text{AlPO}_4\text{-41}$ is the same as that of the calcined dehydrated material, which has never been clearly established.

The aim of the present paper is to reinvestigate the structure of $\text{AlPO}_4\text{-41}$ by solid-state NMR and to bring new information about the framework topology of the as-synthesized, calcined dehydrated, and calcined rehydrated materials.

Experimental Section

Synthesis. $\text{AlPO}_4\text{-41}$ was obtained by hydrothermal crystallization of a precursor gel containing pseudoboehmite (Catapal B, Vista, 74 wt % Al_2O_3), orthophosphoric acid (85 wt %), dipropylamine, and water. Typically, 5 g of Catapal B was slowly added to a solution containing 7 mL of H_3PO_4 in 45 mL of H_2O . The mixture was stirred for 3 h until a homogeneous gel was obtained. Then, dipropylamine was added dropwise, and stirring was maintained for 2 h. The gel, with the composition $4\text{Pr}_2\text{NH}-0.7\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-48\text{H}_2\text{O}$ was then seeded with approximately 50 mg of highly crystalline as-synthesized $\text{AlPO}_4\text{-41}$, transferred in a Teflon-lined stainless steel autoclave, and heated under static conditions for 15 h at 200°C . After cooling, the solid was recovered by centrifugation, washed with distilled water, and dried at 100°C overnight. The calcined material was obtained by heating 1 g of the as-synthesized material in a Pyrex tube at 500°C for 12 h under air. The tube was then evacuated and sealed to prevent rehydration of the solid. The calcined rehydrated material was obtained by contacting dehydrated $\text{AlPO}_4\text{-41}$ with ambient moisture for 24 h.

Characterization. X-ray powder diffraction data used for indexing and least-squares refinement of the unit cell for the as-synthesized and calcined rehydrated materials were collected on a Siemens D-5000 powder diffractometer. Reflection geometry, $\text{Cu K}\alpha$ radiation, variable divergence slits, and a secondary monochromator were used. Patterns were collected in the 2θ range from 2 to 55° . Indexing of the pattern of the calcined rehydrated sample was performed by the TREOR⁶ and ITO⁷ programs, which gave the same results. The LCLSQ program⁸ was used for the least-squares refinement of the unit cell parameters.

All solid-state NMR experiments were performed on a Bruker DSX 400 spectrometer operating at 104.25, 161.2, and 400.13 MHz for ^{27}Al , ^{31}P , and ^1H nuclei, respectively. Conventional MAS NMR spectra were recorded using a double bearing probe head equipped with 4-mm (o.d.) zirconia rotors. Samples were spun at the magic angle with a spinning speed of 14 kHz. The pulse lengths were $2\ \mu\text{s}$ ($\pi/4$) and $0.7\ \mu\text{s}$ ($\pi/6$), and the recycle delays were 30 and 1 s for ^{31}P and ^{27}Al nuclei, respectively.

Two-dimensional five-quantum (2D-5Q) MAS NMR spectra were collected with a standard 4-mm probe head at a spinning speed of 14 kHz and a rf field of 175 kHz, using the reported two-pulse sequence.⁹ In a typical experiment, 80 scans were accumulated for each free induction decay with a recycle delay of 300 ms. One hundred twenty-eight time-domain real data points were acquired in the indirect dimension, and pure phase spectra were obtained by using the TPPI scheme.^{10,11}

$^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP/MAS experiments were performed using a three-channel $^1\text{H}-\text{X}-\text{Y}$ probe head (Bruker) and a conventional spin-lock sequence.¹² The Hartmann-Hahn matching condition,¹³ modified to take into account only the central ^{27}Al transition was set up experimentally on as-synthesized $\text{AlPO}_4\text{-41}$. On a static sample, this condition corresponds to

$$\gamma_{\text{P}}B_{1,\text{P}} = 3\gamma_{\text{Al}}B_{1,\text{Al}}$$

For fast spinning conditions, the matching condition is split up into sidebands shifted once or twice by the spinning frequency:¹³

$$\gamma_{\text{P}}B_{1,\text{P}} = 3\gamma_{\text{Al}}B_{1,\text{Al}} \pm n\nu_{\text{R}} \quad n = 1 \text{ or } 2$$

Cross-polarization involving quadrupolar nuclei may prove difficult as a consequence of the sensitive tune-up required for effective spin-locking of the magnetization. This has been shown to work most effectively for low-power and high-spinning speeds.^{14,15} We used a spin-locking field of 4 and 5 kHz for ^{27}Al and ^{31}P , respectively, which corresponds to matching with $n = 1$ since our spinning rate was approximately 7 kHz. In these conditions, the power level of the irradiation field becomes effective for on-resonance polarization transfer, but it is too weak to thoroughly overcome the dampening effects of the offset. A more homogeneous transfer was achieved by linear amplitude modulation of the spin-locking field on the aluminum.

The contact time was varied between 0.1 and 3.5 ms, and the recycle delay was 0.3 s. Two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP/MAS correlation experiments were performed by encoding the aluminum evolution frequencies in an initial time period after the 90° pulse. Pure absorption phase NMR line shapes in both dimensions were obtained by cycling the phase of the 90° pulse using the TPPI scheme.

$^1\text{H} \rightarrow ^{31}\text{P}$ polarization-transfer experiments were performed at a 9-kHz spinning rate, using a spin-lock field of 115 kHz on both ^1H and ^{31}P nuclei. Two hundred forty scans were accumulated for each experiment, with a recycle delay of 5 s. Twelve different spectra were recorded with mixing times up to 15 ms.

Description of the Cross-Polarization Dynamics. A general treatment for the cross-polarization dynamics between two spins I and S can be found in the literature and involves the relaxation times in the rotating frame $T_{1\rho}^I$ and $T_{1\rho}^S$, as well as the time constant T_{CP} , which is connected to the efficiency of the dipolar contact between the two species in the experimental conditions.^{16,17}

$$S(t) = S_{\max}(a_+ - a_-)[\exp(a_-t) - \exp(a_+t)] \quad (1)$$

where

$$a_{\pm} = c[1 \pm (1 - b/c^2)^{1/2}]$$

$$b = (T_{\text{CP}}/T_{1\rho}^I)(1 + T_{\text{CP}}/T_{1\rho}^S) + \epsilon\alpha^2(T_{\text{CP}}/T_{1\rho}^S)$$

$$c = 0.5(1 + \epsilon\alpha^2 + T_{\text{CP}}/T_{1\rho}^I + T_{\text{CP}}/T_{1\rho}^S)$$

$$\alpha = [(S + 1/2)\gamma_S B_{1,S} \pm n\nu_R]/[(I + 1/2)\gamma_I B_{1,I}] \quad n = 1, 2$$

where ϵ is the scaling factor taking into account the ratio of the number of partners involved in the transfer, N_I/N_S , and α describes the effective amplification experienced by a radio-frequency field when applied selectively to one transition of a multilevel system. Therefore, $\alpha = 1$ in the case of a $^1\text{H} \rightarrow ^{31}\text{P}$ transfer, but $\alpha = 3$ for $^{27}\text{Al} \rightarrow ^{31}\text{P}$. We used eq 1 in all simulations of cross-polarization build-up curves described later in the text, with the approximations suitable for each case.

Results

As-Synthesized AlPO₄-41. The X-ray powder diffraction pattern of as-synthesized AlPO₄-41 is the same as those previously reported^{3,5} and shows that the aluminophosphate is highly crystalline and does not contain detectable impurity phases (Figure 2). Even though the X-ray pattern of the as-synthesized material is very similar to that of the calcined dehydrated AlPO₄-41, many small peaks could not be indexed using the unit cells (monoclinic or orthorhombic) of the calcined material. Actually, these peaks could be indexed by doubling the unit cell in the c direction, thus leading to the following parameters: $a = 9.674(6)$ Å, $b = 13.792(9)$ Å, $c = 16.78(1)$ Å, $\gamma = 110.70(8)^\circ$. The value of the c axis, which is twice that of the calcined dehydrated AlPO₄-41, is a consequence of the presence of the templating molecules in the channels, which either do not fit into one unit cell or have a specific interaction with one specific framework site with a $2c$ periodicity length.

