

Solid-State NMR Studies of Hydrated Porous Aluminophosphate VPI-5

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Abstract: Hydrated aluminophosphate molecular sieve VPI-5 has been studied by variable-temperature (180–370 K) ^{31}P and ^{27}Al magic-angle-spinning (MAS) solid-state NMR spectroscopy. ^1H - ^{31}P and ^1H - ^{27}Al cross-polarization (CP) and, for the first time in variable-temperature MAS studies, ^{27}Al quadrupole nutation were used. The room-temperature ^{31}P MAS spectrum contains three resonances in a 1:1:1 intensity ratio, which have been assigned. The ^{27}Al MAS spectrum is composed of two signals from 4- and 6-coordinated Al in a 2:1 intensity ratio, and quadrupole nutation further resolves two signals which overlap in the MAS signal from 4-coordinated Al. These results are consistent with the $P6_3$ symmetry group. Above 353 K two ^{31}P MAS resonances in a 2:1 intensity ratio are found, and quadrupole nutation gives only one signal from 4-coordinated Al (apart from the signal from 6-coordinated Al), indicating that hydrated VPI-5 undergoes a high-temperature phase transformation to a higher framework symmetry, possibly $P6_3cm$. In parallel, there is a considerable decrease of the intensity of ^{31}P and ^{27}Al CP/MAS signals with increasing temperature, indicating an increased molecular mobility of water caused by the breakdown of its hydrogen-bonded structure inside the pores. In the range 190–220 K the width of the MAS signal from 4-coordinated Al and the quadrupole interaction parameters and isotropic chemical shift of the resonance from 6-coordinated Al (obtained by computer line fitting) all go through extremes. These observations indicate that hydrated VPI-5 undergoes a low-temperature structural transformation. Despite the transformation, the ^{31}P MAS spectrum still contains three resonances, while quadrupole nutation resolves only one signal from 4-coordinated Al, probably because the crystallographically inequivalent ^{27}Al sites have similar quadrupole interaction parameters and isotropic chemical shifts. The high- and low-temperature phase transformations are fully reversible.

Introduction

VPI-5 is a hydrophilic crystalline molecular sieve containing 18-membered rings of Al and P atoms (Figure 1) and having the chemical formula AlPO_4 .^{1,2} The large channel diameter of ca. 12 Å gives the material potential for the separation of large molecules and for catalytic cracking of heavy fractions of petroleum. Several attempts have been made to determine the details of the structure of VPI-5.^{3,4} Rudolf and Crowder⁵ refined the structure of the as-prepared material from the powder X-ray diffraction (XRD) pattern, but their refinement leaves a large difference between the observed and calculated patterns. Also, the ^{31}P and ^{27}Al magic-angle-spinning (MAS) NMR spectra^{6,7} are difficult to reconcile with the proposed structure. First, the space group $P6_3cm$ calls for two crystallographically distinct phosphorus positions with relative occupancies 2:1, while the ^{31}P MAS NMR spectrum contains three resonances. Second, the ^{27}Al MAS NMR spectrum contains signals from 4- and 6-coordinated aluminum, but the latter cannot be accounted for in this model. McCusker et al.⁸ obtained a significantly better refinement in the lower symmetry space group $P6_3$ (see Figure 1), which is fully consistent with the NMR results. This refinement locates all the water molecules inside the large pore of VPI-5: two molecules complete an octahedral coordination sphere around the framework aluminum atom between the fused 4-membered rings; four of the remaining water positions form a hydrogen-bonded chain linking the 6-coordinated aluminum atoms, thus forming a triple helix

of water molecules. The last, less well defined, water position links the helices to one another.

Variable-temperature ^{31}P MAS NMR studies in the range ca. 294–423 K have been reported,^{9,10} but only one of the papers¹⁰ actually shows the spectra. No ^{31}P information is available for temperatures below 294 K, and there is no ^{27}Al information for

