# Variable-temperature Solid State $^{31}P$ NMR Spectroscopic Study of VPI-5

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A reversible change in the $^{31}P$ NMR spectrum of VPI-5 is shown to take place upon increasing the temperature of measurement; in combination with a recently reported crystal structure refinement the data allow a more precise assignment of the NMR signals.

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VPI-5, a crystalline aluminophosphate, the synthesis and basis structural analysis by XRD of which were first reported by Davis *et al.*,[1] possesses micropores of approx. 1.3 nm diameter, which may lend to this material considerable application potential. The large 18-ring pores are circumscribed by 6-rings, connected by fused 4-rings.

Soon after the discovery of VPI-5, $^{31}P$ NMR studies[2] yielded the surprising result that there are three NMR distinct species, in an approximate ratio of 1 : 1 : 1, whereas the structural data from XRD indicated only two crystallographically distinct T-sites, in a 2 : 1 ratio. It has been shown that the spectra are considerably influenced by adsorbed water,[2,3] but a precise explanation of the occurrence of three $^{31}P$ signals has remained elusive. Wu *et al.*,[4] in an impressive demonstration of the power of the recently invented double rotation (DOR) technique, showed that the $^{27}Al$ NMR spectrum, too, consists of three signals, two of which cannot be resolved in normal MAS experiments. Rietveld refinement of XRD data by Rudolf *et al.*[5] yielded the position of water molecules adsorbed in VPI-5, while the presence of octahedrally coordinated framework aluminium species was also accounted for; it was noted, however, that a relatively large refinement residual remained. A significantly better refinement result was recently obtained by McCusker *et al.*,[6] who used a model having a lower symmetry (space group $P6_3$) than the model assumed previously[5] ($P6_3cm$). In the latter model the phosphorus atoms in the 6-rings are equivalent, whereas the former model has two inequivalent T-sites in the 6-rings. The present study indicates that both refinement results may be valid (for the aluminophosphate network at least) but in different temperature regimes; in addition, it allows a more complete assignment of the $^{31}P$ NMR signals.

VPI-5 of excellent X-ray crystallinity was synthesized according to a procedure reported by Davis *et al.*,[7] involving the use of tetrabutylammonium hydroxide (TBAOH) as a template. The product was thoroughly washed with water and dried at 60 °C. Elemental analysis revealed the following composition expressed in molar oxide ratios: 0.003 $TBAOH \cdot 1.0P_2O_5 \cdot 1.2Al_2O_3 \cdot 4.6H_2O$. $^{31}P$ MAS NMR measurements were performed at 121.5 MHz with direct excitation of $^{31}P$ and high-power proton decoupling (spin gas; dry nitrogen). The spinner was sealed by applying Teflon tape over the top before replacing the turbine cap. Achievable spinning speeds turned out to be low (approx. 3 kHz), possibly as a result of the sealing procedure. Temperature increments of 10 °C were applied, *ca.* 15 min being allowed for temperature equilibration. No signs of any transient phenomena were noted during this period. After reaching 120 °C the sample was cooled down and the initial experiment was repeated.

At 60 °C the spectrum had already markedly changed compared with the one recorded at ambient temperature (Fig. 1); the change was even more pronounced at 70 °C, and at 80 °C, the process appeared to be almost complete: between 80 and 120 °C little further change occurred. The three peaks in the original spectrum had approximate intensity ratios of 1 : 1.1 : 1; the ratio of the peak intensities in the final spectrum was 2 : 1. The spectrum obtained after cooling to room temperature was virtually identical with the one measured at the start, demonstrating that the changes were reversible. The transition appears to take place in an inhomogeneous way, not all of the sample being in the same state in the transition regime. The peak at −23 ppm gradually decreases, while the one at −27 ppm grows; one does not observe coalescence of the two.