Chemical analysis of the material gives $\text{P}/\text{Al} = 1 \pm 0.02$, suggesting that all phosphorus and aluminum species are framework species. This result is not in line with that of Kirchner et al.,⁴ who found $\text{P}/\text{Al} > 1$ in as-synthesized AlPO₄-41 and attributed the excess of phosphorus to extraframework species associated with protonated amines in the channels. Indeed, this type of species had been previously found in other as-synthesized aluminophosphates such as AlPO₄-22¹⁸ or AlPO₄-52.¹⁹ On this basis, they concluded that the analysis of as-synthesized AlPO₄-41 could be approximated as $20[\text{AlPO}_4] \cdot 2.0\text{Pr}_2\text{NH}_2^+\text{H}_2\text{PO}_4^- \cdot 1.5\text{H}_2\text{O}$, thus leading to an idealized P/Al ratio of 1.1. The difference with respect to our determination of the P/Al ratio, which lies well outside the range of experimental error, suggests that the material prepared by these authors may have been contaminated by a small amount of an amorphous phosphorus-rich phase.

Thermogravimetric analysis of AlPO₄-41 showed a unique weight loss around 250 °C, corresponding to the decomposition of dipropylamine occluded in the pores. No additional loss was observed at temperatures above 300 °C, which indicated the absence of protonated amines and thus supported the absence of extraframework phosphorus species in our material. The chemical formula derived from thermal data could be estimated as $\text{Al}_{10}\text{P}_{10}\text{O}_{40} \cdot 1\text{Pr}_2\text{NH} \cdot 0.18\text{H}_2\text{O}$.

The ^{31}P MAS NMR spectrum of as-synthesized AlPO₄-41 shows five major resonances between -19 and -37 ppm along

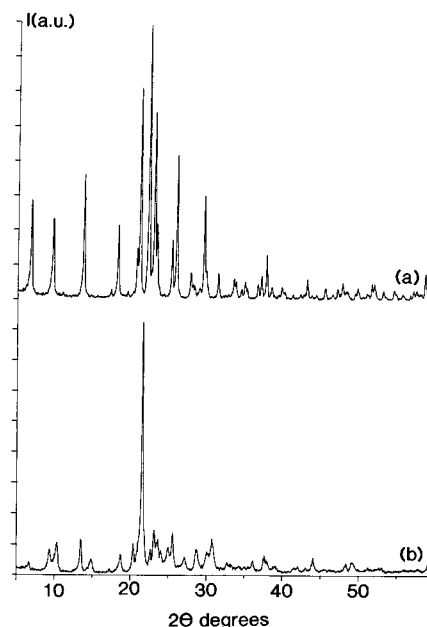


Figure 2. X-ray diffraction powder patterns of as-synthesized (a) and calcined rehydrated (b) AlPO₄-41.

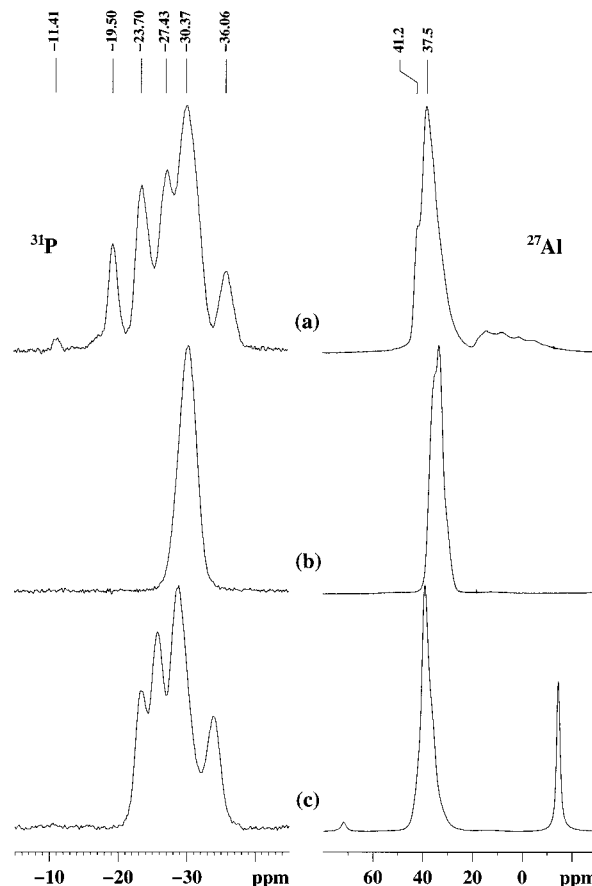


Figure 3. ^{31}P and ^{27}Al MAS NMR spectra of as-synthesized (a), calcined never rehydrated (b), and calcined rehydrated (c) AlPO₄-41.

with two weak signals at -11 and -17 ppm (Figure 3a). The two latter resonances, whose intensity does not exceed 2% of the intensity of the whole signal, are probably associated with framework defects and will not be taken into account in the deconvolution of the NMR spectrum. The resolution of the spectrum is excellent as compared to those already reported,^{3,5,20} particularly in the region between -25 and -33 ppm where

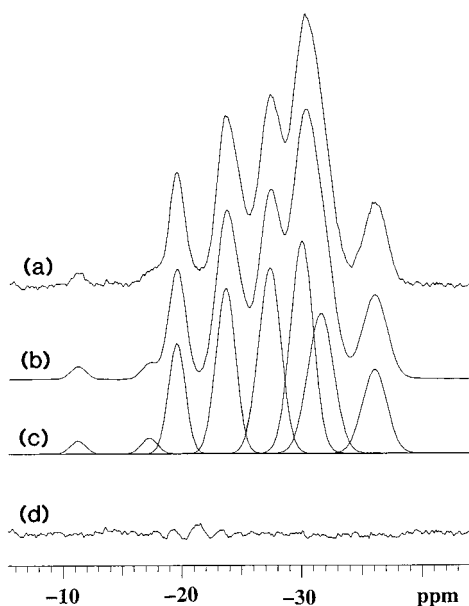


Figure 4. Deconvolution of the ^{31}P MAS NMR spectrum of as-synthesized $\text{AlPO}_4\text{-41}$: (a) experimental spectrum, (b) simulated spectrum, (c) individual signals, and (d) difference between the experimental and simulated spectra.

two resonances are observed at ca. -27.5 and -30.4 ppm. This certainly results from the high crystallinity of our material as already evidenced by X-ray diffraction.

Deconvolution of the ^{31}P MAS NMR spectrum gives six resonances with Gaussian line shapes at -19.5 , -23.9 , -27.3 , -29.9 , -31.5 , and -36 ppm with intensity ratios of 11:20:19:21:19:10 (Figure 4). The relative intensities strongly differ from those reported by Hartmann et al.,⁵ at least for the signals between -23 and -32 ppm. In this region, these authors found relative intensities of approximately 1:1:2:1 for the four major lines, whereas our results clearly indicate that they all possess the same intensity. Actually, Hartmann et al.⁵ used Lorentzian lines to deconvolute the spectrum, which may result in overestimating the relative intensity of the broader signal at ca. -29.5 ppm. On the basis of their deconvolution, those authors assigned only the four NMR lines between -23 and -32 ppm to crystallographic sites, which is consistent with the assumption of an orthorhombic symmetry for the calcined dehydrated $\text{AlPO}_4\text{-41}$. Under such conditions, the signal at -29.5 ppm was assigned to the P_5 atom (Figure 1), whose population in the structure is twice that of the other phosphorus atoms for an orthorhombic symmetry. The two peaks at ca. -19.5 and -36 ppm were attributed to $\text{O}_3\text{P-OH}$ and extraframework phosphorus species, respectively. However, the results of our deconvolution show that these two peaks represent approximately 20% of the phosphorus species in the material, which suggests that such attribution is not correct.