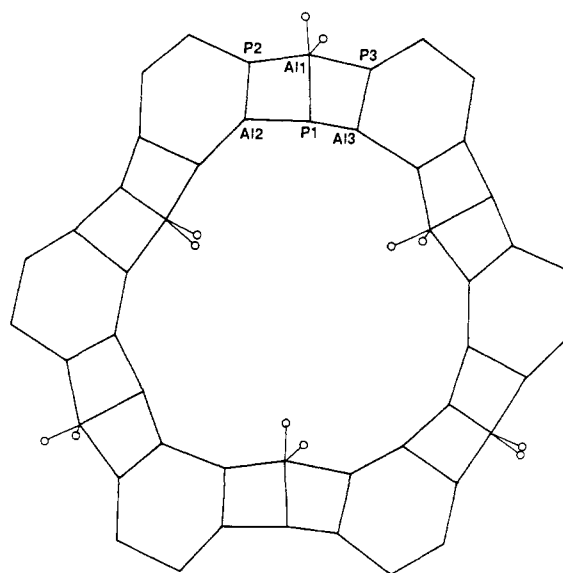


Figure 1. One layer of the framework structure of hydrated VPI-5 taken from the stereoscopic view along the [001] direction according to McCusker et al.⁸ showing the deviation from $P6_3cm$ symmetry. Aluminum and phosphorus atoms, linked via oxygen atoms (not shown for clarity), are located at the apices of the polygons. Sites located between two fused four-membered rings are referred to in the text as 4–4 sites; those located between six-membered and four-membered rings are referred to as 6–4 sites. P2 and P3 sites and Al2 and Al3 sites are inequivalent as a result of the distortion. All Al and P atoms are linked, via oxygens, to atoms in another layer in the structure (not shown), which makes them 4-coordinated, except for the Al1 site which is 6-coordinated as a result of bonding to four bridging oxygens and two “framework” water molecules. Other intracrystalline waters are not shown.

(1) Davis, M. E.; Saldarriaga, C.; Montes, C.; Garces, J.; Crowder, C. *Nature* **1988**, *331*, 698.

(2) Davis, M. E.; Saldarriaga, C.; Montes, C.; Garces, J.; Crowder, C. *Zeolites* **1988**, *8*, 362.

(3) Crowder, C. E.; Garces, J.; Davis, M. E. *Adv. X-Ray Anal.* **1988**, *32*, 507.

(4) Richardson, J. W., Jr.; Smith, J. V.; Pluth, J. J. *J. Phys. Chem.* **1989**, *93*, 8212.

(5) Rudolf, R. R.; Crowder, C. E. *Zeolites* **1990**, *10*, 163.

(6) Davis, M. E.; Montes, C.; Hathaway, P. E.; Arhancet, J. P.; Hasha, D. L.; Garces, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 3919.

(7) Grobet, P. E.; Martens, J. A.; Balakrishnan, I.; Mertens, M.; Jacobs, P. A. *Appl. Catal.* **1989**, *56*, L21.

(8) McCusker, L. B.; Baerlocher, Ch.; Jahn, E.; Bülow, M. *Zeolites* **1991**, *11*, 308.

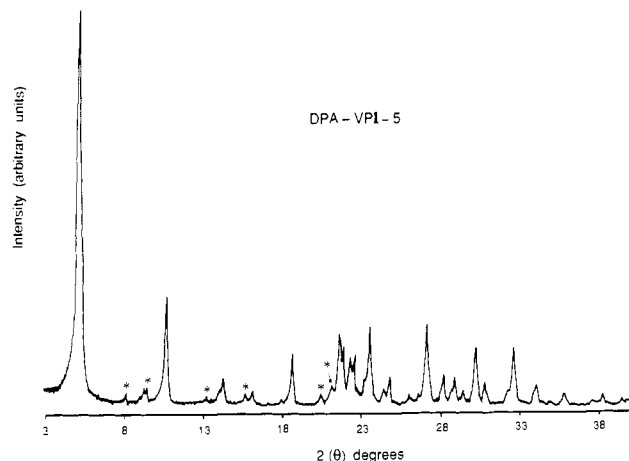


Figure 2. Room-temperature XRD pattern of hydrated VPI-5 collected with a Philips PW-1380 horizontal goniometer using Cu K α radiation with a curved graphite monochromator in the diffracted beam. Asterisks denote AlPO₄-11 impurity peaks.

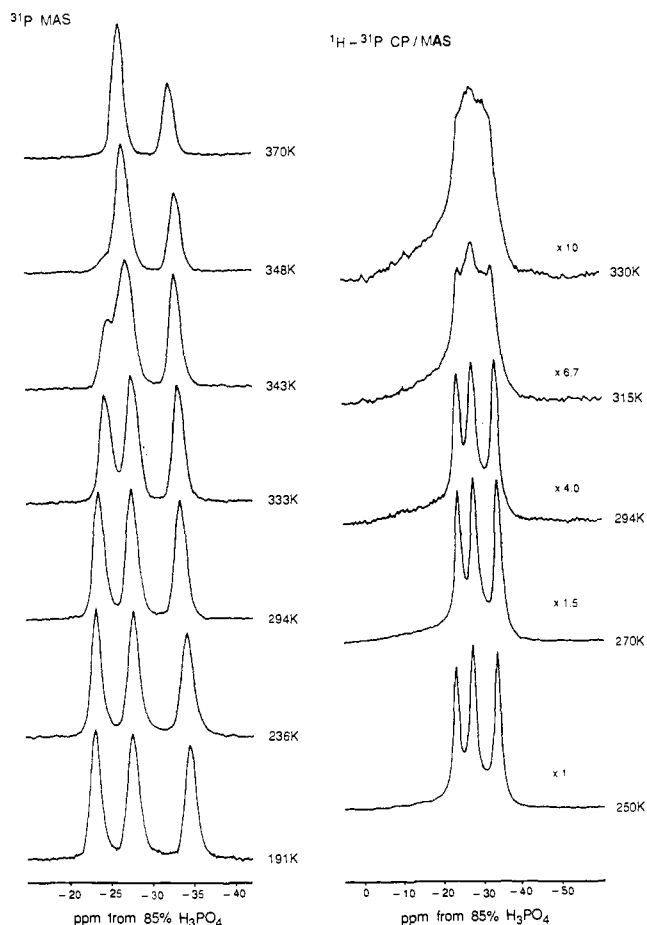


Figure 3. Variable-temperature ³¹P MAS and ¹H-³¹P CP/MAS NMR spectra of hydrated VPI-5. Note the different vertical expansion factors in the CP spectra. The resonances at -23 and -27 ppm are due to P atoms in the 6-4 sites, and the signal at -33 ppm is due to P atoms in the 4-4 sites.¹⁰

