

Solid-State NMR and XRD Study of the Thermal Stability of the Molecular Sieve VPI-5: Conditions for the Transformation Process

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The thermal stability of VPI-5 and the conditions for the transformation of VPI-5 to $\text{AlPO}_4\text{-8}$ have been investigated by X-ray diffraction and *in situ* variable-temperature ^{27}Al and ^{31}P MAS NMR. These results indicate that under normal open air drying conditions, VPI-5 transforms irreversibly to $\text{AlPO}_4\text{-8}$ within 60 min at temperatures $\geq 70^\circ\text{C}$. In contrast, under sealed conditions with the restricted loss of water, the VPI-5 structure is maintained to $> 150^\circ\text{C}$. However, careful low-temperature dehydration *in vacuo* allows the structure to be preserved even after heating to 400°C .

The discovery of the aluminophosphate and related molecular sieve materials has heralded a great variety of novel structure types, augmenting the already large number of known zeolite frameworks. The most recent exciting addition is the elucidation of the structure of VPI-5/ $\text{AlPO}_4\text{-54}$, which has extended the largest channel dimension known, from the earlier 12-membered ring (7 Å diameter), to an 18-membered ring (10 Å diameter).¹ The material in its AlPO_4 form was first observed by d'Yvoire.² The obvious potential for this extra-large pore material, however, to some extent relies on its hydrothermal stability. Recent studies now reveal that under certain relatively mild conditions, the VPI-5 structure undergoes a phase transformation.^{3–6} This new phase has the same XRD pattern as a previously claimed material known as $\text{AlPO}_4\text{-8}$.⁷ The structure of $\text{AlPO}_4\text{-8}$ is now proposed^{3,8} as containing the second largest pores after VPI-5, defined by 14-membered ring (8 Å diameter) channels. The similarity of these two structures is very evident (Fig. 1), and if the suggested partial instability of the conformation of the 4–4 ring portion of the VPI-5 structure is correct,⁹ then the transformation to $\text{AlPO}_4\text{-8}$ is not difficult to envisage.

The obvious interest in characterising the transformation process of the VPI-5 structure has led to a number of primarily XRD studies^{3,4} which, to some extent, present conflicting evidence for the prerequisite conditions and reversibility for the transformation. In addition, a recent study⁶ of the effect of various post-synthesis treatments on the transformation process indicates that even the type of solvent used in the washing may be important. In order to contribute further to the understanding of this issue, we present here a combined XRD and variable-temperature (VT) solid-state ^{27}Al and ^{31}P NMR study of VPI-5, its

transformation to $\text{AlPO}_4\text{-8}$ and of $\text{AlPO}_4\text{-8}$ itself. The application of solid-state ^{29}Si NMR to zeolites is already well known and is now able to give unprecedented information on the structure of these materials.¹⁰ In contrast, earlier ^{27}Al and ^{31}P solid-state NMR studies of AlPO_4 materials^{11,12} appeared less informative, exhibiting simple spectra characterising the tetrahedral Al or P in the framework. More recent studies of SAPO-35 and hydrated AlPO_4 materials,^{13,14} including VPI-5,^{15,16} have shown more complex spectra, which should be able to provide some degree of structural insight into the local environment of the framework atom. This has most recently been vividly illustrated by the results observed in the unique ^{27}Al double-rotation (DOR) study of VPI-5.¹⁷

Experimental

Synthesis of VPI-5. VPI-5 was synthesized according to two different procedures: (1) a slightly modified procedure given by Davis et al. using dipropylamine¹⁸ (DPA) and (2) the recent Mobil patent procedure¹⁹ using 2-amino-2-(hydroxymethyl)-1,3-propanediol (DA) as template.

Procedure 1: $\text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5 : \text{DPA} : 40 \text{ H}_2\text{O}$. Alumina (Catapal B) was dispersed in most of the water, to which was added a solution of phosphoric acid. After the gel had been mixed thoroughly for 1 h, the amine was added and the mixture then blended for 1 h. Thereafter the gel was transferred to a Teflon-lined autoclave and heated to 137°C for 24 h.

Procedure 2: $\text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5 : \text{DA} : 40 \text{ H}_2\text{O}$. Catapal was dispersed in most of the water, to which was added a solution of phosphoric acid. The gel was then left mixing at 80°C on a water bath for 1 h, after which the amine was added. Thereafter the gel was transferred to a Teflon-lined autoclave and heated to 143°C for 16 h.