The ^{27}Al MAS NMR spectrum of as-synthesized $\text{AlPO}_4\text{-41}$ is less informative than the ^{31}P NMR spectrum, as it is essentially composed of a signal around 37.5 ppm along with a shoulder at 41 ppm (Figure 3a). The chemical shift indicates that the corresponding aluminum species are tetrahedrally coordinated in the framework. A weak broad pattern is also observed between -20 and $+20$ ppm, which probably results from interactions between some of the framework Al species with water or template molecules inside the channels. The resolution of the ^{27}Al NMR spectrum can be considerably increased by using a two-dimensional five-quanta (2D-5Q) MAS technique, recently developed by Frydman et al.²¹ for the

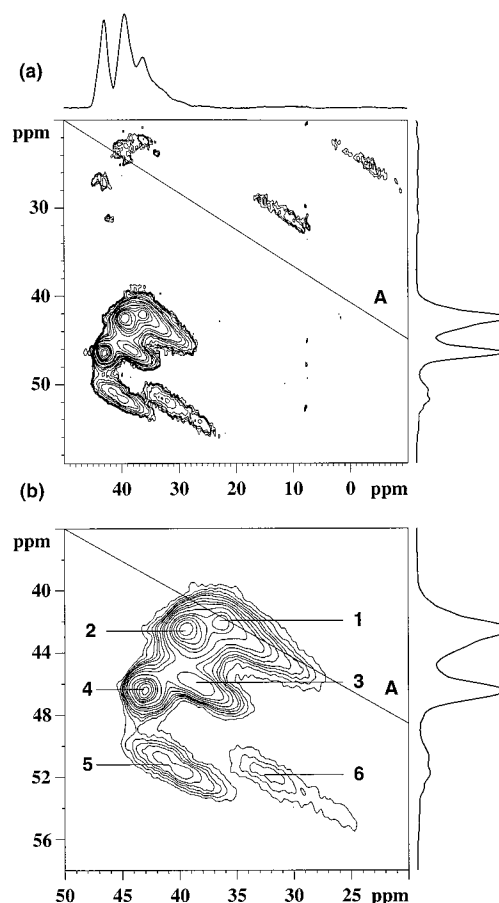


Figure 5. ^{27}Al two-dimensional 5Q MAS NMR spectrum of as-synthesized $\text{AlPO}_4\text{-41}$: (a) full spectrum and (b) detail of the tetrahedral region.

study of quadrupolar nuclei. This method provides enhanced resolution compared to conventional MAS spectra since common sources of spectral broadening, such as the second-order quadrupolar broadening and the chemical shift distribution due to structural disorder, are dispersed over two dimensions. Moreover, the difference in chemical shifts is amplified as it would be in a field approximately five times more intense. It was then possible, by using this technique, to resolve six different aluminum sites in the tetrahedral region, as shown in Figure 5. Moreover, two weak signals were observed at about 10 and -5 ppm, which correspond to the broad pattern observed between 20 and -10 ppm in the MAS spectrum (Figure 3a). If we neglect the weak contribution from those latter ones, the number of aluminum signals that can be distinguished in the 2D-5Q MAS spectrum is thus the same as that obtained for phosphorus using a standard MAS sequence. By contrast to ^{31}P MAS NMR, the relative intensities of the Al sites, and therefore a quantitative estimation of aluminum species, cannot be directly derived from the 2D-5Q MAS signals. However, it is possible to estimate the isotropic chemical shift of a given resonance, δ_{iso} , as well as the corresponding quadrupolar constant by using the relations⁵

$$\delta_{\text{iso}}(i) = x_2(i) - Q_{\text{is}}(i) \quad (2)$$

$$C_Q(i) = (x_1(i) - x_2(i))^{1/2} 1.3 \text{ (MHz)} \quad (3)$$

where $Q_{\text{is}}(i) = 4/9(x_2(i) - x_1(i))$ is the quadrupolar-induced shift and $x_2(i)$ and $x_1(i)$ are the coordinates of the center of gravity of line i .

The results give

$$\delta_{\text{iso}}(1) = 37.3 \text{ ppm } C_Q(1) = 3.0 \text{ MHz}$$

$$\delta_{\text{iso}}(2) = 38.5 \text{ ppm } C_Q(2) = 2.2 \text{ MHz}$$

$$\delta_{\text{iso}}(3) = 40.3 \text{ ppm } C_Q(3) = 3.5 \text{ MHz}$$

$$\delta_{\text{iso}}(4) = 43.0 \text{ ppm } C_Q(4) = 2.4 \text{ MHz}$$

$$\delta_{\text{iso}}(5) = 44.0 \text{ ppm } C_Q(5) = 4.3 \text{ MHz}$$

$$\delta_{\text{iso}}(6) = 39.4 \text{ ppm } C_Q(6) = 5.7 \text{ MHz}$$

The intensity ratios of the ^{31}P NMR lines suggest that the unit cell of as-synthesized AlPO₄-41 contains at least 10 P atoms, provided that all ^{31}P NMR lines can be assigned to framework species. A possibility to discriminate between framework and nonframework phosphorus species is to use a $^{27}\text{Al} \rightarrow ^{31}\text{P}$ cross-polarization technique, since the former species only possess neighboring aluminum sites. The cross-polarization method has been widely applied to materials in which nuclei with a low sensitivity like ^{13}C or ^{29}Si are bonded to protons.^{22,23} By transferring the proton magnetization to these nuclei, it is possible to differentiate those that are directly bonded to protons from the others. Fyfe et al.^{24–26} have shown that the method could be extended to other nuclei, in particular quadrupolar nuclei. Examples include the magnetization transfer from ^{27}Al to ^{29}Si in zeolites or ^{31}P in aluminophosphate molecular sieves. The $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP/MAS NMR spectra of as-synthesized AlPO₄-41 obtained with different contact times show the same resonances as the ^{31}P MAS spectrum (Figure 6). The maximum cross-polarization intensity is obtained for all ^{31}P resonances at ca. 2-ms contact time. The growth of the ^{31}P NMR cross-polarization intensity is a complex function of the contact time involving time constant T_{CP} as well as the $T_1\rho$ values for both nuclei (eq 1).^{16,17} The growth of the signal at short contact times depends on the rate of magnetization transfer characterized by T_{CP} , while the decay of the signal can be described by the spin-lattice relaxation times in the rotating frame, $T_1\rho$, for each nucleus. However, in the case of $^{27}\text{Al} \rightarrow ^{31}\text{P}$ cross-polarization, $T_1\rho^{\text{Al}} \ll T_1\rho^{\text{P}}$ and $T_1\rho^{\text{Al}} \ll T_{\text{CP}}$, which makes that the evolution of the signal intensity with contact time t , can be considerably simplified:²⁴

$$S(t) \approx S_{\text{max}}(T_1\rho^{\text{Al}}/T_{\text{CP}})[\exp(-t(1/T_1\rho^{\text{P}} + 1/T_{\text{CP}})) - \exp(-t/T_1\rho^{\text{Al}})] \quad (4)$$

The $T_1\rho^{\text{Al}}$ values are of the order of 350–400 μs in aluminophosphate or zeolite molecular sieves materials.^{24,26} Therefore, the differences in ^{31}P signal intensities obtained from cross-polarization generally indicate different T_{CP} values for the corresponding phosphorus species. T_{CP} is related to the strength of the dipolar coupling between ^{27}Al and ^{31}P nuclei. Variations in T_{CP} result from more or less efficient polarization transfers due to differences in dipolar coupling between the nearby Al species and the corresponding P species. In particular, the T_{CP} value is very dependent on the mean Al–O–P distance around a phosphorus atom in the framework.²⁶ As a consequence, extraframework phosphorus species will probably show a completely different behavior in the dynamics of the cross-polarization process as compared to framework species. The evolution of ^{31}P NMR signals obtained from cross-polarization with contact time can be compared with that reported by Fyfe

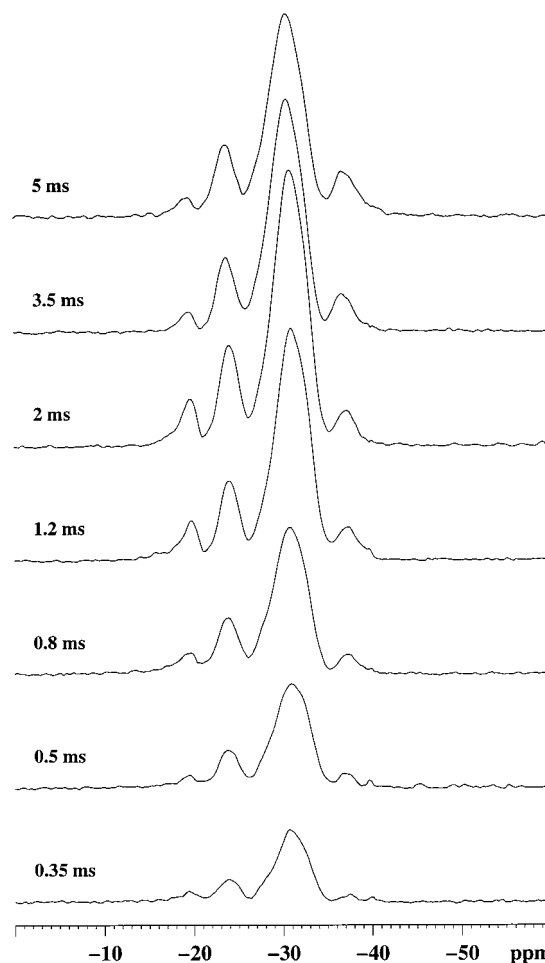


Figure 6. Evolution of the ^{31}P NMR spectrum of as-synthesized AlPO₄-41 with contact time obtained from $^{27}\text{Al} \rightarrow ^{31}\text{P}$ cross-polarization.

