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Further Studies on Aluminophosphate Molecular Sieves

Part 2.—VPI-5 and Related Aluminophosphate Materials

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VPI-5 and $AlPO_4$-H2 are constructed from the same type of chain building unit which contains octahedral Al atoms (coordinated with four framework oxygens and two water molecules). The bonded water molecules are believed to stabilize the chain building unit and play an important role in the crystallization of these materials. This chain building unit limits the possibilities of incorporating silicon into the VPI-5 framework and synthesizing aluminosilicate or pure-silica versions of the VPI-5 structure. VPI-5 and $AlPO_4$-H2 can irreversibly transform to $AlPO_4$-8 and $AlPO_4$-tridymite, respectively, *via* similar bond rearrangements. Several new aluminophosphates with X-ray powder diffraction reflections similar to some of those for VPI-5 are synthesized and their physicochemical properties do not match those for VPI-5. Strong evidence is provided to suggest that previous claims that VPI-5 and $AlPO_4$-H1 are the same phase are unwarranted.

VPI-5 is an aluminophosphate molecular sieve that contains extra-large pores (18-membered rings) and was first reported in 1988.[1,2] Over the past few years, this material has received great attention (more than 80 publications on VPI-5 and related materials have appeared). The rising interest in this material is mainly due to its unusual structure and properties which are not observed in other aluminophosphate ($AlPO_4$-*n*) and aluminosilicate (zeolites) molecular sieves.

VPI-5 can be synthesized in the presence of organic species and yet the organics do not ultimately reside in the channels of the final product.[3,4] Instead, water molecules fill in the void space and account for an amount of *ca.* 25 wt.% of the sample. This is unusual for aluminophosphate molecular sieves.[3] Also, it has been shown that VPI-5 can crystallize from a completely inorganic system.[5,6] Currently, there is much interest in synthesizing silicon-substituted VPI-5 and aluminosilicate or pure-silica versions of the VPI-5 structure. This is because the VPI-5 framework is electroneutral and partial substitution of heteroatoms, *e.g.* Si, for P and Al would create a negatively charged framework which could be protonated to form acid sites. However, the amount of Si incorporated into VPI-5 is usually very small[4,7–9] compared with those in other silicon-substituted aluminophosphate molecular sieves, *e.g.* SAPO-5[10] and SAPO-37.[11] The ^{29}Si NMR data for Si-VPI-5[4,7–9] cannot be used to justify the substitution mechanisms that normally occur in SAPO-*n* molecular sieves:[12] (i) Si substitutes for P and/or (ii) two Si atoms substitute for Al and P pairs. The thermal stability of VPI-5 is dependent on its method of preparation, *e.g.* VPI-5 synthesized with tetrabutylammonium hydroxide shows greater thermal and hydrothermal stability than that made with dipropylamine.[3] At elevated temperatures, VPI-5 can transform to a 14-ring molecular sieve denoted $AlPO_4$-8,[13,14] thereby losing its microporosity.[15] It has been reported that this transformation is reversible,[16] although this has not been confirmed.[17]

The magic-angle-spinning (MAS) ^{31}P NMR spectrum of hydrated VPI-5 is quite unusual, with three peaks at −23.3, −27.2 and −33.1 ppm.[3] Grobet *et al.*[18] explained the spectrum by proposing that half of the Al atoms located at the six-rings in VPI-5 are octahedrally coordinated (two water molecules and four framework oxygens). Recently, McCusker *et al.*[19] determined that the structure of hydrated VPI-5 contains octahedral Al at the centre of the fused 4-rings (rather than at six-rings), and that all the water molecules are located in the 18-ring channels to form a triple helix. In this configuration, the symmetry of the structure is lowered from $P6_3cm$ to $P6_3$, and three different P sites are present in the hydrated VPI-5 framework. Dehydration and rehydration of VPI-5 at variable temperatures may change the symmetry of the structure, and from these results, the ^{31}P NMR peak at −33 ppm has been assigned to P atoms located between the fused four-rings and those at −23 and −27 ppm are due to P atoms in six-rings.[20] Such assignments, however, are not in agreement with the ^{31}P NMR spectrum of $AlPO_4$-8,[21] a 14-ring framework that is formed from VPI-5 and also contains fused four-rings.[13,14] Three ^{31}P NMR peaks are observed for $AlPO_4$-8, and on the basis of the structure model and the relative intensities of the peaks, the resonance at the lowest field is assigned to the P atoms residing between the fused four-rings.[21] This is in conflict with the assignments of ^{31}P NMR peaks for VPI-5.