After recovery of the solid material all samples were thoroughly washed with distilled water and dried at room

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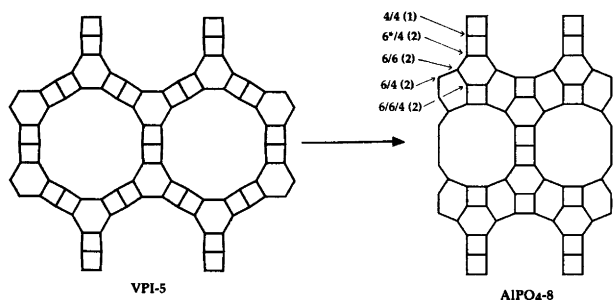


Fig. 1. Representation of the view of the framework outline of VPI-5 and $\text{AlPO}_4\text{-8}$ along the c -axis. The relative numbers of the five non-equivalent crystallographic sites of $\text{AlPO}_4\text{-8}$ are shown in parentheses.

temperature (RT) (22°C). Both procedures produced samples which were confirmed by powder X-ray diffraction to be crystalline VPI-5.

X-Ray diffraction. A $\text{CuK}\alpha$ Siemens diffractometer integrated with a Phillips PW 1710 microprocessor was used for routine studies and a Siemens D500 instrument with a germanium monochromator was applied for high-resolution studies.

Solid-state NMR. The solid-state NMR spectra were recorded on a Varian VXR 300 S WB spectrometer, equipped with both Jakobsen and Doty high spinning speed MAS probes using 7 mm zirconia rotors. The registration conditions were as follows.

^{27}Al . Frequency, 78.157 MHz; sweep width, 50 kHz; pulse width, $3.0\ \mu\text{s}$ (90° pulse, $10.5\ \mu\text{s}$); repetition time, 1.0 s; acquisition time, 0.05 s; number of scans, 1000; MAS spinning speed, 5–6 kHz. The lines were referenced to 1 M Al nitrate solution = 0 ppm.

^{31}P . Frequency, 121.421 MHz; sweep width, 15.5 kHz; pulse width, $8.0\ \mu\text{s}$ (90° pulse, $12.0\ \mu\text{s}$); repetition time, 20 s; acquisition time, 0.5 s; number of scans, 16; MAS spinning speed, 4.6–5 kHz. The lines were referenced to 85 % phosphoric acid solution = 0 ppm.

All NMR analyses were carried out on the VPI-5 material prepared by the first procedure, and a number of parallel experiments were also run on the material prepared using the second procedure. In all these parallel experiments no significantly different results were obtained. The experimental error for the chemical shifts was <0.1 ppm.

Results

X-Ray diffraction studies. The XRD of the 'as-synthesised' VPI-material, shown in Fig. 2a, confirms it as crystalline VPI-5 with very little phase impurities not identified. Earlier attempts at the synthesis of VPI-5 had already indicated the thermal sensitivity of the material, so initial investigations were carried out at 100°C in which separate samples of the VPI-5 material were heated in unstoppered sample

tubes, within an ordinary drying oven. This was done for varying periods of time ranging from 15 to 60 min. As shown in Figs. 2b–2c, there is a drastic change in the XRD pattern with increasing drying times. After 60 min in the oven the material has now transformed completely to $\text{AlPO}_4\text{-8}$, as characterised by the appearance of new lines and the disappearance of lines characterizing VPI-5. There is a complete loss of the VPI-5 phase, mainly characterised by the disappearance of the line at $d = 8.2\ \text{\AA}$. This is an apparently smooth transition from 100 % VPI-5 at $t = 0$, through a coexisting VPI-5/ $\text{AlPO}_4\text{-8}$ phase at intermediate times, to nearly 100 % $\text{AlPO}_4\text{-8}$ after only 60 min drying.