et al.²³ for VPI-5, thus suggesting that all ^{31}P NMR resonances observed between -19 and -37 ppm in the spectrum can be assigned to framework phosphorus species. This result is in contradiction with the conclusion of Hartmann et al.,⁵ who assigned peaks at -19.5 and -36 ppm to extraframework phosphorus species. Their conclusion was supported by the value of the mean P–O–Al bond angle in the structure, calculated using an empirical relation proposed by Müller et al.²⁷ Indeed, a mean P–O–Al angle value of 147° was obtained, very close to that reported by Kirchner et al.⁴ for a monoclinic symmetry. However, the calculation obtained from our deconvolution using the same relation and considering that all ^{31}P NMR signals can be assigned to framework species gives a value of 147.1° , which is also in excellent agreement with that obtained from refinement of the framework topology in the $P112_1$ space group. This demonstrates that the P–O–Al angle value is not a sensible parameter to discriminate between framework and nonframework phosphorus species. Moreover, as previously mentioned, the assignment of the external phosphorus resonances to nonframework species is inconsistent with the measured Al/P ratio, as each of these two signals amounts to approximately 10% of the total NMR signal intensity.

The two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP/MAS correlation spectrum of as-synthesized AlPO₄-41 shows that each of the six ^{31}P resonances is connected to four-coordinated framework Al species (Figure 7). At least five different aluminum sites are resolved in the indirect dimension f_1 with apparent chemical shifts of 31.8, 33.8, 36.5, 37.8, and 42.5 ppm. By comparison of these values with those of the ^{27}Al 2D–5Q MAS spectrum

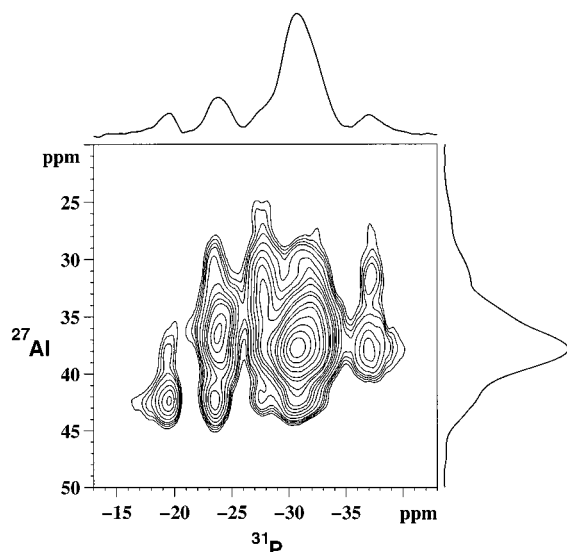


Figure 7. Two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ cross-polarization correlation spectrum of as-synthesized $\text{AlPO}_4\text{-41}$.

(Figure 5), it is reasonable to assign the chemical shifts at 42.5, 37.8, and 31.8 ppm to signals 4, 2, and 6 in Figure 5, respectively. The assignment of the other two correlation peaks is more difficult since the apparent chemical shifts of signals 1, 3, and 5 in Figure 5 are similar. However, the aluminum species at 33.8 ppm could correspond to signal 1 and that at 36.5 ppm to signal 3. Correlations between each phosphorus line and four-coordinated Al species are a definitive confirmation that all ^{31}P NMR signals observed between -19 and -37 ppm in the MAS spectrum can be assigned to framework phosphorus species.

More information about the nature of phosphorus species can be obtained using $^1\text{H} \rightarrow ^{31}\text{P}$ cross-polarization. As will be discussed further, protons of water molecules occluded (not coordinated) in the channels of as-synthesized $\text{AlPO}_4\text{-41}$ are too mobile at room temperature to efficiently transfer their polarization to ^{31}P nuclei. Thus, this method singles out the interactions between templating molecules and framework nuclei. The buildup of the phosphorus signal produced through cross-polarization as a function of transfer time is shown in Figure 8. Because of resonance overlapping, the evolution of signals at -29.9 and -31.5 ppm could not be easily quantified, and signal IV in Figure 8 actually contains the contribution of both intensities. It is apparent that the signals do not decay over the range of mixing times explored, which is an indication of reduced mobility of the protonated (polarizing) species. The polarization dynamics can be then simplified to

$$S(t) \approx S_{\max}(1/\epsilon + 1)[1 - \exp(-t(1 + \epsilon/T_{\text{CP}}))] \quad (5)$$

where ϵ is the scaling factor taking into account the ratio of the number of partners involved in the transfer, $N_{\text{IH}}/N_{^{31}\text{P}}$.

A fit to eq 5 reveals that only the site at -19.5 ppm can be successfully described within these assumptions, while all other signals unveil a biexponential growth (Table 1a). The time constants of the two contributions to the phosphorus polarization are calculated to differ by an order of magnitude. The slower transfer rate could be associated to species either further away or partially mobile (for example, the methyl groups), possibly mediated through spatial proton–proton spin diffusion. This mechanism would be more effective among protons in the aliphatic chain if the amine proton (N–H) is geometrically well-isolated. This latter would transfer its polarization toward its

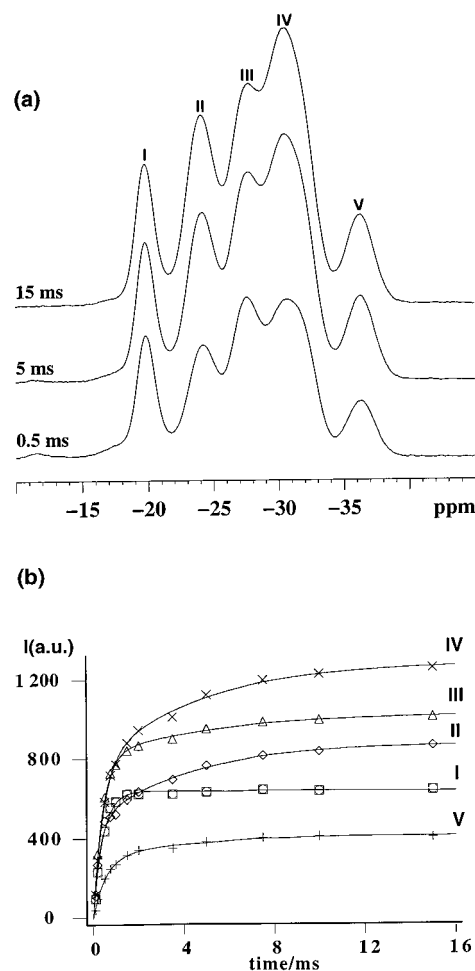


Figure 8. $^1\text{H} \rightarrow ^{31}\text{P}$ CP/MAS NMR spectra of as-synthesized $\text{AlPO}_4\text{-41}$ obtained at three different contact times (a) and evolution of the ^{31}P line intensities with contact time (b). The solid line is calculated using eq 4 with the parameters in Table 1a.

closest neighbor effectively as an isolated proton, thus providing a monoexponential buildup. A thorough analysis would be complicated by the difficulty to ascertain the effective geometry and number of partners involved in the polarization transfer, which determine ϵ . The values reported in Table 1 were calculated assuming $\epsilon = 1$.