In 1961, d'Yvoire[22] reported the synthesis of several aluminophosphate hydrates, H1, H2, H3 and H4 (denoted with prefix $AlPO_4$- in this work). These materials were prepared from dilute aqueous solutions of alumina and phosphoric acid with a $P_2O_5 : Al_2O_3$ ratio of 2.7. Early on, we noticed some similarities in the X-ray diffraction (XRD) patterns of VPI-5 and $AlPO_4$-H1.[2] Nine X-ray reflections were listed by d'Yvoire for $AlPO_4$-H1 that overlap with some peaks of VPI-5. Recently, Duncan *et al.*[5,6] reported an organic-free synthesis of an aluminophosphate which shows the same XRD pattern as VPI-5 and concluded that VPI-5 and $AlPO_4$-H1 do not differ. Perez *et al.*[23] also described the synthesis of $AlPO_4$-H1 with a similar XRD pattern to that of VPI-5, yet with different properties.

To date, many issues regarding VPI-5 are not fully resolved. Many questions remain; *e.g.*, why does VPI-5 crystallize from a gel containing organic amines and yet the organic species do not reside in the 18-ring channels? Why is it difficult to incorporate silicon into the VPI-5 framework? It is possible to synthesize aluminosilicate or pure-silica versions of the VPI-5 structure? Why can VPI-5 transform to $AlPO_4$-8? Is the transformation of VPI-5 to $AlPO_4$-8 reversible? What are the assignments of the ^{31}P NMR peaks for VPI-5? What is $AlPO_4$-H1? Is $AlPO_4$-H1 related to VPI-5?

Very recently, we reported the synthesis and physi-

cochemical properties of pure $AlPO_4$-H2.[24] In this paper we compare VPI-5, $AlPO_4$-H2 and other related aluminophosphates, and discuss the findings to reach a better understanding of some of the 'cloudy' issues surrounding VPI-5.

Experimental

Table 1 summarizes the sample preparations used in this study. By following the procedures reported earlier, two VPI-5 samples were prepared. The synthesis of VPI-5(DPA) and VPI-5(TIPA) involved the use of reactive aluminophosphate gels and the addition of dipropylamine (DPA)[25] and a mixture of triisopropanolamine (1,1',1''-nitrilotripropan-2-ol) (TIPA) and tetramethylammoniun hydroxide (TMA),[26] respectively. Crystallization of VPI-5 was performed at 415 K for 12 h. Longer crystallization times resulted in a material called $AlPO_4$-H3.[27] $AlPO_4$-8 was obtained by heating sample VPI-5(DPA) in air at 383 K for 12 h.

Pure $AlPO_4$-H2 was crystallized from an aluminophosphate gel containing dipentylamine (DPeA).[24] Another synthesis was carried out by slightly modifying the procedures used for the $AlPO_4$-H2 preparation. Dipentylamine was replaced by dibutylamine (DBA) for this synthesis. An aluminophosphate gel was prepared by slowly adding phosphoric acid solution (from Fisher) to Catapal B alumina slurry (from Vista Co.). The gel was statically aged at room temperature for 8 h before adding DBA. The final gel was stirred for 15 min, charged to a Teflon-lined autoclave, and heated at 393 K for 7 days. The product was washed with distilled water and dried at room temperature. This sample is denoted sample(DBA). Sample(mix1) and sample(mix2) were obtained by physically mixing VPI-5(TIPA) and $AlPO_4$-H2 in weight ratios of 1 : 1 and 1 : 4, respectively.