Such a facile transition at these low temperatures proved to be very intriguing, and further studies to determine the exact temperature of transition were again carried out in the drying oven. In this case the samples were heated in unstoppered sample tubes overnight in the temperature range $60\text{--}100^\circ\text{C}$. XRD analysis indicated that the VPI-5 structure was maintained at 60°C , but was completely transformed to $\text{AlPO}_4\text{-8}$ above 70°C . Thus the temperature for the onset of the transformation under these conditions was in the range $60\text{--}70^\circ\text{C}$. To obtain a more detailed analysis of the changes occurring, a further study using a Guinier–Simon camera to monitor the change in the XRD pattern with increasing temperature was performed. The results presented in Fig. 3 show a 2θ range of $10\text{--}90^\circ$ along the x -axis and a temperature range of $20\text{--}260^\circ\text{C}$ with a heating rate of $0.25^\circ\text{C min}^{-1}$ along the y -axis. The low-angle lines of VPI-5 and $\text{AlPO}_4\text{-8}$ are not visible in this range. In this study the VPI-5 phase is apparently unchanged until ca. 120°C , after which there is then a complete transition to $\text{AlPO}_4\text{-8}$. A comparison of the as-synthesised VPI-5 material and the $\text{AlPO}_4\text{-8}$ sample formed after heating at 100 and 400°C overnight is presented in Fig. 4, revealing a slightly different degree of transformation.

The indications from these results were that the transformation process was connected with the dehydration/removal of water. With the obvious interest of seeing whether the VPI-5 structure could be maintained at higher temperatures, further studies were carried out in relation to careful dehydration under controlled conditions. One sample, shown in Fig. 5a, was evacuated for 3 h at RT and then the temperature was raised to 200°C at $0.1^\circ\text{C min}^{-1}$; thereafter the sample was heated to 400°C at $0.2^\circ\text{C min}^{-1}$. As is evident from the presence of only a small amount of the characteristic $\text{AlPO}_4\text{-8}$ line at $d = 13.5\ \text{\AA}$, the VPI-5 phase is to a great degree maintained after this treatment, although there is a small amount of $\text{AlPO}_4\text{-8}$ present.

Another sample was evacuated for 2 h at 22°C and then the temperature was raised slowly to 54°C and maintained *in vacuo* at this temperature for 24 h, with a subsequent raising of the temperature to 250°C . The resulting sample (Fig. 5b) is still a VPI-5 phase, with a very minor amount of the $\text{AlPO}_4\text{-8}$ phase apparent, as shown by the small shoulder at $d = 13.6\ \text{\AA}$.

The apparent importance of the initial low-temperature dehydration stage was confirmed by evacuating a sample at

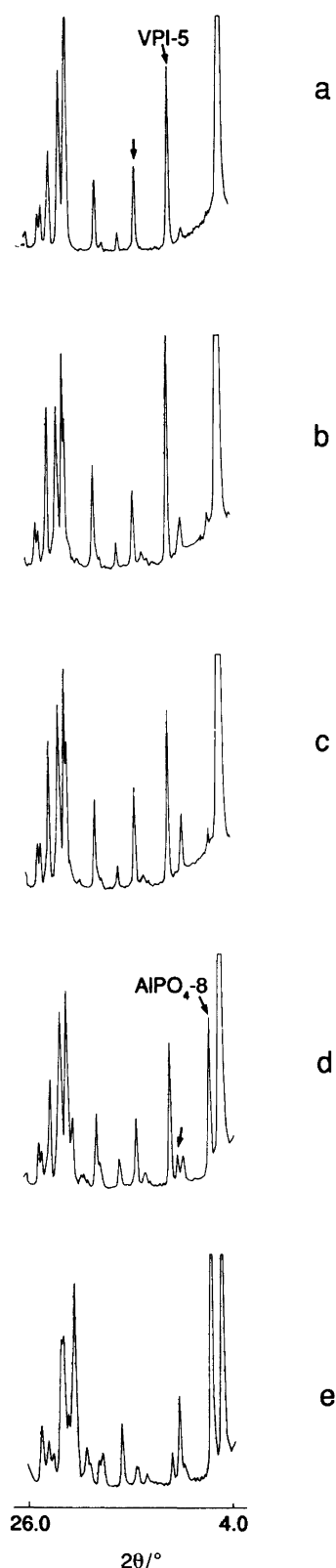


Fig. 2. Effect of drying time at 100°C on the transformation of VPI-5 to $\text{AlPO}_4\text{-8}$, as monitored by XRD. Some of the characteristic lines of the two phases are indicated. (a) Fresh, (b) 15 min, (c) 30 min, (d) 45 min, (e) 60 min.