any temperature apart from room temperature. A recent double-rotation (DOR) NMR study of hydrated VPI-5 has detected two resonances due to 4-coordinated Al and one due to 6-coordinated Al in a 1:1:1 intensity ratio.¹¹ The former peaks are not

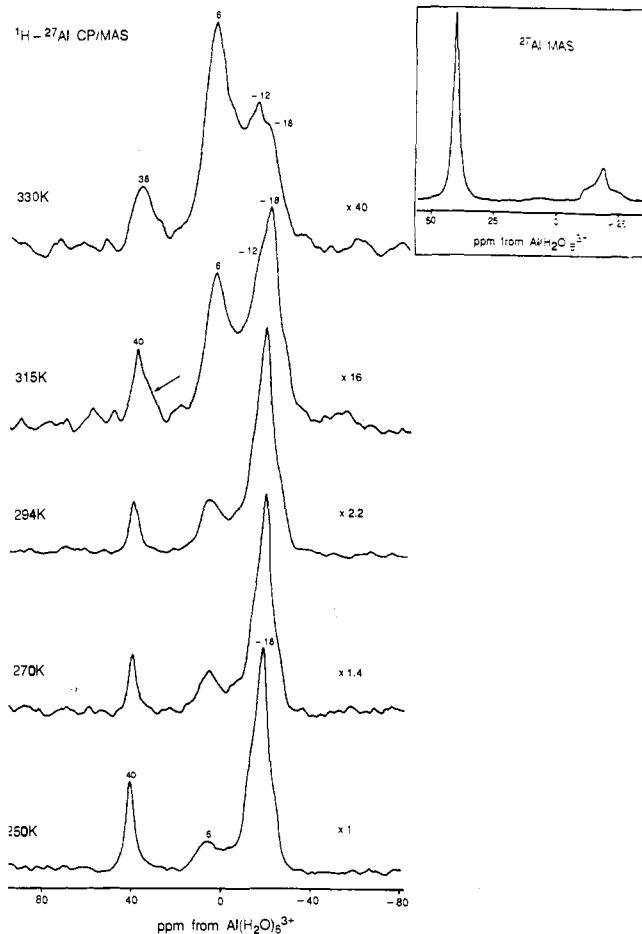


Figure 4. Variable-temperature ¹H-²⁷Al CP/MAS NMR spectra of hydrated VPI-5. Note the different vertical expansion factors. For comparison, the inset shows the room-temperature ²⁷Al MAS NMR spectrum. VPI-5 gives resonances at 40 and -18 ppm from 4-coordinated Al atoms in the 6-4 sites (Al2 and Al3 in Figure 1) and from 6-coordinated Al atoms in the 4-4 sites (Al1), respectively. Impurities give resonances at ca. 38, 6, and -12 ppm.

resolved in the ordinary ²⁷Al MAS NMR spectrum, and it is of interest to establish whether their quadrupole interaction parameters are sufficiently different to be profitably studied by quadrupole nutation NMR spectroscopy.¹² If so, the technique should provide valuable insights into the temperature-induced structural transformations of VPI-5. We have carried out variable-temperatures ²⁷Al, ³¹P MAS, and ²⁷Al quadrupole nutation NMR measurements in the range 180-370 K, using fast (7-12 kHz) spinning rates. These are the first variable-temperature quadrupole nutation studies using MAS.

Experimental Section

Samples. VPI-5 was prepared according to Davis et al.¹³ using di-*n*-propylamine (DPA) as a template, hydrated for 12 h (ca. 25 wt % water) over a saturated solution of NH₄Cl, and characterized by XRD, Fourier transform infrared spectroscopy, and ¹H, ²⁷Al, and ³¹P solid-state NMR spectroscopy. Elemental analysis indicates that the DPA content in the samples corresponds to about one molecule per three unit cells. The powder XRD pattern of the product given in Figure 2 shows that the sample is highly crystalline and contains less than ca. 3% AlPO₄-11 impurity.

Techniques. ²⁷Al NMR Bloch decays were recorded on a Bruker MSL-400 spectrometer at 104.26 MHz (9.4 T) with very short, 0.6- μ s (less than 10⁶), radiofrequency pulses and 0.4-0.5-s recycle delays.