The techniques used to characterize the samples have been described in our accompanying paper.[24]

Results and Discussion

VPI-5 *vs.* $AlPO_4$-H2

McCusker *et al.*[19] have shown that in the hydrated VPI-5 structure, Al atoms between the fused four-rings are octahedrally coordinated with two water molecules and four framework oxygens. The remainder of the water molecules create triple helices in the 18-ring channels. Using the space group $P6_3$ and the atomic positions provided by McCusker *et al.*,[19] three XRD powder diffraction patterns are calculated and displayed in Fig. 1 in the absence of water molecules [Fig. 1(*a*)], in the presence of two water molecules bonded to Al atoms between fused four-rings [Fig. 1(*b*)], and in the presence of all water molecules in the 18-ring channel [Fig. 1(*c*)]. The experimental XRD pattern of VPI-5(TIPA) is plotted in Fig. 1(*d*). It can be seen that all the calculated patterns have reflections matching the experimental data. The differences in these patterns are the relative intensities of the calculated peaks and these depend upon the positions of the water molecules. For $AlPO_4$-H2, it is clear that two water molecules must bond the Al at the centre of the fused four-rings in order to yield calculated XRD reflections that match the experimental data.[24] Thus, the probability that octahedral aluminium resides at the centre of the fused four-rings is much higher in $AlPO_4$-H2 than in VPI-5. Since $AlPO_4$-H2 is composed of the same building units at VPI-5,[24] the octahedral Al positioning in $AlPO_4$-H2 supports the assignment of McCusker *et al.*[19]

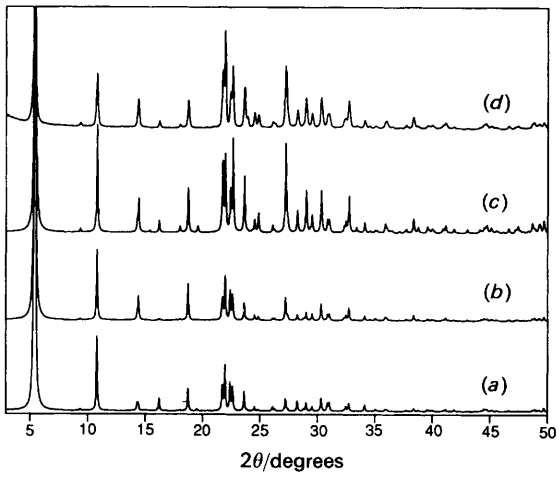

Fig. 1 Calculated (based on atomic positions given in ref. 19) and experimental X-ray powder diffraction patterns of VPI-5: (*a*) calculated in the absence of H_2O, (*b*) calculated with two H_2O molecules bonded to the Al atom at the centre of fused four-rings, (*c*) calculated with all H_2O molecules in the main channel and (*d*) experimental pattern of VPI-5(TIPA)

Like the VPI-5 synthesis,[3,4,25] the synthesis of pure $AlPO_4$-H2 employs an organic additive (dipentylamine) in the reaction mixture and yet the final product does not contain organic species. The organic species do not function as structure-directing agents, rather they probably serve as pH moderators. Water molecules may play an important role in the crystallization of these two materials. The pore volume of the 18-ring channels in VPI-5 is *ca.* 0.25 $cm^3\ g^{-1}$,[3] while the volume of the highly elliptical 10-ring channels (2.9 Å by 7.6 Å) in $AlPO_4$-H2 is *ca.* 0.14 $cm^3\ g^{-1}$ (see Table 2). According to the water adsorption isotherms, the water contents of VPI-5 and $AlPO_4$-H2 correspond to compositions of $AlPO_4 \cdot 2.1H_2O$ and $AlPO_4 \cdot 1.3H_2O$, respectively. If all the water molecules are in the main channels of the structures, as suggested by McCusker *et al.*[19] for VPI-5, the densities of the water in the pores of VPI-5 and $AlPO_4$-H2 would be 1.24 g cm^{-3} and 1.36 g cm^{-3}, respectively. However, it is most unlikely that all the water molecules are located in the main channels of these structures. Alternatively, water could reside

