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Hydration of AlPO₄-11 Studied with X-ray Powder Diffraction and ²⁷Al and ³¹P NMR

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The influence of water adsorption in AlPO₄-11 has been studied with X-ray powder diffraction and ²⁷Al and ³¹P NMR. With X-ray powder diffraction, a change of the crystal symmetry from *IMA2* to *PNA2*₁ is observed upon water adsorption, resulting in a diminished unit-cell volume and more elliptical pores. NMR was used to study the hydration on an atomic scale. With ²⁷Al double rotation (DOR) and magic angle spinning (MAS) NMR, the quadrupole coupling constants (*C_Q*) and asymmetry parameters (*η*) of the different Al sites in dry and wet AlPO₄-11 were determined and correlated with the symmetry of the Al site obtained from literature data. In contrast with earlier ²⁷Al DOR measurements,¹ spectral simulations of ²⁷Al MAS and DOR NMR spectra measured at 7.0 T prove the preferential hydration of one tetrahedral aluminum site in AlPO₄-11 (five crystallographically different sites), transforming this site reversibly into octahedrally coordinated aluminum.² From the observed correlation between the XRD data and *C_Q*, it was concluded that the Al₂ site becomes preferentially octahedrally coordinated. On the basis of ²⁷Al DOR and ³¹P MAS NMR measurements performed on the partially hydrated samples, it is shown that the transformation upon hydration is a local process, comparable to the symmetry change observed upon adsorption of sorbates in ZSM-5.^{3,4}

Introduction

AlPO₄-11 is one of a range of crystalline aluminophosphates first synthesized by Union Carbide.⁵ The structure is built of alternating AlO₄⁻ and PO₄⁺ tetrahedra linked together via joined oxygen atoms to form a microporous three-dimensional network with a unidimensional pore system of 4.4 × 6.7 Å. The crystal structure of the calcined dehydrated material has been solved based on partial refinement of powder data obtained using a pulsed neutron source.⁶ The structure calls for three different T sites in the ratio 2:2:1. Meinhold et al.⁷ observed that AlPO₄-11 reversibly adsorbs water after calcination. X-ray diffraction measurements indicated that upon hydration the crystal symmetry changes from body-centered orthorhombic (space group *IMA2*, *a* = 13.54, *b* = 18.51, *c* = 8.37 Å) to primitive orthorhombic (space group *PNA2*₁, *a* = 13.54, *b* = 18.02, *c* = 8.12 Å) within 2 h. Due to the lowering of the symmetry, the calcined rehydrated sample is expected to contain five distinct crystallographic sites for Al and P with a ratio 1:1:1:1:1.¹

With ²⁷Al MAS NMR measured at 4.7 T, Meinhold et al.⁷ observed significant differences between the dry and the wet samples; however, no octahedral aluminum was reported. IR measurements indicated the presence of physisorbed water only. Upon hydration, the ³¹P MAS NMR spectrum also changes. The dry sample exhibits only a single peak at -31.6 ppm, while the wet sample shows two peaks with ratios 1:4 (-23.8 and -30.0 ppm, respectively, referenced to (NH₄)H₂PO₄). The downfield signal was tentatively assigned to the P atom in a 6-6 site, which became resolved from the other P sites.

Barrie et al.¹ studied fully hydrated AlPO₄-11 using ²⁷Al MAS and DOR NMR (see below) measured at 9.4 and 11.7 T. The MAS spectrum at 9.4 T of the hydrated sample (five crystallographically different T sites) showed three peaks in the tetrahedral region with intensity ratios of 21.3:60.2:18.5, together with an octahedral signal (approximately 20% of the total area). As a consequence, simulation of the tetrahedral region of the MAS spectrum measured at 11.7 T was performed using five signals. Furthermore, DOR resulted in a significant decrease of the line widths of two resolved peaks in the tetrahedral region while the line width of the octahedral signal did not decrease.

This lead to the conclusion that all five aluminum sites are hydrated to about the same extent.