(9) Stöcker, M.; Akporiaye, D.; Lillerud, K.-P. *Appl. Catal.* **1991**, *69*, L7.

(10) van Braam Houckgeest, J. P.; Kraushaar-Czarnetzki, B.; Dogterom, R. J.; de Groot, A. *J. Chem. Soc., Chem. Commun.* **1991**, 666.

(11) Wu, Y.; Chmelka, B. F.; Pines, A.; Davis, M. E.; Grobet, P. J.; Jacobs, P. A. *Nature* **1990**, *346*, 550.

(12) Samoson, A.; Lippmaa, E. *J. Magn. Reson.* **1988**, *79*, 255.

(13) Davis, M. E.; Montes, C.; Hathaway, P. E.; Carces, J. M. In *Zeolites: Facts, Figures, Future*; Jacobs, P. A., van Santen, R. A., Eds.; Elsevier: Amsterdam, 1989, p 199.

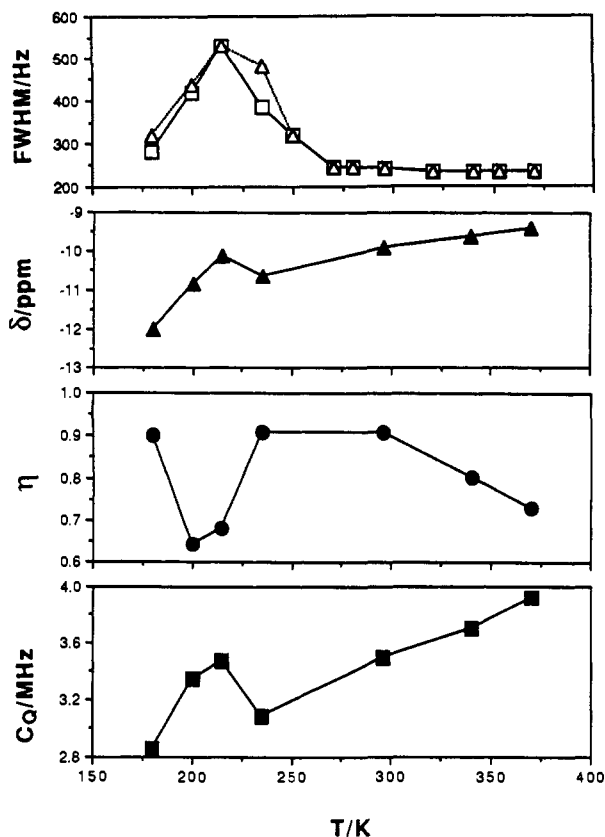


Figure 5. Variation of the fwhm of the ^{27}Al MAS NMR signal from 4-coordinated Al and quadrupole parameters, C_Q and η , and the isotropic chemical shift, δ , obtained by simulation of the 6-coordinated Al signal (see also Figure 5), as a function of temperature. In the top plot the solid and dashed lines link points obtained from spectra recorded with and without ^1H decoupling, respectively. Note that all plots go through an extremum at 190–220 K. The error of the measurement is represented by the diameter of the points.

Tightly closed double-bearing zirconia rotors, 4 mm in diameter, were spun in nitrogen at 8–10 kHz in the temperature range 180–294 K and at 12 kHz in the 294–370 K range. ^1H - ^{27}Al CP/MAS spectra¹⁴ were recorded with a single contact, a contact time of 500 μs , a ^1H 90° pulse of 3.5 μs , a recycle delay of 4 s, and a spinning rate of 8 kHz. The Hartmann–Hahn condition was established in one scan on a sample of pure and highly-crystalline kaolinite using similar acquisition parameters. Because only the central ($-1/2 \leftrightarrow +1/2$) transition is observed, excitation is selective and therefore the Hartmann–Hahn condition is

$$3\gamma_{\text{Al}}B_{\text{Al}} = \gamma_{\text{H}}B_{\text{H}}$$

Quadrupole nutation spectra were recorded with a radiofrequency field $\omega_{\text{rf}}/2\pi$ of 115 ± 5 kHz and with MAS at 8–12 kHz. Forty to sixty-four data points were collected in the t_1 dimension in increments of 0.5 and 1 μs , the damping of the t_1 FID being ca. 30 μs . A sine-bell digitizer filter and zero filling were used in the t_1 dimension and the FIDs were doubly Fourier transformed in the magnitude mode. ^{31}P MAS NMR spectra were measured at 162.0 MHz with 30° pulses and 30-s recycle delays with rotors spinning in nitrogen at 8–12 kHz. All ^{31}P spectra were also recorded with high-power ^1H decoupling, but no significant differences were found. ^1H - ^{31}P CP/MAS NMR spectra were recorded with a 5-ms (optimized) contact time, a 5-s recycle delay, and a 3.1- μs ^1H 90° pulse with rotors spinning in nitrogen at ca. 8 kHz. In all NMR experiments the temperature was varied in steps of 5–20 K and 15 min was allowed for equilibration.