Table 1 Preparation of samples

sample	starting mixture[a]	*T*/K	*t*/h
VPI-5(DPA)	DPA : Al_2O_3 : P_2O_5 : $40H_2O$	415	12
VPI-5(TIPA)	TIPA : 0.025TMA : Al_2O_3 : P_2O_5 : $40H_2O$	415	12
$AlPO_4$-H2	DPeA : Al_2O_3 : P_2O_5 : $50H_2O$	393	15
$AlPO_4$-H3	TIPA : 0.025TMA : Al_2O_3 : P_2O_5 : $40H_2O$	415	24
$AlPO_4$-8	VPI-5(DPA) transformation	383	12
sample(DBA)	DBA : Al_2O_3 : P_2O_5 : $40H_2O$	393	168
sample(mix1)	50% VPI-5–50% $AlPO_4$-H2	(physically mixed)	
sample(mix2)	20% VPI-5–80% $AlPO_4$-H2	(physically mixed)	

[a] DPA = diproylamine; TIPA = triisopropanolamine; TMA = tetramethylammonium hydroxide; DPeA = dipentylamine; DBA = dibutylamine.

Table 2 Pore volume and water content of VPI-5 and $AlPO_4$-H2

parameter	VPI-5[a]	$AlPO_4$-H2[b]
framework density (FD)/TO_2 nm^{-3}	14.2	18.4
ring size	4, 6, 18	4, 6, 10
free diameter of channels[c]/Å	12.1 (circular)	2.9 × 7.6 (elliptical)
unidimensional pore volume/cm^3 g^{-1}	0.25	0.14
water content[d]/g g^{-1}	0.31	0.19

[a] From ref. 3. [b] Derived from crystal structure. [c] Based on an oxygen atom radius of 1.32 Å. [d] From water adsorption data.

in the six-rings lined along the *c* axis, as well as in the main channels. Complete pore filling by water is consistent with the water contents found for all other zeolites and aluminophosphates.[3]

Possibility of Silicon Substitution

The structures of VPI-5 and $AlPO_4$-H2 are constructed from the same type of building unit, *i.e.* triple crankshaft chains. Their [001] projections (Fig. 2 of ref. 24) show fused four-rings that are connected in different ways. Two water molecules bond to Al at the centre of the fused four-rings. We believe that the water molecules stabilize the aluminophosphate triple-chain building unit and probably play a key role in the crystallization of VPI-5 and $AlPO_4$-H2. Octahedral aluminium has been found in aluminophosphate structures, *e.g.* $AlPO_4$-H3,[27] VPI-5 and $AlPO_4$-H2 [containing $P—O—Al(H_2O)_2$ linkages]. Si^{4+} is always tetrahedrally coordinated in silicate materials when the materials are synthesized under hydrothermal conditions. However, Al^{3+} ions can be coordinated tetrahedrally as well as octahedrally with oxygens in silicates.[28] For example, Al^{3+} in silicate minerals such as the clay mineral kaolinite [$Al_2Si_2O_5(OH)_4$] can reside in octahedral coordination.[29] However, in continuous, three-dimensional structures, such as zeolites, framework Al^{3+} is always tetrahedrally coordinated, whereas non-framework Al^{3+} ions can be octahedral. Since no octahedral Al species have been found in four-connected three-dimensional aluminosilicate frameworks, the aluminosilicate form of the triple crankshaft chain [or the $Si—O—Al(H_2O)_2$ linkage] is not likely to occur. Also P—O—Si linkages will not occur in silicon-substituted aluminophosphate molecular sieves.[30] Thus, substitutions of Si for P and Al in VPI-5 or $AlPO_4$-H2 are not likely to take place during hydrothermal synthesis and we believe that phosphorus-free structures analogous to VPI-5 and $AlPO_4$-H2 will not be formed *via* hydrothermal syntheses.