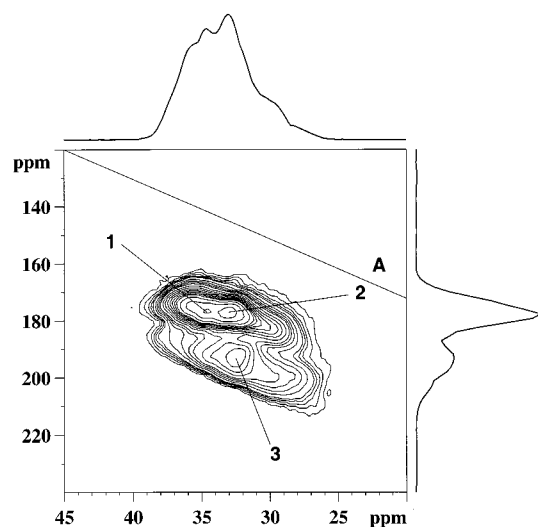
Hartmann et al.⁵ had previously reported a more qualitative analysis of the cross-polarization dynamics, in which they suggested that the ^{31}P NMR line at -19.5 ppm was the only signal enhanced by the cross-polarization process. This amounts to stating that two different reservoirs of proton magnetization can be assumed, so they concluded that this resonance could be assigned to extraframework phosphorus species, probably in the form of H_2PO_4^- groups. However, our results show that the peculiar behavior of this resonance under cross-polarization derives rather from a different number of protons contributing to the transfer. Indeed, the results in Table 1a show that the intensity of this peak evolves as a function of the contact time with parameters very similar to the other resonances.

Calcined Never Rehydrated $\text{AlPO}_4\text{-41}$. The X-ray powder diffraction pattern of calcined never rehydrated $\text{AlPO}_4\text{-41}$ is similar to that of the as-synthesized material, indicating that the framework topology is maintained upon removal of the organic molecules.^{3,5} The ^{31}P MAS NMR spectrum of the material is composed of a unique broad asymmetric signal at ca. -30.5 ppm (Figure 3b). Assuming that the chemical shift of a phosphorus species is approximately proportional to the

TABLE 1: ¹H–³¹P Cross-Polarization in As-Synthesized AlPO₄-41^a (Section a) and in Calcined and Rehydrated AlPO₄-41^b (Section b)

Section a					
P sites ^c					
	I	II	III	IV ^d	V
S_{\max}^A /a.u.	1278 ± 12	958 ± 80	1616 ± 90	1514 ± 112	602 ± 54
T_{CP}^A /ms	0.84 ± 0.04	0.54 ± 0.08	0.80 ± 0.08	0.88 ± 0.10	1.04 ± 0.12
S_{\max}^B /a.u.	0	800 ± 70	442 ± 72	1062 ± 88	232 ± 44
T_{CP}^B /ms	0	8.3 ± 2.2	10.2 ± 5.4	9.0 ± 2.0	8.4 ± 3.6
R^2	0.99309	0.99125	0.99562	0.99735	0.99678
Section b					
P sites ^e					
	I	II	III ^f	IV	
S_{\max} /a.u.	464 ± 33	1838 ± 38	2400 ± 88	1380 ± 54	
$T_{1\rho}$ /ms	6.6 ^g	6.8 ± 0.6	6.7 ± 0.6	6.3 ± 0.5	
T_{CP} /ms	6.9 ± 0.9	1.8 ± 0.1	1.02 ± 0.09	3.1 ± 0.2	
R^2	0.974 07	0.989 17	0.981 18	0.995 74	

^a Results of a fitting of the experimental data to eq 5. In most cases, a simple monoexponential model did not reproduce the data and a second reservoir had to be introduced. A scaling factor, ϵ , of 1 was assumed. See text for comments. ^b Results of a fitting of the experimental data to eq 1. ^c P sites refer to numbers in Figure 8. ^d Site IV is composed of two ³¹P NMR signals at –29.9 and –31.5 ppm. ^e P sites refer to numbers in Figure 11. ^f Site III contains the contributions of signals at –28.5 and –29.7 ppm. ^g $T_{1\rho}$ was fixed at the average of the other $T_{1\rho}$ values.

**Figure 9.** ²⁷Al two-dimensional 5Q MAS NMR spectrum of calcined never rehydrated AlPO₄-41.

mean P–O–Al angle in the structure,²⁷ the absence of several well-resolved signals in the ³¹P MAS spectrum suggests that all phosphorus atoms in the unit cell possess very similar environments. The ²⁷Al MAS NMR spectrum of the same material shows only signals characteristic of framework four-coordinated Al species (Figure 3b). The broad pattern observed between –20 and +20 ppm in the spectrum of the as-made AlPO₄-41 is not present anymore, which supports its interpretation as being due to framework Al species in interaction with templating and/or water molecules in the channels. Contrary to the ³¹P MAS spectrum, the ²⁷Al spectrum clearly shows two distinct signals at ca. 32 and 34 ppm. The existence of different species is clearly evidenced in the 2D–5Q MAS NMR spectrum where at least three signals can be resolved (Figure 9). The corresponding Al species are characterized by

$$\delta_{\text{iso}}(1) = 35.5 \text{ ppm} \quad C_Q(1) = 3.2 \text{ MHz}$$

$$\delta_{\text{iso}}(2) = 34.6 \text{ ppm} \quad C_Q(2) = 3.6 \text{ MHz}$$

$$\delta_{\text{iso}}(3) = 35.7 \text{ ppm} \quad C_Q(3) = 4.4 \text{ MHz}$$

All isotropic shifts are very close to each other, which indicates that, similarly to the neighboring phosphorus atoms, all aluminum atoms in the structure possess very similar environments. Unfortunately, the resolution of the 2D–5Q MAS technique in the present case was not sufficient to distinguish between the orthorhombic (four nonequivalent *T* sites) and the monoclinic (five nonequivalent *T* sites) symmetries.

Calcined Rehydrated AlPO₄-41. The X-ray powder pattern of calcined never rehydrated AlPO₄-41 is very similar to that of the as-synthesized material, but it is strongly modified after rehydration (Figure 2). The differences between the patterns of the calcined never rehydrated and calcined rehydrated materials are so large that it is not possible to reveal the similarities of the unit cells by a simple comparison. Indexing the pattern gives a monoclinic symmetry with $a = 9.542(4)$ Å, $b = 13.269(6)$ Å, $c = 8.213(3)$ Å, $\gamma = 101.70(4)^\circ$. These parameters are close to those reported by Kirchner et al.⁴ for dehydrated AlPO₄-41. Nevertheless, we observe a slight contraction of the unit cell axes, principally the *b* axis, upon adsorption of water. The main difference between the dehydrated and the hydrated materials appears to be a decrease by about 10% of the γ angle.

The ³¹P MAS NMR spectrum of calcined rehydrated AlPO₄-41 is composed of four well-resolved resonances between –23 and –34 ppm with intensity ratios of 1:1:2:1 (Figure 3c). The deconvolution of the spectrum with Gaussian lines gives five peaks of the same intensity at –23.6, –25.8, –28.5, –29.7, and –34.0 ppm, indicating that there are five nonequivalent P sites in the structure. The ²⁷Al MAS NMR spectrum shows two signals at 38 and –15 ppm, assigned to four-coordinated and six-coordinated aluminum species, respectively. Shoulders are observed on the main signal in the tetrahedral region, which could result either from quadrupolar line shapes or from various aluminum species that cannot be resolved under MAS conditions. The presence of a signal at –15 ppm is an indication that some of the framework aluminum species changed their coordination in the presence of water. The relative intensity of this signal corresponds to approximately 20% of the total NMR intensity.