Recently, Prasad et al.⁸ reported the preferential adsorption of water on the T₃ site (located at the junction of 6-, 6-, and 10-membered rings) according to MNDO calculations using the crystal structure of the as-synthesized AlPO₄-11. The calculations suggested that the oxygen atom of the water molecule interacts with the T atom on a T₃ position while the hydrogen atoms of the water molecule interact with two of the surrounding oxygen atoms. The T₃ site is the site with the largest T-O-T angle and hence posing minimum steric hindrance and offering maximal polarity and electrostatic field. On the basis of this result, both the ²⁷Al and ³¹P MAS NMR spectra were interpreted. The downfield signal in the ³¹P NMR spectrum was ascribed to octahedrally coordinated phosphorus, although the MNDO calculations clearly showed that the Al₃ was much more favored for water adsorption than the P₃ site. It was not taken into account in the calculations that the crystal symmetry changed upon water adsorption, resulting in five different T sites.

Double rotation (DOR) and dynamic angle spinning (DAS) NMR are useful advances in the study of quadrupolar nuclei by solid-state NMR. In MAS NMR, the readily observed central spin transition (+1/2 ↔ -1/2) is principally broadened by first-order chemical shift anisotropy (CSA) and second-order quadrupolar interactions. Although the CSA can be reduced or eliminated by magic angle spinning, the second-order quadrupolar interactions cannot be removed by spinning at any single axis. DOR and DAS techniques, however, provide us with the possibility to greatly diminish the influence of these anisotropies.

Quadrupolar nuclei are subject not only to magnetic fields but also to electric field gradients. The observed center of mass of the MAS NMR powder pattern, or the peak position in the DOR spectrum (*δ_{obs}*), is therefore the sum of two isotropic shifts (in ppm):

$$\delta_{\text{obs}} = \delta_{\text{iso}}^{\text{CS}} + \delta_{\text{iso}}^{\text{Q}}$$

where the first term represents the isotropic chemical shift and the second term is the isotropic quadrupolar shift. While the isotropic chemical shift (in ppm) is field independent, the isotropic quadrupolar shift of the central transition is given by the following

expression:

$$\delta_{\text{iso}}^Q = -\frac{3}{40} \left(\frac{C_Q}{\nu_L} \right)^2 \left[\frac{I(I+1) - 3/4}{I^2(2I-1)^2} \right] \left[1 + \frac{\eta^2}{3} \right] \times 10^6$$

where C_Q represents e^2qQ/h and ν_L the Larmor frequency of the nucleus at the magnetic field. The quadrupolar asymmetry parameter (η) describes the deviation of the local electric field gradient from cylindrical symmetry, while the quadrupolar coupling constant (C_Q) is defined as the product of the electrical field gradient (eq) and the nuclear quadrupole moment (eQ) divided by h and is thus proportional to the magnitude of the electrical field gradient. From the above formula, it can be observed that δ_{iso}^Q is inversely proportional to the square of ν_L . So, by performing DOR or DAS experiments at different magnetic fields, $\delta_{\text{iso}}^{\text{CS}}$ and δ_{iso}^Q can be determined. The calculated δ_{iso}^Q can be used for an approximation of C_Q , since η is between 0 and 1, so C_Q is between δ_{iso}^Q and $0.866\delta_{\text{iso}}^Q$ (MHz). Computer simulation of MAS spectra is necessary to yield the two parameters (C_Q and η) independently.

In a previous communication,² we reported the preliminary results of a combined MAS and DOR NMR study performed on fully hydrated $\text{AlPO}_4\text{-11}$. Here, the results of a combined X-ray powder diffraction and ^{27}Al and ^{31}P NMR study are reported. ^{27}Al DOR and MAS NMR spectra of dry and fully hydrated $\text{AlPO}_4\text{-11}$ were measured at 4.7, 7.0, 9.4, and 11.7 T. Partially hydrated samples were studied by ^{27}Al DOR NMR, ^{31}P MAS NMR, and ^{31}P T_2 measurements, performed at 9.4 T. Relations between the spectral parameters and structural data are proposed and discussed.