Thermal Transformation

The thermal stability of VPI-5 depends on the quality of the samples. Usually, VPI-5 synthesized with dipropylamine is thermally unstable. Sample VPI-5(DPA) easily transforms to $AlPO_4$-8 when heated at 383 K. For the VPI-5 material made with DPA, it was found that the P : Al ratio is below 1 and many hydroxy groups are present.[31] VPI-5(TIPA) is relatively stable. We have shown that the transformation of this VPI-5 material depends on the heating rate employed to remove water from the pores, and such a transformation is irreversible.[17] In d'Yvoire's report,[22] it was mentioned that $AlPO_4$-H2 transforms to $AlPO_4$-tridymite on heating at 383 K. Pure $AlPO_4$-H2 synthesized here also irreversibly converts to $AlPO_4$-tridymite at *ca.* 373 K. Apparently the hydrated triple crankshaft chains are not thermally stable units. (If water is removed from VPI-5 prior to heating, $AlPO_4$-8 is not formed. This is not the case with $AlPO_4$-H2. Upon dehydration of $AlPO_4$-H2, a significant quantity of structural defects are observed.[24] Heating dehydrated $AlPO_4$-H2 still yields $AlPO_4$-tridymite.) Fig. 2 shows schematic illustrations of the transformations of VPI-5 and $AlPO_4$-H2 to $AlPO_4$-8 and $AlPO_4$-tridymite, respectively. Both transformations occur *via* similar bond rearrangements. At elevated temperatures, the bonds from the centre chain atoms tend to break and reconnect to form rings that are more stable than the fused four-rings. Statistically, the bond cleavage for VPI-5 may occur at every set of fused four-rings, and thus a faulted $AlPO_4$-8 structure is generated. An argon adsorption isotherm shows little microporosity[15] and high-resolution TEM indicates the presence of stacking disorders[32] for $AlPO_4$-8.

^{31}P NMR

^{31}P MAS NMR spectra of hydrated VPI-5, $AlPO_4$-H2 and $AlPO_4$-8 are presented in Fig. 3. VPI-5 shows three peaks at −23.3, −27.2 and −33.1 ppm with an intensity ratio of 1 : 1 : 1. The spectrum of $AlPO_4$-8 also has three resonances at −22.1, −26.1 and −30.7 ppm with an intensity ratio of 1 : 2 : 6. Although the ^{31}P resonances for $AlPO_4$-H2 are not well resolved like those of VPI-5, three peaks can be observed at −24.1, −29.4 and −33.0 ppm.

In tetrahedrally linked frameworks such as $AlPO_4$-tridymite and berlinite, the chemical shifts (δ) of the ^{31}P NMR peaks usually have a linear correlation with the mean P—O—Al angles (0.57 ppm $degree^{-1}$, relative to $AlPO_4$-tridymite).[33] The ^{31}P NMR shifts and the mean P—O—Al angles for aluminophosphate molecular sieves such as $AlPO_4$-5 also follow this correlation.[34] However, the use of such a correlation has not been studied for aluminophosphate frameworks with framework Al in octahedral coordination. We have recorded the ^{31}P MAS NMR spectra of $AlPO_4$-H3 and $AlPO_4$-C (dehydrated $AlPO_4$-H3), and attempted to correlate the ^{31}P chemical shifts to the mean P—O—Al angles obtained from structural data.[27,35] Two different phosphorus sites are present in $AlPO_4$-H3 as well as in $AlPO_4$-C. Indeed, two ^{31}P NMR peaks are observed for both materials, at −23.5 and −27.1 ppm for $AlPO_4$-H3, and at −26.2 and −31.2 ppm for $AlPO_4$-C. In $AlPO_4$-H3, half of the framework Al atoms are octahedrally coordinated with two water molecules in addition to four framework