RT for 24 h, followed by heating to 400°C at 0.1°C min⁻¹. As shown in Fig. 5c, the original crystalline VPI-5 is still present after cooling to RT, with no detectable transformation to $\text{AlPO}_4\text{-8}$. However, when this sample was heated overnight at 100°C in the oven, it had completely transformed to $\text{AlPO}_4\text{-8}$.

²⁷Al MAS NMR studies. The ²⁷Al NMR spectra of the as-synthesised material, shown in Fig. 6a, are in complete agreement with earlier studies, characterised by the sharp signal at about 40 ppm (linewidth 283 Hz) and the broad signal in the range -10 to -45 ppm. ²⁷Al NMR studies of the samples heated at 100°C for varying lengths of time up to 60 min (not *in situ*) (Figs. 6b–6e) reveal no real changes in the resonance around 40 ppm, except for an increased linewidth of 838 Hz for the sample heat-treated for 60 min. However, the broad high-field resonance exhibits minor changes up to drying at 45 min, with appearance of more well defined maxima at 6.6, -14.7 and -27.8 ppm. After 60 min heat treatment, this broad resonance with lower intensity is now being dominated by the maximum at 6.9 ppm.

The spectra for the samples heated overnight in air at 100 and 400°C are shown in Figs. 6f and 6g. Both spectra show the loss of the broad high-field signal in the range -10 to -45 ppm, and the strong signal originally at about 40 ppm now appears in the range 34.4–36.9 ppm with a considerably greater linewidth of 794 Hz. The 100°C sample, however, still contains a line at ca. 8 ppm, whereas the 400°C sample only exhibits the signal at 36.9 ppm (linewidth 917 Hz).

The samples dehydrated *in vacuo* separately under different conditions are presented in Fig. 7 (not *in situ*). The sample heated to 400°C in two stages exhibits the sharp resonance at 34.4 ppm, centred on a broad hump. The additional line at 66.6 ppm comes from the Macor material

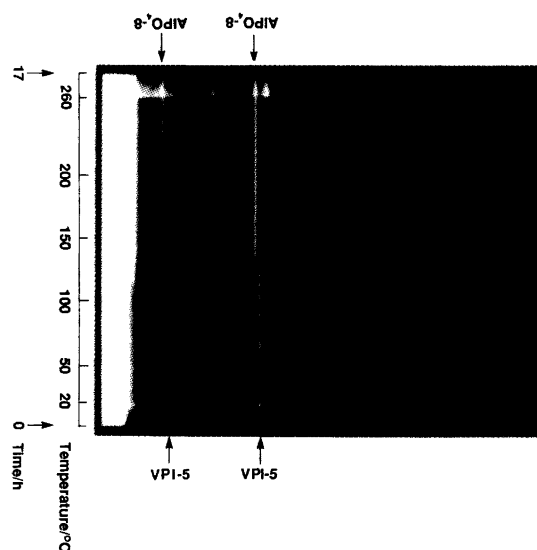


Fig. 3. Results of a Guinier-Simon X-ray study of the effect of temperature on the transformation of VPI-5.