Experimental Section

$\text{AlPO}_4\text{-11}$ was prepared by a method described in the patent literature.⁹ A gel with a molar composition of $\text{P}_2\text{O}_5\text{:Al}_2\text{O}_3\text{:DPA:}40\text{H}_2\text{O}$ was prepared (DPA represents *n*-dipropylamine). Crystallization was performed at 463 K for 48 h in Teflon-lined stainless steel static autoclaves. After quenching of the autoclaves, the crystals were separated from the mother liquor by sedimentation. Calcination of the sample was performed by heating the sample in a flow of dry oxygen at a rate of 5 K min^{-1} to 873 K and keeping them at the final temperature for 5 h. The Al/P ratio of the product was checked using atomic absorption spectroscopy (Al) in combination with a photometric determination of phosphate.¹⁰ The pore volume was measured using *n*-butane adsorption of a Cahn 2000 electrobalance. Hydration was performed by storing the samples in a desiccator with water for several days. The water content of the samples before and after the NMR measurements was determined with TGA.

X-ray diffraction measurements were performed on a Philips PW 7200 diffractometer at room temperature. X-ray diffraction patterns were recorded between $2\theta = 5^\circ$ and $2\theta = 40^\circ$ with a scanning rate of $2^\circ/\text{min}$.

^{27}Al DOR and MAS NMR spectra at different magnetic fields were measured using Bruker MSL spectrometers. The pulse length was varied between 1 and 3 μs , corresponding to a flip angle of approximately 20° ; the recycle delay was 1 s. For the DOR measurements, the outer rotor was spun at 850–1000 Hz with the inner rotor spinning at 4–5 kHz. MAS spectra were recorded at a spinning speed of 5 kHz. Typically 800–1000 pulses were accumulated. Simulations of the DOR and MAS NMR spectra were performed with the program QNMR.¹¹

^{31}P MAS NMR and T_2 measurements were recorded on a Bruker MSL 400 spectrometer. A recycle delay of 60 s was found sufficiently long to record spectra that were unaffected by further enlarging of the delay. The Carr–Purcell–Gill–Meiboom echo train was used on static samples for the T_2 measurements. The interval between two consecutive 180° pulses ($2\tau_1$) was equal to 20 μs .¹² The decrease of the echo height was fitted with a

Figure 1. X-ray diffraction patterns of $\text{AlPO}_4\text{-11}$: (a) as synthesized; (b) calcined, dehydrated; (c) calcined, rehydrated.

Figure 2. X-ray diffraction patterns of $\text{AlPO}_4\text{-11}$ after a certain period of water adsorption from ambient air (indicated in minutes).

biexponential decay of a Lorentzian shape:

$$I(t) = I(0) \exp(-t/T_2) + I''(0) \exp(-t/T_2'')$$

Results and Discussion

The X-ray powder diffraction spectra of the crystallization product and the calcined products (dehydrated and rehydrated) are given in Figure 1. The X-ray diffraction spectra demonstrate the pure and highly crystalline nature of the products. The Al/P ratio of the sample was 1.03; the pore volume as determined with *n*-butane was 0.098 mL/g. Upon water adsorption, the intensity of the reflections at a lower angle ($2\theta = 8\text{--}10^\circ$) decreases in intensity. This reduction in intensity may be an indication of the interaction of water molecules with framework T sites.⁸ In Figure 2, the evolution of the X-ray diffraction spectrum upon hydration is plotted for a selected region ($15^\circ < 2\theta < 24^\circ$). It can be seen that the most pronounced peak at $2\theta = 21.22^\circ$ vanishes upon hydration, and a new peak at $2\theta = 21.85^\circ$ appears. The observed changes are a consequence of the symmetry change from $IMA2_1$ to $PNA2_1$.

Khouzami et al.¹³ also measured X-ray powder diffraction patterns of $\text{AlPO}_4\text{-11}$ after water adsorption. The measured diffraction patterns were described as a combination of the dry and the wet spectrum; the same appears to be the case here. The crystal structures derived from X-ray diffraction data are displayed in Figures 3 and 4. Atomic positions were obtained

Figure 3. Crystal structure of as-synthesized $\text{AlPO}_4\text{-11}$.

Figure 4. Crystal structure of calcined and rehydrated $\text{AlPO}_4\text{-11}$.

from refs 14 and 13. From these figures, it can be observed that upon water adsorption the pores become more elliptical; after water adsorption the pore diameter is just big enough to accommodate the water molecules.