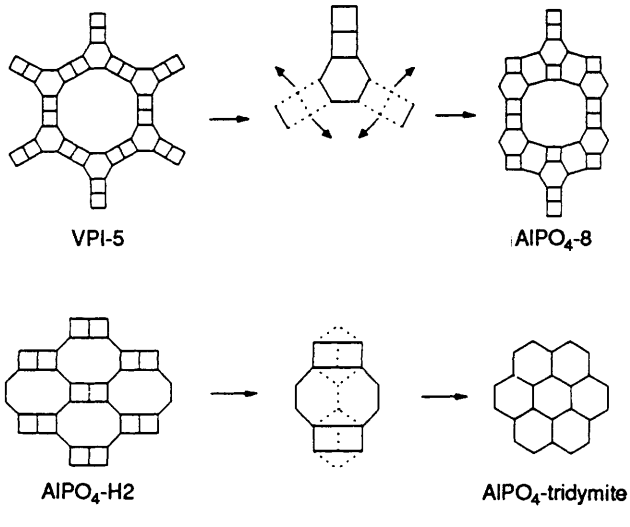

Fig. 2 Schematic illustrations of the transformations of VPI-5 to $AlPO_4$-8 and $AlPO_4$-H2 to $AlPO_4$-tridymite

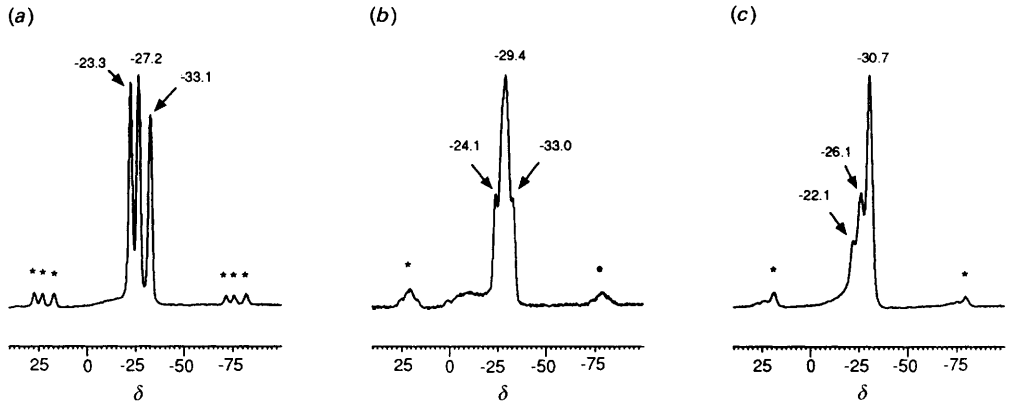

Fig. 3 ^{31}P MAS NMR spectra of (*a*) VPI-5, (*b*) $AlPO_4H2$ and (*c*) $AlPO_4$-8 (asterisks denote spinning side bands)

oxygens.[27] For $AlPO_4$-H3, the mean P—O—Al angles are 145.7° for P1 (specific crystallographic site for phosphorus) and 144.2° for P2, and for $AlPO_4$-C these values are 144.9° for P1 and 153.1° for P2. $AlPO_4$-C is a completely tetrahedral framework. For $AlPO_4$-C, we assign the peak at −26.2 ppm to P1 (mean P—O—Al angle 144.9°; calculated $\delta = -26.6$ ppm) and the one at −33.1 ppm to P2 (mean P—O—Al angle 153.1°; calculated $\delta = -31.1$ ppm). Thus, the relationship between the ^{31}P NMR shifts and mean P—O—Al angles for $AlPO_4$-C appears to agree well with the correlation reported by Müller *et al.*[33] However, this correlation cannot be applied to the ^{31}P NMR shifts and mean P—O—Al angles for $AlPO_4$-H3 where octahedral Al atoms are present. It appears that octahedral Al in the framework has some influence on the phosphorus environment because the chemical shift values are higher than those calculated using the correlation based on the mean P—O—Al angles. In $AlPO_4$-H3, site P1 is coordinated through oxygen atoms to one octahedral Al atom and three tetrahedral Al atoms, while site P2 is linked to three octahedral Al atoms and one tetrahedral Al atom. Although octahedral Al causes the ^{31}P NMR peaks to shift to lower field, it seems that there is poor correlation between the shifted value and the number of octahedral Al atoms surrounding P. We tentatively assign the peak at −25.1 ppm to P1 (mean P—O—Al angle 145.7°; calculated $\delta = -27.1$ ppm) and one at −23.7 ppm to P2 (mean P—O—Al angle 144.2°; calculated $\delta = -26.2$ ppm) for $AlPO_4$-H3.