Results

^{31}P MAS NMR Studies. The MAS spectra of hydrated DPA-VPI-5 at temperatures in the range 191–370 K are shown

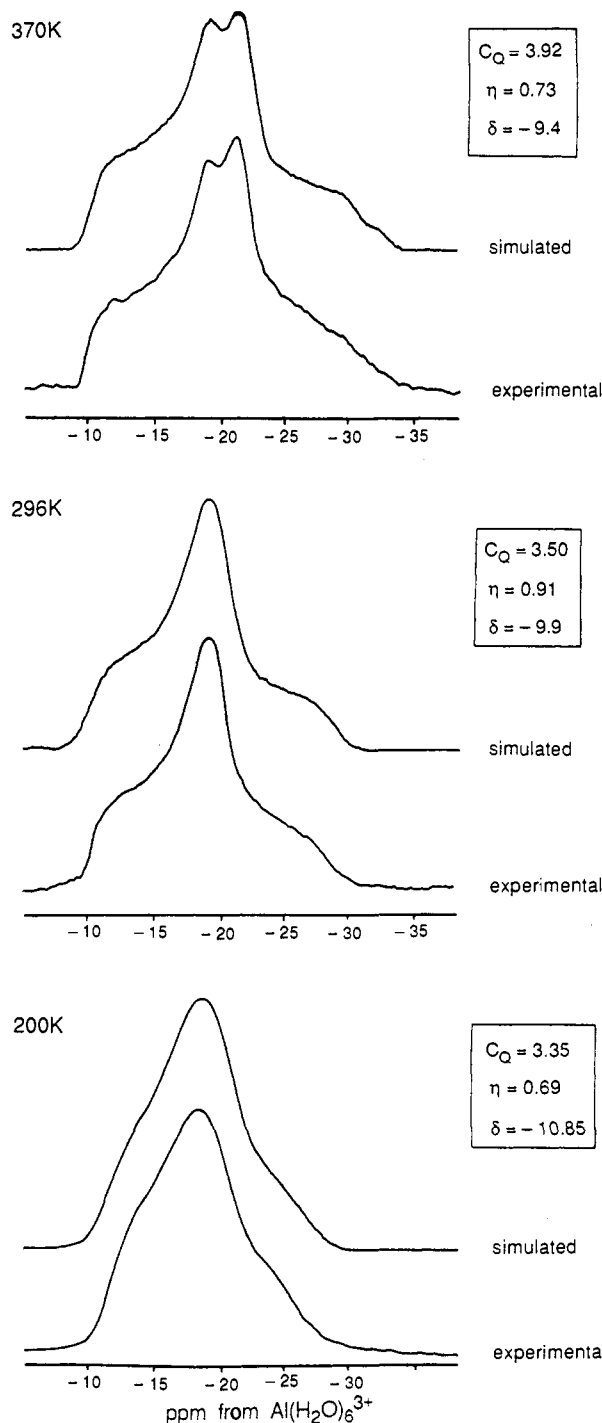


Figure 6. Comparison of the experimental and simulated 6-coordinated Al second-order quadrupole line shapes at several temperatures.

in Figure 3. Below room temperature (294 K) all spectra contain three resonances in a 1:1:1 intensity (peak area) ratio and only minor differences in chemical shifts and full-width-at-half-maximum (fwhm) are observed. ^{31}P spin-lattice relaxation times of the three signals are the same within the limits of error, 19 ± 2 s at 250 K and 26 ± 2 s at 294 K (MAS at 7.2 kHz).

In agreement with the results reported in ref 10, the spectra change considerably above room temperature. Changes are observed already at 333 K and become prominent at 343 K. The resonance at -27 ppm grows at the expense of that at -23 ppm. The two peaks do not coalesce, and the growing peak only shifts slightly from -27.7 ppm at 294 K to -26.6 ppm at 348 K, while the resonance decreasing in intensity shifts gradually from -23.6 to -25.0 ppm. The transformation is complete at 353 K, and the final spectral intensity ratio is 2:1. The phase transformation

(14) (a) Blackwell, C. S.; Patton, R. L. *J. Phys. Chem.* **1984**, *88*, 6135. (b) Morris, D. H.; Ellis, P. J. *Am. Chem. Soc.* **1989**, *111*, 6045. (c) Rocha, J.; Liu, X.; Klinowski, J. *Chem. Phys. Lett.* **1991**, *182*, 531.