The ^{27}Al DOR NMR spectra of the dehydrated $\text{AlPO}_4\text{-11}$ sample measured at different magnetic fields are given in Figure 5. The best resolution is obtained at low magnetic fields. At 4.7 T, two clearly separated peaks are visible (ratio 1:4), while on the basis of neutron scattering three peaks are expected (ratio 2:2:1). Deconvolution of the DOR spectrum measured at 4.7 T was performed with three signals with intensity ratios 1:2:2. It was indicated in the Introduction that the peak positions of quadrupolar nuclei are inversely proportional to $(B_0)^2$; for the dry sample, this is displayed in Figure 6. Extrapolation of the three lines in Figure 6 yields three isotropic chemical shifts and three approximate quadrupolar coupling constants: 36.75 ppm (0.45 MHz), 37 ppm (2.15 MHz), and 38 ppm (2.65 MHz). The more precise values of the quadrupolar coupling constants and the η values were obtained from simulation of the DOR and MAS spectra at 4.7 and 7.0 T with the program QNMR.¹¹ Centers of gravity were taken from the DOR spectrum at 4.7 T. Combination of the centers of gravity and the isotropic shifts yields information regarding the quadrupolar interaction parameters e^2qQ/h and η . Simulation of the MAS spectra allows the determination of the two parameters separately. The values obtained in this way are listed in Table I.

The ^{27}Al DOR NMR spectra of fully rehydrated $\text{AlPO}_4\text{-11}$ at various magnetic fields are given in Figure 7. In contrast with

Figure 5. ^{27}Al DOR NMR spectra of dehydrated $\text{AlPO}_4\text{-11}$ at different field strengths (* denotes spinning sideband).

Figure 6. ^{27}Al DOR NMR line positions of dehydrated $\text{AlPO}_4\text{-11}$ as a function of $100/(B_0)^2$.

TABLE I: Parameters Used for the Simulation of the NMR Spectra of Dry $\text{AlPO}_4\text{-11}$

isotropic chemical shift (ppm, ± 0.15)	relative area (% , ± 1.5)	e^2qQ/h (MHz, ± 0.02)	η (± 0.05)
36.8	20	0.5	0.5
37.0	40	2.15	0.35
38.0	40	2.60	0.45

the dry sample, here the best resolution is observed at 7.0 T. Four different lines in the tetrahedral region, together with an octahedral signal of equal area, are observed. At higher as well as lower magnetic fields, the resolution decreases. Extrapolation of the chemical shifts to infinite magnetic field yields the isotropic chemical shifts at 32.6, 40.8, 42.1, and 46.1 ppm and a signal of octahedral aluminum at -11 ppm (Figure 8 and Table II).

The MAS and DOR spectral simulations were performed with four different tetrahedral sites of equal intensities, assuming preferential hydration of one aluminum site. The octahedral signal was not fitted because of the broad and featureless shape of this part of the MAS spectrum. The fit between experiment and simulated curve which was achieved using four peaks with equal areas in the tetrahedral region did not improve using five tetrahedral sites (random hydration). The results of the DOR

Figure 7. ^{27}Al DOR NMR spectra of fully hydrated $\text{AlPO}_4\text{-11}$ samples at different field strengths (* denotes spinning sideband).

Figure 8. ^{27}Al DOR NMR line positions of hydrated $\text{AlPO}_4\text{-11}$ as a function of $100/(B_0)^2$. No octahedral signal could be observed at 4.7 T.

and MAS NMR (7.0 T) simulations are shown in Figure 9. The parameters used for the simulations are listed in Table II. Simulations of the DOR spectra measured at different magnetic fields are displayed in Figure 10. All spectra were simulated with four Gaussian lines with equal areas. The experimental spectra show slightly broader signals, especially near the bottom of the signals; i.e., the signals are not perfectly Gaussian. This will affect both sides of all signals. At 7.0 T, the low-field side of the signal happens to be affected by a spinning sideband of the 32.6 ppm signal. Integration of the DOR spectra measured at 9.4 and 11.7 T (including spinning sidebands) confirmed the 1:2:1 ratio of the tetrahedral signals, consistent with the simulations.