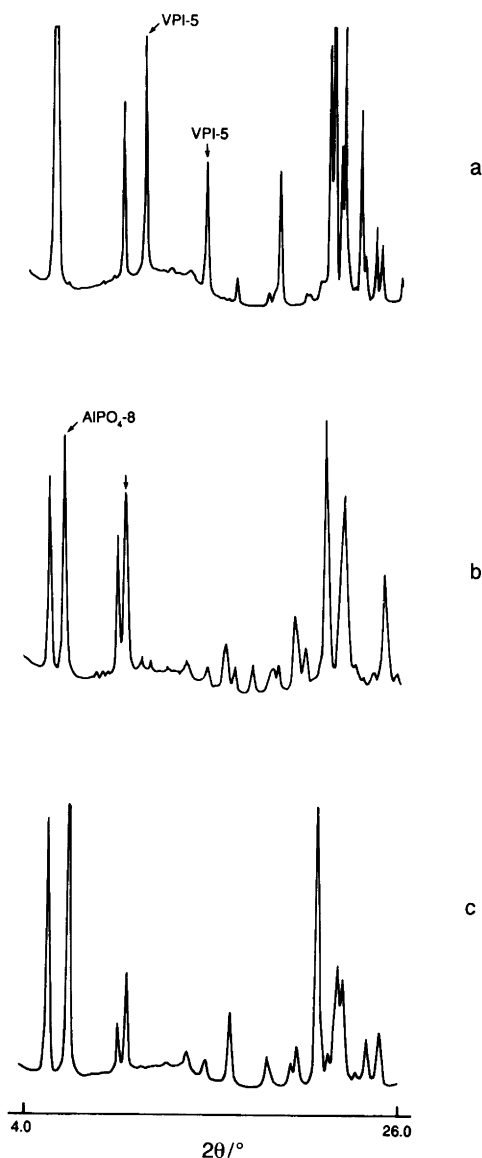


Fig. 4. Comparison of the XRD of VPI-5 (a) and $\text{AlPO}_4\text{-8}$, obtained from the same VPI-5 sample after calcining overnight at 100°C (b) and 400°C (c).

forming the rotor cap, which had to be used during the VT experiments. The second sample dehydrated at 54°C before heating to 250°C has a spectrum very similar to the original VPI-5 sample, with the broad maxima centred around -10 to -45 ppm and the strong resonance at 41.3 ppm. The third sample, dehydrated at RT before being heated to 400°C, has only a single resonance at 34.6 ppm, centred on a broad hump. These three samples again all exhibit relatively broad lines, in comparison to the original fresh samples, in the range 800–900 Hz.

^{31}P MAS NMR studies. The ^{31}P NMR spectrum of the as-synthesised VPI-5 sample shown in Fig. 8a is again in agreement with earlier literature results, exhibiting three well defined resonances at -24.1 , -27.8 and -33.5 ppm, linewidths 273, 285 and 272 Hz, respectively. The spectra

of the samples heated overnight at 100 and 400°C (not *in situ*) are almost identical (Figs. 8b and 8c), both showing the dramatic loss of the three lines and the appearance of a strong broad resonance at -29.4 to -29.8 ppm (linewidths 550–620 Hz) and a small resonance at -11 to -12 ppm due to P–OH sites.

The samples dehydrated separately under vacuum employing different temperature treatments are presented in Figs. 8d and 8e. The sample evacuated at 54°C and then heated to 250°C shows a complex spectrum, with lines at -11 , -23 , -28 to -30 and -33 ppm, whereas the samples calcined at 100 and 400°C and heated slowly *in vacuo* from RT to 400°C ($0.1^\circ\text{C min}^{-1}$) are very different, having a strong, broad resonance around -29 ppm and a small line at -11 to -12 ppm. The peak for the latter sample, at -29.3 ppm, is particularly broad (linewidth 1019 Hz).

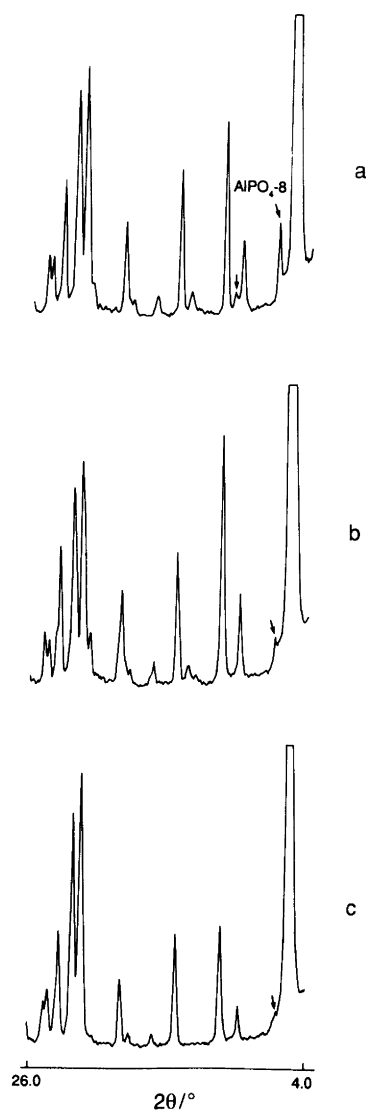


Fig. 5. The effect of various evacuation (evac.) and calcination treatments on VPI-5, as monitored by XRD: (a) evac. RT/3 h, RT \rightarrow 200°C at $0.1^\circ\text{C min}^{-1}$, 200 \rightarrow 400°C at $0.2^\circ\text{C min}^{-1}$; (b) evac. RT/2 h, RT \rightarrow 54°C/24 h, 54 \rightarrow 250°C at 1°C min^{-1} ; (c) evac. RT/24 h, RT \rightarrow 400°C at $0.1^\circ\text{C min}^{-1}$.