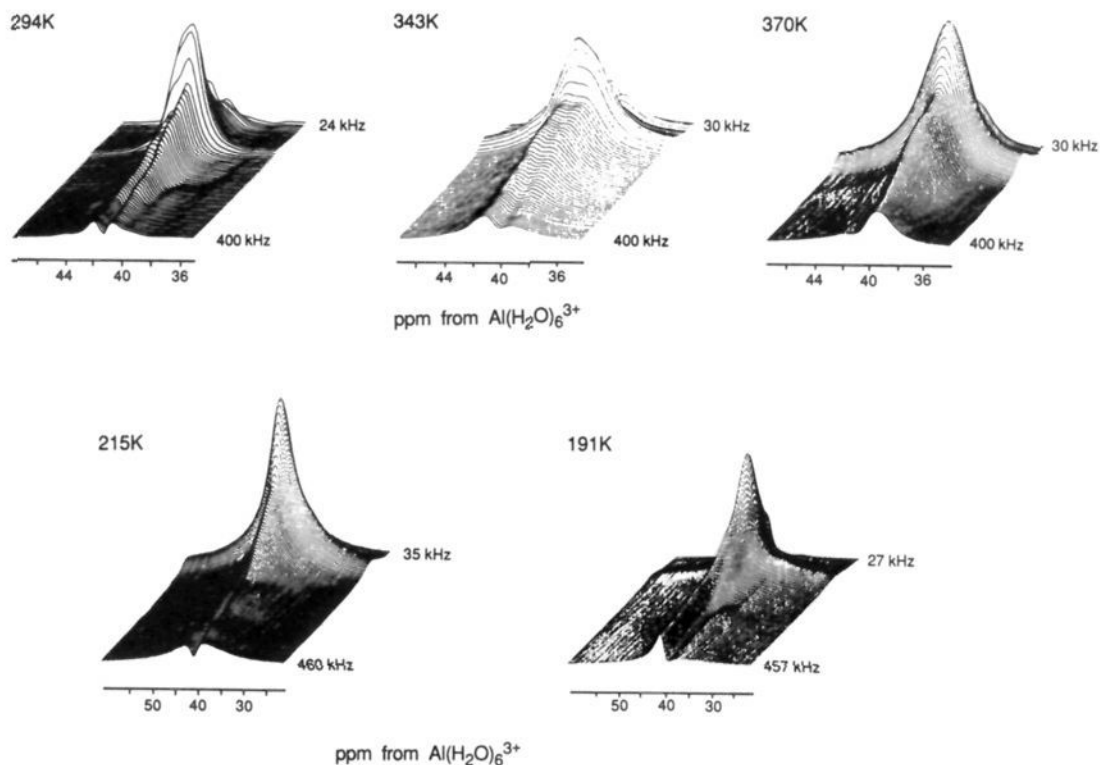


Figure 7. Variable-temperature ^{27}Al quadrupole nutation spectra in the region of 4-coordinated Al of hydrated VPI-5 measured with an $\omega_{rf}/2\pi = 115 \pm 5$ kHz radio-frequency field.

appears to be inhomogeneous,¹⁰ with some sample domains remaining untransformed even at 348 K (note the shoulder at -25.0 ppm). Cooling the sample to room temperature (spectra not given) shows that the transformation is fully reversible. We found a 10-fold decrease in intensity of the ^1H - ^{31}P CP/MAS signal (Figure 3) when the temperature was raised from 250 to 330 K. Above 315 K a broad impurity peak dominates the spectra.

^{27}Al MAS NMR and Quadrupole Nutation Studies. The ^{27}Al MAS NMR spectrum of VPI-5 (see inset in Figure 4) shows two signals in the 2:1 intensity ratio centered at 40 and -18 ppm, respectively, the latter displaying a characteristic second-order powder pattern. The less shielded signal is composed of two overlapping resonances from 4-coordinated Al in a 1:1 ratio, while the more shielded resonance is due to 6-coordinated Al.¹¹ At all temperatures the intensity ratio of 4-coordinated to 6-coordinated Al signals is ca. 2:1. The fwhm of the ^{27}Al MAS NMR spectra at 40 ppm as a function of temperature is plotted in Figure 5. No change is observed above room temperature, between 294 and 370 K (not even when high-power proton decoupling is used), despite the fact that the line shape changes from slightly asymmetric to approximately Gaussian (not shown). By contrast, the second-order powder pattern at -18 ppm changes significantly with temperature and can be simulated to yield the quadrupole coupling constant, C_Q , the asymmetry parameter, η , and the isotropic chemical shift, δ (Figures 5 and 6). C_Q and δ increase from 3.5 MHz and -9.9 ppm (at 294 K) to 3.9 MHz and -9.4 ppm (at 370 K), while η decreases from 0.91 to 0.73. Below room temperature, the fwhm of the 40 ppm line changes considerably, and at 235 and 180 K, ^1H decoupling produces a significant line narrowing. Figure 5 also suggests that some structural transformation, not previously reported, occurs at 190–220 K. As expected, ^1H - ^{27}Al CP/MAS spectra recorded in the range 250–294 K (Figure 4) show a considerable enhancement of the signal from 6-coordinated Al at -18 ppm relative to the signal from 4-coordinated Al at 40 ppm in comparison with spectra measured without CP. This indicates that water is coordinated to aluminum atoms on 6-coordinated sites. In parallel with the ^{31}P evidence, a considerable loss of CP signal is observed when the temperature is increased from 250 to 330 K. At ca. 330 K three impurity resonances, at 38, 6, and -12 ppm, dominate the

spectrum, indicating the presence of 4-, 5-, and 6-coordinated Al. The reason is presumably that the impurities retain strong ^1H - ^{31}P dipolar couplings at higher temperatures.