These results are not in agreement with those published by Barrie et al. In that study, the ^{27}Al MAS NMR spectrum taken at 11.7 T was simulated, resulting in five tetrahedral and one octahedral site with equal areas. The explanation was given in terms of equal (20% each) hydration of all five tetrahedral sites. In our study, the simulations of the DOR spectrum measured at 11.7 T leads to a different result. The tetrahedral region together with the spinning sidebands can be fitted with three sites (ratios 1:2:1), together with an octahedral signal of intensity 1. So, the present study leads unequivocally to the conclusion that one site is hydrated (selective hydration). As such, it is in accordance

Figure 9. ^{27}Al NMR spectra of wet $\text{AlPO}_4\text{-11}$ at 7.0 T: DOR simulation, DOR spectrum, MAS spectrum, and MAS simulation.

TABLE II: Parameters Used for the Simulation of the NMR Spectra of Fully Rehydrated $\text{AlPO}_4\text{-11}$

isotropic chemical shift (ppm, ± 0.15)	rel area (% ± 1.5)	e^2qQ/h (MHz, ± 0.02)	η (± 0.05)
46.1	20	2.23	0
42.1	20	2.69	0.5
40.8	20	1.63	0.5
32.6	20	2.63	0.95
-11.0	20	3.9	ND ^a

^a Not determined. The e^2qQ/h parameter was determined from slope of the curve in Figure 8.

Figure 10. ^{27}Al DOR NMR spectra and simulations of wet $\text{AlPO}_4\text{-11}$: 4.7 T (traces 1, 2), 9.4 T (traces 3, 4), and 11.7 T (traces 5, 6). Odd-numbered traces are simulations; even-numbered traces are experimental spectra. The spectrum at 4.7 T was obtained from a $\text{CoAlPO}_4\text{-11}$ sample containing 1 wt % cobalt. The presence of cobalt leads only to some additional broadening.

with the predictions published by Prasad et al., who based their conclusions mainly on a theoretical approach with MNDO. In the calculations of Prasad et al., site T_3 of the as-synthesized sample was found to have the highest energy of hydration.

TABLE III: Bond Angles and Bond Lengths in $\text{AlPO}_4\text{-11}$ and Corresponding Spectral Parameters for ^{27}Al NMR

T site	%	δ_{iso} (ppm)	C_Q (MHz)	distances (Å)		angles (deg)			
				Al–O	$\sigma_{\text{Al–O}}$	O–Al–O	$\sigma_{\text{O–Al–O}}$	Al–O–P	$\sigma_{\text{Al–O–P}}$
Dry ^a									
Al ₁	40	38.0	2.60	1.730	0.016	109.37	3.26	154.78	14.0
Al ₂	40	37.0	2.15	1.693	0.019	109.44	2.07	161.0	8.9
Al ₃	20	36.8	0.5	1.683	0.049	109.45	1.63	172.0	4.0
Wet ^b									
Al ₁	20	42.1	2.69	1.7065	0.0103	109.46	1.460	161.56	12.19
Al ₂	20	−11.0	3.9	1.707	0.0171	109.47	2.426	151.48	9.43
Al ₃	20	46.1	2.23	1.708	0.0088	109.47	1.222	158.09	10.42
Al ₄	20	40.8	1.63	1.709	0.0062	109.46	1.107	156.78	11.60
Al ₅	20	32.6	2.63	1.715	0.0117	109.46	1.417	149.32	10.20

^a Calculated based on atomic positions given in ref 14. ^b Calculated based on atomic positions given in ref 13.

Figure 11. Correlation between the quadrupolar coupling constants and the standard deviations of the O-Al-O angle at the different Al sites.

An interesting question would be to try and indicate the site of hydration experimentally. Our experiments should allow us, in principle, to indicate which site in $\text{AlPO}_4\text{-11}$ is preferentially hydrated. The correlation between the quadrupolar coupling constant (C_Q) of a nucleus and the symmetry around this site opens such a possibility. The symmetry around a site can be characterized by the distribution in Al-O bond lengths and the Al-O-P or O-Al-O bond angles obtained from Rietveld refinement of X-ray diffraction data. The first two parameters have been suggested to correlate with the isotropic chemical shifts of heavy nuclei (e.g., ^{29}Si and ^{27}Al in zeolites).^{16,17} However, a logical parameter to correlate with the C_Q would be the local symmetry around the nucleus under consideration (here ^{27}Al). A similar suggestion was recently made for ^{17}O NMR by Mueller et al.¹⁸ Relevant values for as-synthesized $\text{AlPO}_4\text{-11}$ and rehydrated $\text{AlPO}_4\text{-11}$ are listed in Table III. The local symmetry was calculated using framework atoms only. It can be expected that the electrical field gradient at the Al₂ site is enhanced by the presence of two water molecules, approaching this T-site in an asymmetric way.