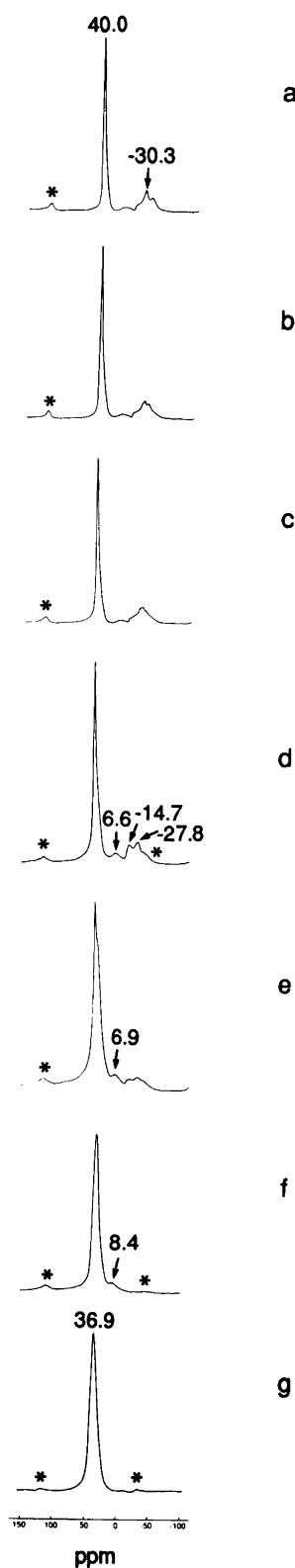


Fig. 6. ^{27}Al MAS NMR study of VPI-5 following various separate heat treatments (not *in situ*). (a) Fresh VPI-5, (b) 100°C/15 min, (c) 100°C/30 min, (d) 100°C/45 min, (e) 100°C/60 min, (f) 100°C/24 h, (g) 400°C/24 h.

Discussion

Conditions for the transformation. A previous study by Richardson *et al.*¹⁹ on the transformation of VPI-5 to $\text{AlPO}_4\cdot 8$ stressed that the important factors promoting the process were the presence of noncrystalline impurities, the presence of moisture, and low heating rates. Importantly, they also indicated that the process was reversible, with some samples returning to the VPI-5 structure when cooled back to RT after a high-temperature treatment. Further work by Davis *et al.*,⁴ however, mainly stressed the importance of water removal, either by pre-evacuation at RT, or by rapid heating of the sample. No indications were given that the transformation process was reversible.

The XRD results presented here confirm the importance of the presence of water at lower temperatures, as is evi-

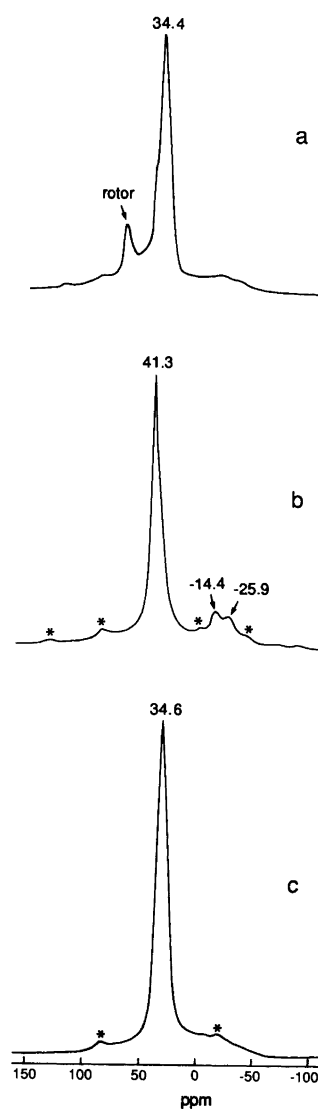


Fig. 7. ^{27}Al MAS NMR study of VPI-5 after various separate evacuation (evac.) and calcination treatments (not *in situ*): (a) evac. RT/3 h, RT \rightarrow 200°C at 0.1°C min⁻¹, 200 \rightarrow 400°C at 0.2°C min⁻¹; (b) evac. RT/2 h, RT \rightarrow 54°C/24 h, 54 \rightarrow 250°C at 1°C min⁻¹; (c) evac. RT/24 h, RT \rightarrow 400°C at 0.1°C min⁻¹.