Quadrupole nutation spectra in the region corresponding to 4-coordinated Al (shown in Figure 7 with F_1 cross sections in Figure 8), provide further insights into the low- and high-temperature transformations. The room-temperature spectrum has one signal at $\omega_{rf}/2\pi$ and two signals between $\omega_{rf}/2\pi$ and ca. $3\omega_{rf}/2\pi$. This shows that the two signals from 4-coordinated Al, which overlap in the ordinary MAS NMR spectrum, have slightly different quadrupole interaction parameters. The relatively weak spectral feature at 38 ppm and $3\omega_{rf}/2\pi$ is due to a small amount of impurities. When the temperature is increased from 294 to 343 K, the resolution of the two peaks from 4-coordinated Al decreases considerably, and above 343 K only one signal is detected (see Figure 7). This suggests that, in parallel with the ^{31}P NMR evidence, above ca. 343 K the two 6–4 aluminum sites collapse into one type of 6–4 site. If two 6–4 aluminum sites are still present, they must have similar quadrupole interaction parameters and similar isotropic chemical shifts. C_Q may increase with temperature, since the signal intensity between $\omega_{rf}/2\pi$ and $3\omega_{rf}/2\pi$ appears to increase slightly (see F_1 cross sections in Figure 8). This conclusion should, however, be regarded with caution: it has been shown that, in order to avoid interference of the spinning-dependent phase of the magnetization vector, the duration of the strong radio-frequency pulse, t_1 , should be less than a quarter of the sample-spinning period.¹² Hence, unless theoretical spectra are calculated by taking MAS into account, accurate values for C_Q and η cannot be given. It is also apparent that the width of the F_1 cross sections, in particular at $\omega_{rf}/2\pi$, also increases above room temperature, and while this could be due to an increase in C_Q or to a distribution of sites with slightly different quadrupole parameters, it may also be connected with $T_{1\rho}$ relaxation effects caused by rapid fluctuations of the electric field gradient at the aluminum sites coming from the movement of the water molecules.¹⁵ At 215 K, the two resonances from 4-coordinated Al

(15) Janssen, R.; Tijink, G. A. H.; Veeman, W. S. *J. Chem. Phys.* 1988, 88, 518.

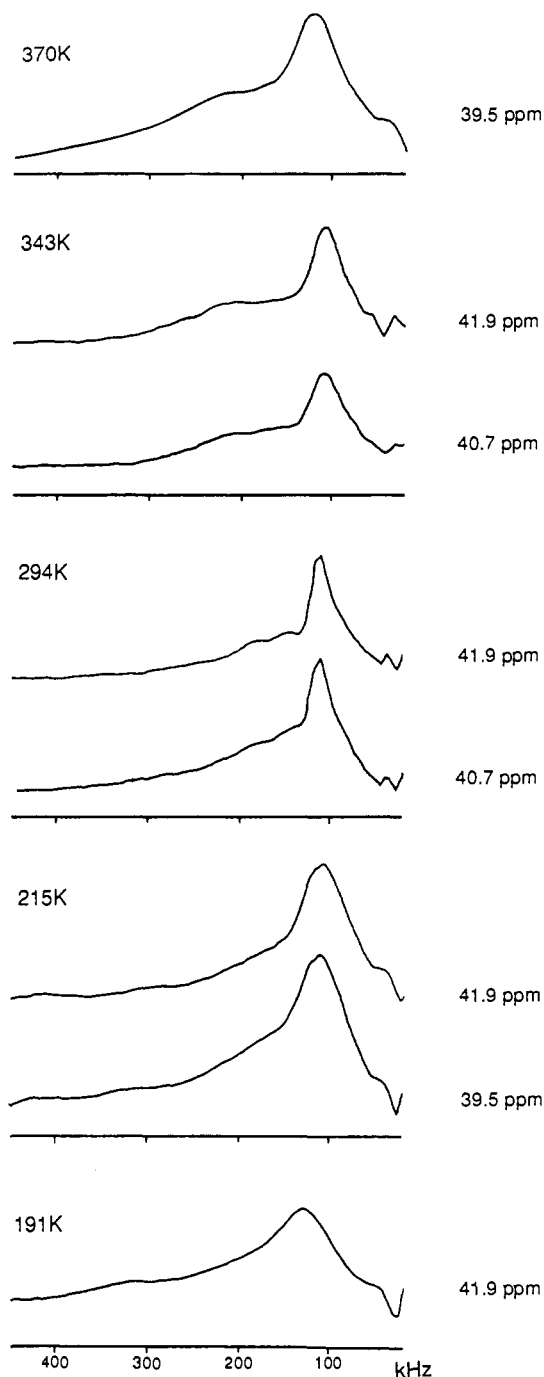


Figure 8. Cross sections parallel to the F_1 axis of the ^{27}Al quadrupole nutation spectra ($\omega_{rf}/2\pi = 115 \pm 5$ kHz) at the F_2 maxima with the coordinates given.

are still present, but less well resolved, since the nutation signal broadens along F_2 . However, at 191 K, in the temperature range of the low-temperature phase transition, the nutation spectrum is significantly different. In particular, only one resonance from 4-coordinated Al, asymmetric along F_2 , is observed, while its cross section along F_1 broadens considerably. The low-temperature transformation is fully reversible.