VPI-5 has octahedral Al atoms in the framework. The ^{31}P MAS NMR spectrum of VPI-5 has three peaks. Based on the structural refinement by McCusker *et al.*,[19] the mean P—O—Al angles of the three phosphorus sites (P3, P2 and P1) are 145.5°, 146.1° and 154.6°, respectively. Although octahedral Al influences the ^{31}P NMR, the P—O—Al angles still affect the chemical shift. There is no doubt that P1, which is the P site at the centre of the fused four-rings of VPI-5 with the highest mean P—O—Al angles, corresponds to the ^{31}P resonance at −33.1 ppm.[3,20,36] The resonances at −23.3 and −27.2 ppm are related to other P2 and P3 atoms located in the six-rings of VPI-5. Both P2 and P3 are connected to one octahedral and three tetrahedral Al atoms. The difference in the mean P—O—Al angles between P2 and P3 is not large enough for a ^{31}P chemical shift difference of *ca.* 4 ppm. Although Kolodziejski *et al.*[36] assigned the signal at −23.3 ppm to P2 and the one at −27.2 ppm to P3, no reason was given for the substantial peak splitting other than the crystallographic data.[19] The significant difference in chemical shifts of the P2 and P3 sites could be caused by the differences in the crystallographic sites,[19] the octahedral Al, the water molecules located in the void space of VPI-5 or all of the above. Although the mean P—O—Al angles for P2 and P3 are similar, each of the four individual P—O—Al angles at these two sites has a quite different value. The four P—O—Al angles for P2 are 136.6°, 147.2°, 151.6° and 149.0°, while the values for P3 are 140.2°, 138.2°, 141.58° and 162.2°. Notice that one of P—O—Al angles for the P3 site is 162.2°, which is significantly higher than the mean P—O—Al angles of P2 and P3. This higher P—O—Al angle may cause the ^{31}P NMR resonance of the P3 site to shift to higher field than that of the P2 site. This is also the case for Al sites. Grobet *et al.*[37] pointed out that ^{27}Al NMR shifts do not correlate with the average Al—O—P angles, and the dispersion of the Al—O—P angles around the Al site is responsible for the ^{27}Al chemical shift value. Dehydrated VPI-5 shows only two ^{31}P NMR peaks at −27 and −34 ppm with an area ratio of 2 : 1.[25] The P sites in the six-rings are equivalent when VPI-5 is dehydrated. The discrepancy between the P2 and P3 in the six-rings of hydrated VPI-5 is most likely caused by the octahedral Al located at the centre of the fused four-rings. Goldfarb *et al.*[38] showed that dehydrated VPI-5 with adsorbed ammonia also gives three ^{31}P NMR peaks at −24.9, −27.7 and −33.3 ppm. The adsorption of ammonia affects the chemical shift of the peak at low field compared with that obtained from hydrated VPI-5.[38] Fig. 4 shows the XRD patterns of VPI-5 which has been hydrated, dehydrated under vacuum (10^{-3} Torr† for one day), and with ammonia adsorbed ($P = 1$ atm‡). Ammonia-containing VPI-5 exhibits

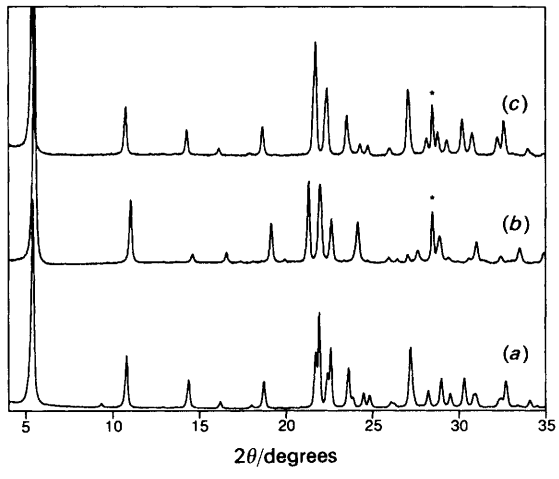

Fig. 4 XRD patterns of VPI-5: (*a*) hydrated, (*b*) dehydrated and (*c*) adsorbed with ammonia (asterisks indicate reflections from silicon standard)