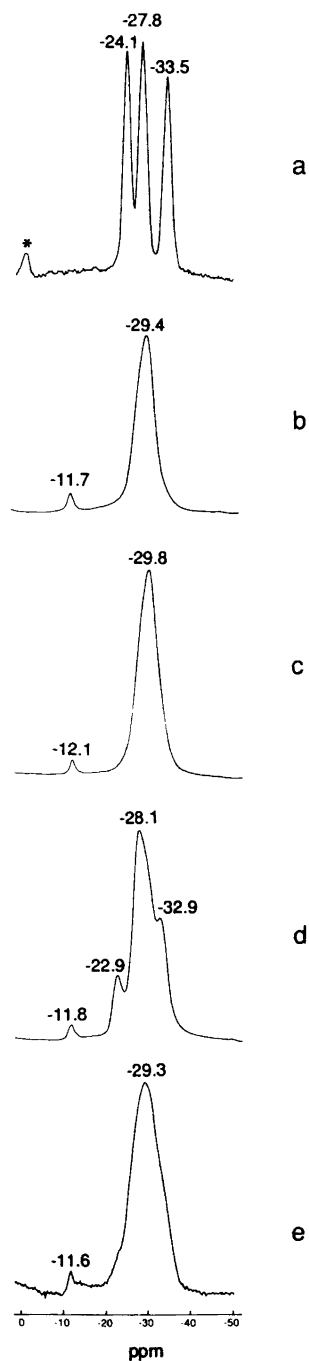


Fig. 8. ^{31}P MAS NMR study of VPI-5 following various separate heat treatments (not *in situ*). (a) Fresh VPI-5; (b) 100°C /overnight; (c) 400°C /overnight; (d) evac. RT/2 h, RT \rightarrow 54°C /24 h, $54\rightarrow 250^\circ\text{C}$ at 1°C min^{-1} ; (e) evac. RT/24 h, RT \rightarrow 400°C at $0.1^\circ\text{C min}^{-1}$.

dent from Fig. 2. At temperatures above 60°C the effect of the removal of the water by drying rapidly is to cause the conversion of the VPI-5 material to $\text{AlPO}_4\cdot 8$. The conclusions from the various evacuation and temperature treatments, as shown from the XRD patterns in Figs. 5–7, is that the presence of minor amounts of $\text{AlPO}_4\cdot 8$ after the thermal treatment is direct evidence of the initial *incomplete* low-temperature water removal, resulting in some degree

of transformation during subsequent raising of the temperature. These results are in agreement with those of Davis *et al.*⁴ So far we have no unequivocal evidence refuting the reversibility of the transformation process as suggested by Richardson *et al.*;³ however, all indications are that, in our case, it is not reversible. All the samples studied, irrespective of any previous pretreatment procedures, were always irreversibly transformed to $\text{AlPO}_4\cdot 8$ under subsequent open air heating conditions, and the Guinier–Simon studies confirm this fact. However, the evidence for the prerequisite conditions for the transformation and a possible reversibility may not be conflicting, since slightly different treatment conditions could lead to different results.

Therefore, with thorough evacuation at RT there appears to be no problem in heating the material to high temperatures thereafter. The exact temperature at which the transformation occurs appears to be, to some degree, dependent on the opportunity for the loss of water from the solid material. Thus, drying of the sample in open air results in the transformation at low temperatures ($> 70^\circ\text{C}$), whereas under the conditions of, for example, the Guinier–Simon VT experiment (for which the sample is tightly packed within a capillary tube), the restricted escape of water delays the transformation to 120°C . This is again confirmed by the VT NMR experiments reported in another study,²⁰ for which the conditions of the sample again consist of tight packing inside a capped rotor. This provides little opportunity for water escape and enables the VPI-5 structure to be maintained to 150°C , the highest accessible temperature in the instrument. Final confirmation of this fact was obtained by tightly packing the as-synthesised VPI-5 material in a sealed ampoule and heating overnight at 110°C . Under normal open drying conditions, complete transformation to $\text{AlPO}_4\cdot 8$ occurs within 1 h. However, under the sealed conditions from which the water does not escape, the VPI-5 structure was unchanged after 12 h heating. The effect of these sealed conditions is probably to ensure a critical partial pressure of water vapour over the sample, preventing the transformation. This is similar to the results of Davis, in which samples were heated *in situ* under saturated water vapour conditions.