Discussion

In view of the recently published XRD structure of hydrated VPI-5⁸ (Figure 1) and our results, we have to address the valuable paper by Wu et al.¹¹ The authors explain the ^{27}Al DOR spectra of hydrated and partly hydrated samples by reference to the two-site model of Crowder et al.,³ which incorrectly predicts two ^{31}P and two ^{27}Al resonances for hydrated VPI-5 instead of three of each. Wu et al. assumed that half of the Al2 (6-4) sites

chemisorb water to acquire octahedral coordination and give a ^{27}Al signal at -18.4 ppm and that the remaining tetrahedral Al2 sites together with Al1 (tetrahedral 4-4) sites produce two partly resolved signals at ca. 41 ppm. The main argument for such an assignment, based on unpublished results, was that the signals at 41 ppm have very different quadrupole interaction parameters. Inspection of the F_1 cross sections of our quadrupole nutation spectra in Figure 8 does not support this conclusion. Moreover, the two 4-coordinated Al signals collapse into one at higher temperatures (Figure 7), suggesting that both are from the 6-4 sites. On the other hand, the low magnetic field ^{27}Al spectrum of Davis et al.,⁶ in which those signals were claimed to be resolved, suggests some difference in quadrupole interaction parameters between the two 4-coordinated Al sites. However, the spectrum is of relatively low quality, since it was recorded with MAS at ca. 4 kHz and, as the authors admit, spinning sidebands overlap with the main signals. An insufficient amount of data does not allow us to provide a satisfactory explanation of the DOR experiments on partially hydrated VPI-5.¹¹ It is likely that the initial rehydration leading to the formation of 5-coordinated Al is a random process and therefore the twice as populated 6-4 Al site (giving the peak at 35.9 ppm) is more often affected by water coordination than the 4-4 site (the peak at 33.3 ppm). At higher water content, coordination of two water molecules to the 4-4 Al site, anchored to a hydrogen-bonded network of noncoordinated water molecules, may prevail. Our NMR results support rather the XRD structure of hydrated VPI-5 proposed by McCusker et al.⁸ We assign the room-temperature ^{31}P and ^{27}Al NMR resonances as follows: (i) the ^{31}P resonances at -23 and -27 ppm to P atoms in 6-4 sites and the signal at -33 ppm to P atoms in 4-4 sites (P1) (see ref 10); (ii) the two ^{27}Al resonances at 40 ppm to 4-coordinated Al atoms in 6-4 sites (Al2 and Al3) and the signal centered at -18 ppm to 6-coordinated Al atoms in the 4-4 sites (Al1).

The structure of hydrated VPI-5 undergoes a transformation to higher framework symmetry at 343-353 K, and two resonances are detected for both ^{31}P and ^{27}Al . It has been suggested that this transformation could be due to a breakdown of the triple-helix structure of water inside the pores, leading to increased molecular mobility and to the $P6_3cm$ space group.¹⁰ Indeed, our results show the loss of both ^{31}P and ^{27}Al CP signals with increasing temperature and thus indicate that dipolar interactions with water molecules are greatly reduced, probably because of an increased degree of water motion. On cooling, the CP signal of the 4-coordinated Al increases more than the 6-coordinated Al signal. This supports the presence of at least two types of water molecules, the signals from which are not resolved by ^1H NMR spectroscopy:¹⁶ (a) noncoordinated, more mobile, molecules which constitute the main CP pool for 4-coordinated Al2 and Al3 sites and (b) coordinated, less mobile, molecules which constitute the main CP pool for the 6-coordinated Al1 site. Quadrupole nutation and line simulations of the second-order powder pattern of 6-coordinated Al indicate that the higher framework symmetry observed above ca. 353 K is obtained at the expense of a larger local distortion (larger C_Q) of the aluminum sites. Hydrated VPI-5 undergoes a second transformation at 190-220 K, and our preliminary ^1H MAS NMR results¹⁶ suggest that this is caused by the quenching of the motion of water molecules. In addition, three resonances are detected for ^{31}P but only two for ^{27}Al . We note that the cross section along F_2 at $3\omega_{rf}/2\pi$ and 191 K is asymmetric. We cannot imagine how VPI-5 could possibly have two crystallographically inequivalent aluminum sites but three inequivalent phosphorus sites. We conclude that two of the three aluminum sites are not resolved, probably because their quadrupole interaction parameters and isotropic chemical shifts are similar.

Acknowledgment. We are grateful to Unilever Research, Port Sunlight, and the University of Aveiro for support.