The following explanation may be suggested for these observations. Up to *ca.* 60 °C adsorbed water assumes a hydrogen-bonded structure that distorts the framework in such a way as to produce three crystallographically inequivalent sites.[6] Between 60 and 80 °C these constraints are relaxed, allowing a transition to higher framework symmetry with two inequivalent P-species only: the peak at −23 ppm disappears, while the one at −27 ppm simultaneously increases to twice its original intensity (and undergoes a slight shift to −26 ppm). Two possible mechanisms may be at work here: either partial dehydration, or a breakdown of the structure of the adsorbate, leading to increased mobility (but not necessarily any desorption). We favour the latter hypothesis, for the following reasons: (i) under the conditions of the measurement no significant desorption can occur, the spinner being sealed; (ii) The change is rather abrupt, and complete at 90 °C; (iii) a cross-polarisation spectrum was almost unobservable at >60 °C, showing that the static dipolar interaction of the framework phosphorus with water was greatly reduced; (iv) a repeated experiment, in which the spinner turbine cap had been drilled through in order to allow any desorbed water to leave the system, again showed the transition to be reversible. (No data shown for iii and iv.) Regardless of the strength of these arguments, however, we consider the

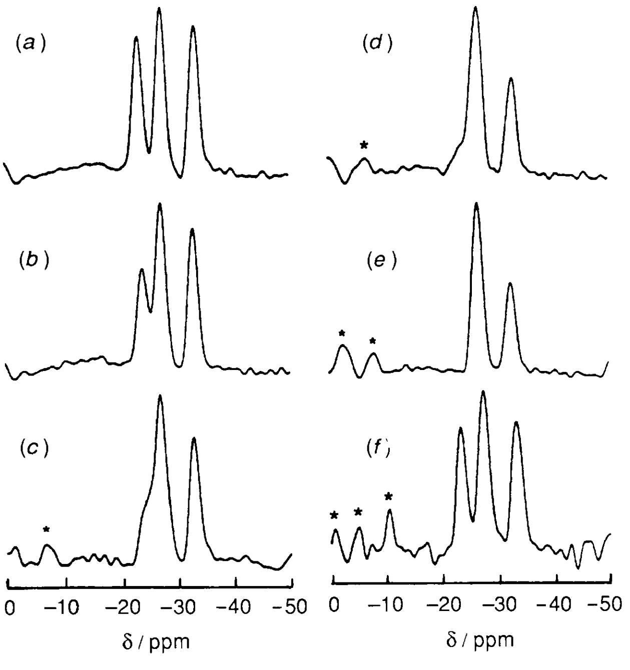

**Fig. 1** $^{31}P$ MAS NMR spectra of VPI-5 measured at various temperatures. An asterisk denotes spinning side-bands. (*a*) 25 °C; (*b*) 60 °C; (*c*) 70 °C; (*d*) 80 °C; (*e*) 120 °C; (*f*) 25 °C, after cooling from 120 °C.

essential point to be the lowering of the crystal symmetry through the structure of the hydrogen-bonded adsorbed water, and the transition to higher symmetry upon breakdown of this structure. Exactly what form this breakdown takes is not essential to the conclusions reached.

In order to obtain more direct proof of the reduction of crystal symmetry by adsorbed water, the experiments were repeated on a sample dehydrated prior to the NMR measurements, the MAS-spinner having been filled under dry nitrogen. This attempt was unsuccessful, however, because it was found (XRD and NMR) that irreversible transformation into $AlPO_4$-8 had occurred.

We conclude that the presence of three equal signals in the $^{31}P$ NMR spectrum at ambient temperature is due to lowered symmetry of the $P6_3$ space group reported by McCusker.[6] At higher temperatures the breakdown of the hydrogen-bonded structure of adsorbed water permits a transition to a higher framework symmetry, *i.e.* that of the $P6_3cm$ space group, which implies the presence of two crystallographically distinct phosphorus species, in the ratio 2:1.

On the basis of these data the peaks at −23 and −27 ppm may now be assigned to phosphorus atoms in the 6-rings, and the one at −33 ppm to phosphorus between the fused 4-rings.

A variable-temperature XRD study should confirm the symmetry change form $P6_3$ to $P6_3cm$ around 70 °C.

Further confirmation might come from similar experiments on fully dehydrated VPI-5, if this can be obtained.

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