The ^{31}P and ^{27}Al NMR characterisation of the transformation process is related to (i) in the ^{31}P spectra, the loss of the three peaks at -24.1 , -27.8 and -33.5 ppm with the appearance of the single, very broad signal at -29.3 ppm, and (ii) in the ^{27}Al spectra, to the loss of the broad signal at -10 to -45 ppm and the up-field shift of the sharp signal at 38.8 ppm to form a broad signal at 34.4 ppm. Samples shown by XRD to be partially transformed exhibit a ^{31}P NMR spectrum consisting of a composite formed from the superimposition of the separate spectra for VPI-5 and $\text{AlPO}_4\cdot 8$ or dehydrated VPI-5. The changes observed in the ^{27}Al NMR spectra correlate with the loss of the framework Al-coordinated water, as characterised by the loss of the broad lines at -10 to -45 ppm.

The changes in the ^{31}P and ^{27}Al spectra are thus associated with the dehydration of the VPI-5 material, and, under open air conditions, are to some extent simultaneously related to the structural transformation. However, it was not possible to assign unequivocally the dehydrated spectra of VPI-5 to either of the two structures. This is because of the close similarity between the ^{31}P and ^{27}Al spectra of carefully *dehydrated* VPI-5 (Figs. 7c and 8e), retaining the VPI-5 structure as indicated by XRD, and the ^{31}P and ^{27}Al spectra of *dehydrated* $\text{AlPO}_4\text{-8}$ (Figs. 6g and 8c) formed from the transformation from VPI-5 as confirmed by XRD. Thus for partially transformed samples dried in open conditions, the parts of the spectra corresponding to the dehydrated material may result from the presence of both (i) dehydrated VPI-5 that has not yet transformed and (ii) dehydrated $\text{AlPO}_4\text{-8}$ formed from partially transformed VPI-5.

One final comment relates to the recent study by Maistriau *et al.*⁶ on the effect of different solvent washings on the ^{31}P spectra of MCM-9, a SAPO variant with the same structure as VPI-5. In this study, the authors indicate that the ^{31}P peak at -20.06 ppm (referenced to H_3PO_4) characterises an amorphous AlPO_4 phase which is removed after washing with acetonitrile. This would thus indicate that the characteristic spectra of VPI-5/MCM-9 consists of the two signals at -27 and -33 ppm. Our results, however, are not consistent with this analysis. ^{31}P MAS NMR results of all our samples, representing a number of syntheses making use of three different procedures and templates, have reproducibly shown the same spectra: three signals with the ratio 1:1:1. Such a wide variety of conditions would be unlikely to produce the same level of amorphous impurities. Thus we would indicate that the three signals are in fact characteristic of *hydrated* VPI-5. This is confirmed by VT studies by our group.²⁰ However, it should also be noted that the ^{31}P spectra reported by the authors of Ref. 6 are significantly different in appearance to those obtained by us, particularly the low-field peak, which has a much narrower linewidth and lower chemical shift than we have ever recorded. It could be the case that in these particular syntheses there is a level of impurities which we do not observe in our case.

Conclusions

Under normal open air drying conditions, VPI-5 is irreversibly converted to $\text{AlPO}_4\text{-8}$ at temperatures $> 70^\circ\text{C}$. The enhancement of the thermal stability of the VPI-5 material can apparently be achieved by heating under sealed condi-

tions for which water loss is prevented or by careful dehydration at low temperatures. The transformation process is linked to the removal of water during the heating process, as indicated by ^{27}Al MAS NMR studies. The changes in the structure of the VPI-5 material by the loss of framework-associated water and the structural conversion to $\text{AlPO}_4\text{-8}$ are reflected by dramatic changes in the ^{31}P spectra. Further analyses of the significance of these changes are in preparation. We also confirm that *hydrated* VPI-5 is characterised by three signals at -23 , -27 and -33 ppm.

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