Since five signals are observed in the ³¹P MAS spectrum of calcined rehydrated AlPO₄-41, at least five geometrically nonequivalent Al sites are expected to be present in the structure. Two scenarios can be invoked to account for the relative intensity of the ²⁷Al NMR line at –15 ppm. Water can be randomly located on 20% of the aluminum atoms, which means that each of the five Al sites possesses both tetrahedral and octahedral coordinations. However, it is difficult to imagine a direct interaction between site 3 (Figure 1) and water molecules, since this site is located inside the pore walls and is not easily accessible to water molecules from the channels. The other possibility is that one specific site becomes six-coordinated, whereas the other four remain in a tetrahedral coordination. The distinction between these two possibilities would be provided by the 2D–5Q MAS technique, for example, if several contributions to the octahedral or tetrahedral signals should be unfolded. The 2D–5Q MAS NMR spectrum of calcined rehydrated AlPO₄-41 shows five signals, only four of them being attributed to four-coordinated Al species and one to six-coordinated aluminum (Figure 10). This demonstrates that water

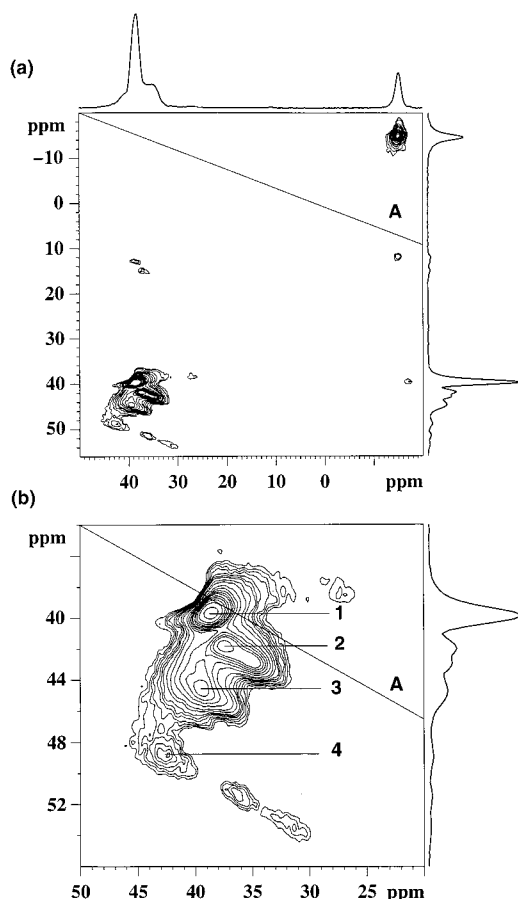


Figure 10. ^{27}Al two-dimensional 5Q MAS NMR spectrum of calcined rehydrated $\text{AlPO}_4\text{-41}$.

specifically coordinates one of the aluminum sites in the structure. The isotropic chemical shift and quadrupolar constant of the five aluminum species are

$$\delta_{\text{iso}}(1) = 39.4 \text{ ppm} \quad C_Q(1) = 1.7 \text{ MHz}$$

$$\delta_{\text{iso}}(2) = 39.5 \text{ ppm} \quad C_Q(2) = 2.8 \text{ MHz}$$

$$\delta_{\text{iso}}(3) = 41.8 \text{ ppm} \quad C_Q(3) = 2.9 \text{ MHz}$$

$$\delta_{\text{iso}}(4) = 44.1 \text{ ppm} \quad C_Q(4) = 4.4 \text{ MHz}$$

$$\delta_{\text{iso}}(5) = -9.7 \text{ ppm} \quad C_Q(5) = 1.3 \text{ MHz}$$

The location of water molecules in the channels can be specified by analyzing the connectivities in the $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP/MAS correlation spectrum of the hydrated material (Figure 11). The spectrum shows that each of the five P atoms of the structure is connected to four-coordinated aluminum. By contrast, the six-coordinated Al site is only connected to three phosphorus atoms, which is clearly evidenced in the one-dimensional trace taken at $\delta_1(\text{Al}) = -15 \text{ ppm}$ (Figure 11).

In an aluminophosphate, the Al–O–P bond length does not vary to the first order. Consequently, the dipolar coupling, and thus the cross-polarization time constant, can be safely assumed to be the same for all different Al–P pairs. The intensities in a cross-polarization phosphorus spectrum corresponding to a single aluminum site are then approximately proportional to the number of neighboring phosphorus sites. The intensity ratios of the ^{31}P NMR lines connected to the six-coordinated aluminum

species are 1:2:1, which indicates that the latter is connected with two symmetrically equivalent P atoms in the structure.

$^1\text{H} \rightarrow ^{31}\text{P}$ CP/MAS experiments at various contact times have been performed to estimate the proximity of the protons to framework phosphorus atoms. The intensities of ^{31}P NMR lines first increase with contact time and then decrease because of relaxation of the proton magnetization (Figure 12). As for the as-prepared material, signal III actually contains the contributions of two signals which could not be quantitatively deconvoluted. The evolution is different from the one observed for as-synthesized $\text{AlPO}_4\text{-41}$ where no decrease in magnetization was observed at long contact times. This means that the coordinated water molecules probably possess a higher mobility in the channels as compared to dipropylamine, which is consistent with the structuring role of this latter. In this case, we can safely neglect the contribution of phosphorus relaxation in eq 1. At very short contact times (typically 100 μs), only three signals are observed, with the same chemical shifts and relative intensities as those observed in the one-dimensional trace at $\delta_1 = -15 \text{ ppm}$ in the $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP/MAS correlation spectrum (Figure 13). This indicates that the protons which are in strong interaction with the framework P atoms are those of water molecules bonded to the six-coordinated Al atoms. The analysis of the build-up curves (Table 1b) shows that the resonance at -23.6 ppm increases much slowly than the others, as expected within the assumption that this peak corresponds to the internal phosphorus site P_3 (Figure 1).

Since thermal analysis data of calcined rehydrated $\text{AlPO}_4\text{-41}$ show that the material contains approximately 7 water molecules per 10 phosphorus (or aluminum) atoms, the channels probably contain water that does not interact directly with the framework. However, $^1\text{H} \rightarrow ^{31}\text{P}$ CP/MAS experiments indicate that these molecules are probably too mobile and/or too far from the pore walls to transfer their polarization to phosphorus nuclei.

Discussion

The published structure for the calcined dehydrated $\text{AlPO}_4\text{-41}$ suggests a monoclinic symmetry, due to a slight deviation from perfect ellipticity of the pores. On the other hand, NMR spectroscopy appears not to be very informative in this case, as the resonances of the 10 possible distinguishable sites (Al or P) collapses within a too small spectral region to be effectively resolved, because of its structural symmetry. The rather dramatic changes in the NMR spectra of the as-synthesized material should be ascribed to minor internal rearrangements of the bond angles. In fact, since the removal of the template does not significantly affect the X-ray pattern of as-synthesized $\text{AlPO}_4\text{-41}$, both as-made and calcined dehydrated materials probably possess the same topology with similar unit cell parameters. In particular, if the structure of the calcined dehydrated $\text{AlPO}_4\text{-41}$ is effectively monoclinic and assuming that the pore distortion already exists before calcination, it is reasonable to describe the topology of the precursor in monoclinic symmetry. Actually, we have found that the presence of templating molecules inside the channels doubles the c axis so that the unit cell contains 20 P and 20 Al atoms along with 2 dipropylamine molecules. In the absence of organic molecules, aluminophosphate layers at $z \approx 0$ and $z \approx 0.5$, which are connected together by narsarsukite-type UDUD (up–down) chains to form the $\text{AlPO}_4\text{-41}$ framework, are structurally identical. Each tetrahedral site $T(x, y, z \approx 0)$ is equivalent to the site $T(1-x, 1-y, z \approx 0.5)$ located in the adjacent layer. Therefore, the structure contains five nonequivalent T sites (Figure 1). The $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP/MAS correlation spectrum of as-synthesized $\text{AlPO}_4\text{-41}$ clearly shows that all six

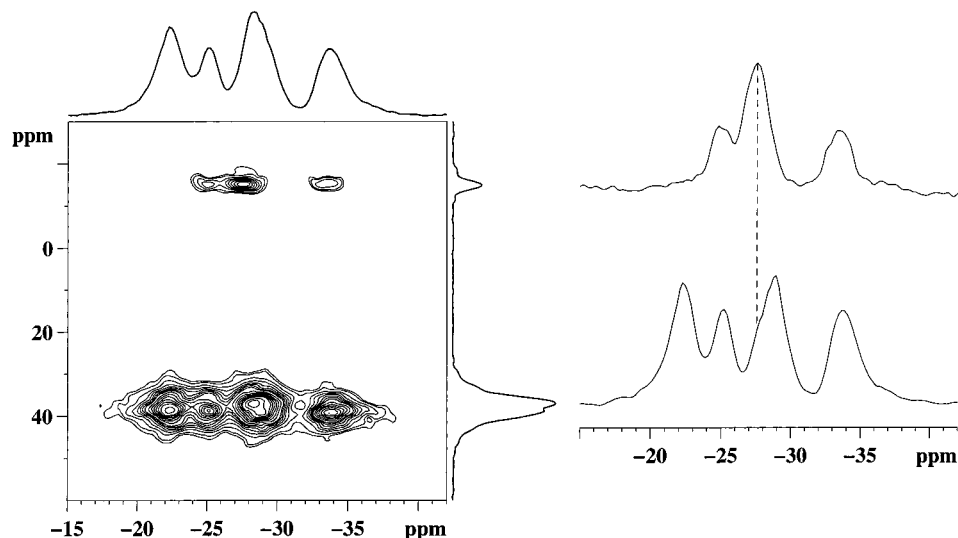


Figure 11. Two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ cross-polarization correlation spectrum of calcined rehydrated $\text{AlPO}_4\text{-41}$ and one-dimensional traces at tetrahedral and octahedral aluminum sites.