There exists a fair agreement between the $\sigma_{\text{O-Al-O}}$ and the e^2qQ/h for the wet sample. A nearly linear correlation between these two parameters is observed (Figure 11), even for the octahedral signal, which passes through the origin, as expected for symmetry reasons.¹⁹ The relation between $\sigma_{\text{O-Al-O}}$ and e^2qQ/h for the dry sample is not as clear as that for the wet sample, but in our view it is still acceptable (Figure 11). A possible reason for this deteriorated fit lies in the fact that the atomic positions for the dry sample have been assumed to be the same as those for the as-synthesized sample. It is very likely, however, that the

Figure 12. Correlation between the isotropic chemical shifts and the average Al-O-P angles at the different Al sites.

crystal symmetry changes slightly after calcination (see Figure 1). At this time, no analysis of XRD data of calcined dehydrated $\text{AlPO}_4\text{-11}$ is available in the literature, to the best of our knowledge.

On the basis of the observed correlation between C_Q and $\sigma_{\text{O-Al-O}}$, we conclude that it is the Al₂ site which becomes preferentially hydrated and is transformed into octahedrally coordinated aluminum. This finding is supported by the atomic coordinates supplied by Khouzami et al.¹³ While the mean Al-O distance around the Al₂ site is the same as for the other Al sites, the $\sigma_{\text{Al-O}}$ increases strongly, indicating that some Al-O bonds are significantly longer.

In the literature, a correlation between the isotropic chemical shifts of aluminum and the Al-O-Si¹⁷ or Al-O-P¹⁶ bond angle is suggested. This correlation can be used to check the assignment of the different sites in $\text{AlPO}_4\text{-11}$. In Figure 12, the isotropic chemical shift is correlated with the average Al-O-P bond angle. Two almost straight lines are observed but with different slopes. This difference in slopes might be caused by the same fact that led to the deteriorated fit of the C_Q for the dry sample. Apparently, the discrepancies between the real and the assumed (as-synthesized) geometries have a larger influence on the calculated shifts than on the C_Q values. Previously published relations between the isotropic chemical shifts and the average angles around the surrounding oxygen atoms also point to deshielding when deviating from perfect tetrahedral symmetry.¹⁶ The octahedrally coordinated aluminum strongly deviates from the observed relationships.

In order to follow the course of the hydration, partially hydrated samples were studied using ^{31}P MAS, ^{31}P T_2 , and ^{27}Al DOR NMR measured at 9.4 T. The ^{27}Al DOR spectra are displayed

Figure 13. ^{27}Al DOR spectra of partially hydrated $\text{AlPO}_4\text{-11}$ samples measured at 9.4 T. Water content (wt %): 0 (bottom), 1, 3, 3.6, 5.0, 5.9, 6.5, 10.9, and 15.0 (top).

Figure 14. ^{31}P T_2 relaxation behavior as a function of the water content (indicated in wt %).

in Figure 13. Upon hydration, two extra bands appear in the tetrahedral region, at the same position as in the fully hydrated sample, together with an octahedral signal. The intensities of these bands increase linearly with the intensity of the octahedral signal. At intermediate water contents, the central band is split into three bands but finally splits into two peaks for the fully hydrated sample. Even at very low water concentrations, octahedrally coordinated aluminum is formed. There are no indications for pentacoordinated aluminum. The spectra can be described as being a mixture of a dry and a wet part, of which the wet part increases linearly with the octahedral signal. This process is reminiscent of the adsorption of sorbates in dealuminated zeolites (silicalites), which also causes a local structural deformation.^{3,4}

The observation that the structure is locally transformed is confirmed by the ^{31}P measurements. The ^{31}P MAS NMR spectra

Figure 15. ^{31}P MAS NMR spectra of partially hydrated $\text{AlPO}_4\text{-11}$ samples measured at 9.4 T. Water content (wt %): 0 (bottom), 3, 5.2, 7.2, 7.9, and 15.0 (top).