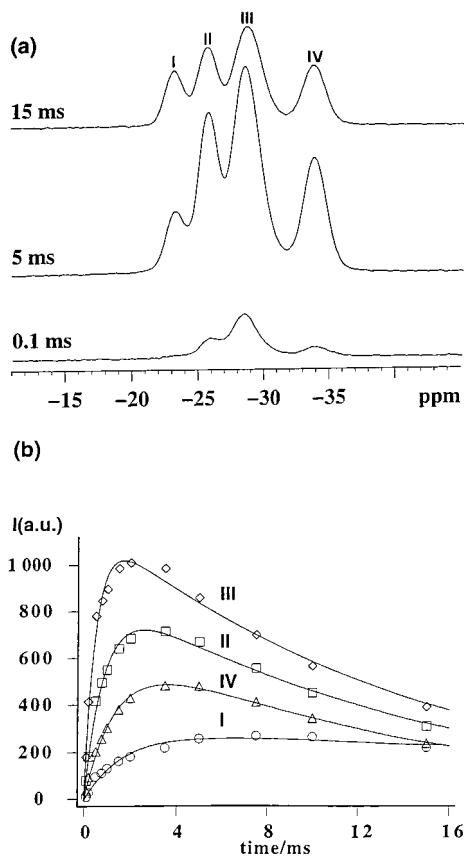


Figure 12. $^1\text{H} \rightarrow ^{31}\text{P}$ CP/MAS NMR spectra of calcined rehydrated $\text{AlPO}_4\text{-41}$ obtained at three different contact times (a) and evolution of the ^{31}P line intensities with contact time (b). The solid line is calculated using eq 4 with the parameters in Table 1b.

^{31}P NMR resonances observed between -19 and -37 ppm can be assigned to phosphorus nuclei bonded to tetrahedrally coordinated framework aluminum species, as each of them correlates with more than one Al site (Figure 7). The presence of 6 lines in the ^{31}P MAS spectrum with intensity ratios of approximately 1:2:2:2:2:1 confirms that the unit cell contains 10 nonequivalent *T* sites. $^1\text{H} \rightarrow ^{31}\text{P}$ CP/MAS NMR experiments have shown that protons of the dipropylamine molecule are in strong interaction with some of the framework P atoms, suggesting that the organic molecule is not located at the center

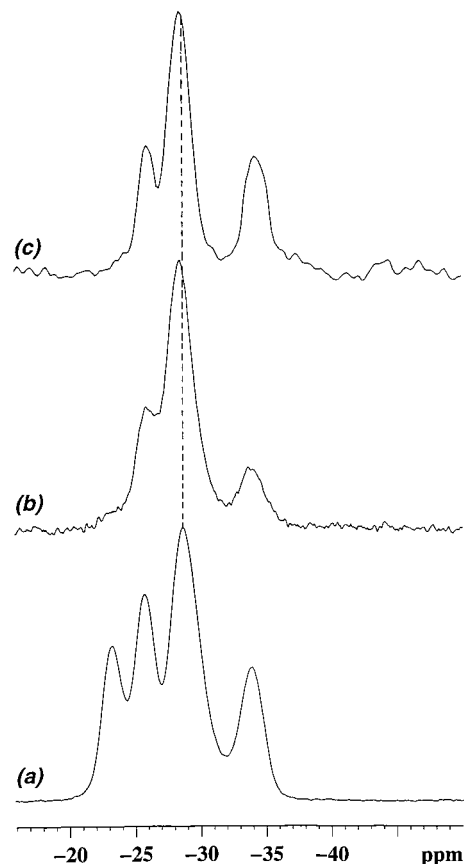
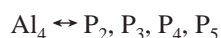


Figure 13. ^{31}P NMR signals of calcined rehydrated $\text{AlPO}_4\text{-41}$ obtained using a MAS sequence (a), $^1\text{H} \rightarrow ^{31}\text{P}$ cross-polarization with $100 \mu\text{s}$ contact time (b), and comparison with the one-dimensional trace of the two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ cross-polarization correlation spectrum corresponding to octahedral aluminum sites (c).

of the channels. This was supported by the presence of a broad signal between $+20$ and -20 ppm in the ^{27}Al MAS spectrum of the material (Figure 3a), probably resulting from a modification of the coordination of framework Al species in the vicinity of the template. A possibility could be that the amine interacts with a framework oxygen via a hydrogen-bonding interaction, as was previously observed for other microporous molecular sieves.²⁸ As a consequence, aluminophosphate layers at $z \approx 0$ and $z \approx 0.5$ are no longer identical and the unit cell contains

10 nonequivalent *T* sites, which is consistent with our ^{31}P NMR data and the doubling of the *c* edge of the unit cell. The ^{31}P NMR signal at -19.5 ppm is the ideal candidate for localizing the $\text{N}-\text{H}\cdots\text{O}-\text{P}$ interaction. In fact, its intensity buildup with contact time in $^1\text{H} \rightarrow ^{31}\text{P}$ cross-polarization experiments suggests proximity with a well-isolated proton (the $\text{N}-\text{H}$), contrary to the other polarized *P* sites which show a more complex behavior (Figure 8). Moreover, its chemical shift is in the region characteristic of $\text{P}-\text{O}\cdots\text{H}$ groups and could thus be assigned to the phosphorus atom bonded to the oxygen interacting with the organic molecule.

Upon removal of the template, the ^{31}P MAS NMR spectrum collapses to a single broad signal at ca. -30.5 ppm, indicating that all phosphorus atoms in the structure possess very similar environments in terms of $\text{P}-\text{O}-\text{Al}$ bond lengths and angles (Figure 3b). These environments are modified in the presence of water molecules, as evidenced by ^{31}P and ^{27}Al NMR (Figure 3c). As already mentioned, the monoclinic structure is preserved upon hydration of the molecular sieve. A slight decrease in the unit cell parameters, particularly the *b* axis but also the γ angle, is observed. From the new values, it is reasonable to assume that the unit cell of the hydrated material also contains 10 *P* and 10 *Al* atoms. The significant decrease in the *b* axis as compared to the *a* and *c* ones may indicate that the pores of the molecular sieve become more elliptical upon adsorption of water. ^{31}P and ^{27}Al NMR spectra show that the structure contains five nonequivalent *T* sites and that water modifies the coordination of one specific aluminum site. Therefore, there are two equivalent octahedrally coordinated *Al* species per unit cell in the hydrated $\text{AlPO}_4\cdot 41$. One is located in the aluminophosphate layer at $z \approx 0$, whereas the other is located in the layer at $z \approx 0.5$. The one-dimensional trace at $\delta = -15$ ppm in the 2D $^{27}\text{Al} \rightarrow ^{31}\text{P}$ correlation spectrum shows that the octahedrally coordinated aluminum is bonded to three nonequivalent phosphorus atoms (Figure 11). The position of this six-coordinated *Al* species in the unit cell can be determined by looking at framework $\text{Al}-\text{O}-\text{P}$ connectivities. Since the dehydration/rehydration process is reversible, the structure modifications occur without bond rearrangements, in contrast to the transformation of VPI-5 to $\text{AlPO}_4\cdot 8$.²⁹ As a consequence, framework connectivities are the same for the dehydrated and rehydrated materials. From Figure 1, these connectivities are



The only aluminum species connected to only three different phosphorus atoms is Al_1 . The octahedrally coordinated Al_1 species is not located near the center of the channel but is located where the pore curvature is maximum (Figure 1). Very similar observations have been reported by Peeters et al.^{30,31} for the calcined rehydrated $\text{AlPO}_4\cdot 11$. $\text{AlPO}_4\cdot 11$ is an aluminophosphate molecular sieve with 1-dimensional 10-membered-ring elliptical channels with a diameter of 3.9×6.4 Å. Upon hydration of the calcined material, Peeters et al.³¹ have observed that the orthorhombic symmetry was preserved with a small contraction of unit cell parameters, particularly for the *b* axis, thus leading to more elliptical pores. ^{27}Al MAS and DOR NMR

showed the preferential hydration of one of the five nonequivalent sites of the structure, thus transforming this site into an octahedrally coordinated aluminum species. By using a correlation between the standard deviations of the $\text{O}-\text{Al}-\text{O}$ angles obtained from Rietveld refinement of the X-ray pattern and the quadrupolar coupling constants obtained from ^{27}Al DOR NMR spectra, the authors came to the conclusion that water preferentially coordinates one specific *Al* site of the structure. As for $\text{AlPO}_4\cdot 41$, the position of this site corresponds to the maximum curvature of the elliptical pore. In $\text{AlPO}_4\cdot 41$, the six-coordinated *Al* species is connected to two P_1 , one P_2 , and one P_5 sites. On the basis of NMR signal intensities in the region of the 2D $^{27}\text{Al} \rightarrow ^{31}\text{P}$ correlation spectrum corresponding to octahedrally coordinated *Al* species, the ^{31}P NMR signal at -28.5 ppm can be unambiguously assigned to P_1 (Figure 13). Assignment of lines at -25.8 and -33.9 ppm, which also show connectivities with the six-coordinated *Al* site, is not possible since the intensities of their correlation peaks are similar. In the same manner, signals at -23.5 and -29.7 ppm, which correspond to the two phosphorus sites P_3 and P_4 bonded exclusively to four-coordinated *Al* species, cannot be distinguished. However, because of its peculiar behavior under $^1\text{H} \rightarrow ^{31}\text{P}$ cross-polarization, in particular the long T_{CP} value (Table 1b), it is reasonable to assign the ^{31}P NMR line at -23.5 ppm to the internal phosphorus site P_3 .

As already mentioned, NMR signals at -23.5 , -27.3 , -29.9 , and -31.5 ppm in the ^{31}P MAS NMR spectrum of as-synthesized $\text{AlPO}_4\cdot 41$ possess the same intensity, which is twice that of the lines at -19.5 and -36 ppm. The analysis of the $^1\text{H} \rightarrow ^{31}\text{P}$ cross-polarization buildup shows that the resonance at -19.5 ppm has a rather peculiar behavior, probably arising from a specific interaction of the proton of the amine ($\text{N}-\text{H}$) with a neighboring oxygen. This suggests that the modification of the environment of phosphorus atoms resulting from the interaction between the framework and the organic molecule is a local process that affects only the phosphorus species involved in the $\text{P}-\text{O}\cdots\text{H}$ bond. As a consequence, NMR signals at -19.5 and -36.0 ppm could result from the splitting of a unique signal corresponding to two *P* atoms otherwise equivalent in the absence of template or in the presence of coordinated water. Indeed, a major difference between phosphorus environments in as-synthesized and calcined rehydrated $\text{AlPO}_4\cdot 41$ materials is the presence of one $\text{P}-\text{O}\cdots\text{H}$ bond in the unit cell of the as-synthesized compound.

Qualitatively, the ^{31}P MAS NMR spectrum of calcined rehydrated $\text{AlPO}_4\cdot 41$ is similar to the region of the spectrum of the as-made aluminophosphate between -23 and -36 ppm (Figure 3). Signals are slightly shifted toward low fields for the rehydrated compound, which results from the modification of the unit cell and from the presence of water molecules in the pores. Despite that, the main difference concerns the relative intensity of the high-field peak. If such an analogy holds, one could infer that the -19.5 and -36 ppm resonances in the as-made solid originate from the same two phosphorus nuclei which resonate at -34 ppm after calcination and rehydration of the molecular sieve. These atoms would be magnetically equivalent in the presence of water but not in the presence of the amine. The nonequivalence is clearly evidenced in the ^{31}P NMR spectrum: the hydrogen-bonding interaction shifts one of the signals by more than 15 ppm downfield (Figure 3a).

Similar observations can be made by comparing the ^{27}Al 2D-5Q MAS NMR spectra of both materials (Figures 5 and 10). High- and low-field peaks at ca. 36 and 43 ppm in the spectrum of the as-synthesized material (signals 4 and 6 in Figure 5) are

no longer present in the spectrum of the calcined rehydrated $\text{AlPO}_4\text{-41}$, consistent with a nonequivalence of two aluminum atoms due to the presence of the amine. This attribution is supported by Al—O—P framework connectivities, as the $^{27}\text{Al} \rightarrow ^{31}\text{P}$ cross-polarization shows that ^{31}P signals at -19.5 and -36 ppm are strongly connected to ^{27}Al signals at 43 and 36 ppm, respectively (Figure 6). Moreover, $^1\text{H} \rightarrow ^{27}\text{Al}$ CP/MAS (not shown) experiments have demonstrated that the signal at 43 ppm is enhanced at short contact times along with resonances of Al species between -20 and 20 ppm.

As previously mentioned, the line at ca. -34 ppm in the ^{31}P MAS NMR spectrum of calcined rehydrated $\text{AlPO}_4\text{-41}$ can be assigned to P_2 or P_5 sites. In as-synthesized $\text{AlPO}_4\text{-41}$, one of the two P_2 (or P_5) sites is modified by interaction of the amine with one of the neighboring oxygen atoms. The hydrogen-bond interaction probably causes a slight displacement of the oxygen atom and thus a change in pore width. This could explain the special topology of the channels and, therefore, the monoclinic structure suggested by Kirchner et al.⁴ for calcined dehydrated $\text{AlPO}_4\text{-41}$.

Conclusion

A highly crystalline microporous aluminophosphate $\text{AlPO}_4\text{-41}$ has been synthesized hydrothermally using dipropylamine as the structure-directing molecule. $\text{AlPO}_4\text{-41}$ is one of a few $\text{AlPO}_4\text{-}n$ materials that display a multiple-line ^{31}P MAS NMR spectrum. The spectrum is composed of essentially six lines with chemical shifts ranging from -19.5 to -36 ppm and intensity ratios of 1:2:2:2:2:1. Six signals are also observed in the region characteristic of four-coordinated Al species of the ^{27}Al two-dimensional 5Q-MAS spectrum. $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP/MAS correlation spectroscopy indicates that all lines can be assigned to framework atoms, contrasting with previous studies that attributed ^{31}P NMR lines at -19.5 and -36 ppm to extraframework species. The relative intensities of ^{31}P NMR lines suggest that the structure contains 10 nonequivalent P and Al atoms, along with 1 Pr_2NH molecule that interacts with a specific framework oxygen atom by a hydrogen-bond interaction. The resonance at -19.5 ppm has been assigned to the phosphorus atom bonded to the oxygen involved in the hydrogen bonding. The presence of one $\text{P}-\text{O}\cdots\text{H}$ group makes the aluminophosphate layers perpendicular to [001] nonequivalent, as is the case for the calcined dehydrated material. However, the hydrogen-bonding interaction has only a local influence and does not significantly affect the environment of other phosphorus atoms since they cannot be distinguished by ^{31}P NMR.

$^1\text{H} \rightarrow ^{31}\text{P}$ CP/MAS experiments as well as the similarity that exists between ^{31}P MAS spectra of as-synthesized and calcined rehydrated materials allowed us to propose an approximate location for the organic molecules in the channels. The amine is not located at the center of the channel, which could explain their nonelliptical opening after calcination, proposed in a previous study.

While calcination does not significantly modify the X-ray pattern, the ^{31}P MAS NMR spectrum of the calcined never rehydrated $\text{AlPO}_4\text{-41}$ shows only a single broad resonance at ca. -30.5 ppm. Upon rehydration, the X-ray pattern is modified, which results from a contraction of the unit cell, particularly along [010]. Five signals are observed in both ^{31}P MAS and

^{27}Al 5Q MAS NMR spectra. Water preferentially coordinates one of the five nonequivalent aluminum atoms of the structure and transforms it into a six-coordinated species. This six-coordinated aluminum site has been located at the maximum curvature of the pores (site Al_1 in Figure 1) by two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ correlation spectroscopy and by one-dimensional $^1\text{H} \rightarrow ^{31}\text{P}$ CP/MAS experiments.

On the basis of its reversibility, unit cell changes, and location of water molecules in the channels, the dehydration/rehydration process in $\text{AlPO}_4\text{-41}$ is very similar to that observed in $\text{AlPO}_4\text{-11}$.

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