TABLE IV: ^{31}P T_2 Values (Static Samples) and Relative Contributions of ^{31}P MAS NMR Lines

water content (wt %)	rel area ^a of -20 ppm peak	$I(0)$ (%)	T_2 (ms)	$I''(0)$ (%)	T_2'' (ms)
0	0	93.1	322.5	6.57	24.09
1	1.8	—	—	—	—
3	6.4	80.9	128.0	19.8	5.03
5.2	9.9	60.3	119.2	42.4	4.5
7.2	15.5	35.1	84.7	70.5	4.2
7.9	18.4	27.7	79.1	77.3	4.3
15.0	21.1	60.0	9.97	48.2	3.3

^a Relative area of the -20 ppm MAS NMR line with respect to the total intensity.

of $\text{AlPO}_4\text{-11}$ with different water contents are given in Figure 15. The dry sample exhibits only one peak, at -27 ppm. Upon hydration, an extra peak at -20 ppm appears. The intensity of this peak increases with the water content of the samples (Table IV).

In previous publications,^{12,20} it was indicated that the T_2 relaxation time of ^{31}P is dramatically decreased upon water adsorption and that only a very small contribution of the dipolar coupling of phosphorus with the protons of the water molecule is apparent. The major reduction of the relaxation time stems from other influences. One possible source of ^{31}P spin relaxation could be the change in symmetry brought about by the hydration. This same loss of symmetry is reflected in the overall increase of the C_Q values for ^{27}Al upon adsorption of water. The lower symmetry enhances the electrical field gradients at the aluminum nuclei, resulting in a faster transversal relaxation. Dipolar coupling of the ^{27}Al nuclei with the ^{31}P nuclei results in a reduced T_2 value of the surrounding phosphorus nuclei. The results of the ^{31}P T_2 measurements (with high-power proton decoupling) are listed in Table IV and displayed in Figure 14. The observed decays were fitted with a biexponential Lorentzian function. The existence of several P sites is not responsible for the observed biexponential decay. Comparing the contributions of the two exponential functions with the ratio of the P sites, this becomes clear. In a previous publication,¹² we reported ^{31}P T_2

measurements at two different magnetic fields. The ratio of the two contributions shifted with the magnetic field, so we think that the biexponential decay for the dry sample stems from the choice of the time between two consecutive 180° pulses ($2\tau_1$ periods). Only measurements performed at the same magnetic field with the same τ_1 period should be compared.¹² The gradual increase of the fast relaxing component observed upon gradual hydration is a strong indication that the observed biexponential decay is realistic and not due to the choice of the τ_1 value. With increasing water content, the contribution of the fast relaxing component increases, up to approximately 8 wt % water (equal to the amount of water needed for octahedral coordination of 20% of the aluminum). Further enlarging of the water content reduces the relaxation time of the slowest relaxing component significantly. The contributions of the two exponential decays are based on the total intensity (static samples show only one broad signal).

Integration of the ^{31}P MAS NMR spectra also seems to indicate that the hydration is completed after approximately 8 wt % water adsorption. The contribution of the peak at -20 ppm has reached the maximum value after 8 wt % water adsorption.

Both the ^{27}Al and the ^{31}P NMR measurements indicate that the symmetry change upon water adsorption is a local process. Upon water adsorption, part of the structure is quickly transformed, while the dry parts remain in the old symmetry.

Conclusions

With ^{27}Al DOR and MAS NMR, it was shown that the hydration of $\text{AlPO}_4\text{-11}$ is a selective process. The correlation between the C_Q and the symmetry around an aluminum site, characterized by the standard deviation from the average O-Al-O angle, enabled us to indicate which aluminum site becomes octahedrally coordinated. Upon water adsorption, the Al_2 site becomes hydrated, transforming this site selectively into octahedrally coordinated aluminum. NMR measurements performed on partially hydrated samples have shown that the transformation is a local process.

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