† 1 Torr = (101 325/760) Pa.
‡ 1 atm = 101 325 Pa.

an XRD pattern that is similar to that of the hydrated material, except for the fact that the [211] and [311] reflections become shoulders rather than distinct peaks as observed for hydrated VPI-5. Since ammonia molecules also bond to Al to produce octahedral coordination but do not form the same type of structure in the VPI-5 channels as water molecules,[38] the change of the symmetry of the VPI-5 structure from dehydrated ($P6_3cm$) to hydrated ($P6_3$) or ammonia-containing ($P6_3$) is mainly due to the octahedral coordination of Al at the centre of the fused four-rings. Perez *et al.*[39] have shown that when dehydrated VPI-5 adsorbs ethanol, the ^{31}P NMR spectrum is the same as that of the dehydrated VPI-5. Ethanol molecules occupy the channels of VPI-5 but do not coordinate to Al, and thus, the P sites in the six-rings remain equivalent. Therefore, the discrepancy between P2 and P3 sites in hydrated or ammonia-containing VPI-5 is caused by the octahedral aluminium located at the fused four-rings and not by the adsorbed species in the channels.

The ^{31}P MAS NMR spectrum of $AlPO_4$-H2 also shows three peaks at −24.1, −29.4 and −33.0 ppm, respectively. Like VPI-5, the peak at −33.0 ppm can be assigned to the P atoms at the centre of the fused four-rings. The remaining peaks, however, cannot be assigned to specific P sites at the this time. Complete understanding of the ^{31}P NMR spectra for VPI-5 and $AlPO_4$-H2 will require further investigation.

Since $AlPO_4$-8 also contains fused four-rings,[13,14] it is expected to have a ^{31}P NMR resonance near −33 ppm. However, the ^{31}P NMR spectrum for $AlPO_4$-8 shows three peaks at −22.1, −26.1 and −30.7 ppm, respectively, and the ratio of these peaks (1 : 2 : 6) corresponds well to the crystallographically unique sites of the ideal structure of $AlPO_4$-8.[21] The peak at higher field (−30.7 ppm) is not assigned to the P atoms at the centre of the fused four-rings.[21] As mentioned above, when VPI-5 transforms to $AlPO_4$-8, bonds at every set of fused four-rings may break and generate structural disorder. The ideal topology of $AlPO_4$-8 will not occur in the real material. The hydrated triple crankshaft chains observed in VPI-5 may not exist in $AlPO_4$-8 after thermal transformation. It is therefore possible that $AlPO_4$-8 would not show a ^{31}P resonance similar to that which corresponds to P atoms at the centre of triple crankshaft chains in VPI-5 and $AlPO_4$-H2. In addition to the structural disorder for $AlPO_4$-8, other data are available to support these speculations. Fig. 5A shows the ^{27}Al NMR spectra of hydrated and dehydrated $AlPO_4$-8. Compared with the MAS spectra, the CP MAS experiments substantially enhance the signals for non-tetrahedral aluminium species (7.8 ppm in dehydrated $AlPO_4$-8), indicating that significant amounts of hydroxyl groups are present in $AlPO_4$-8. The ^{31}P CP MAS NMR spectra of hydrated and dehydrated $AlPO_4$-8 (Fig. 5B) show that there are a large number of P—OH groups in $AlPO_4$-8. Mid-infrared spectroscopy in the hydroxyl vibrational region also reveals that a considerable amount of hydroxyl groups are generated when VPI-5 transforms to $AlPO_4$-8. The increased amount of hydroxyl groups indicates that defect sites are generated during the transformation process and many of the triple crankshaft chains are most likely dissociated in $AlPO_4$-8.

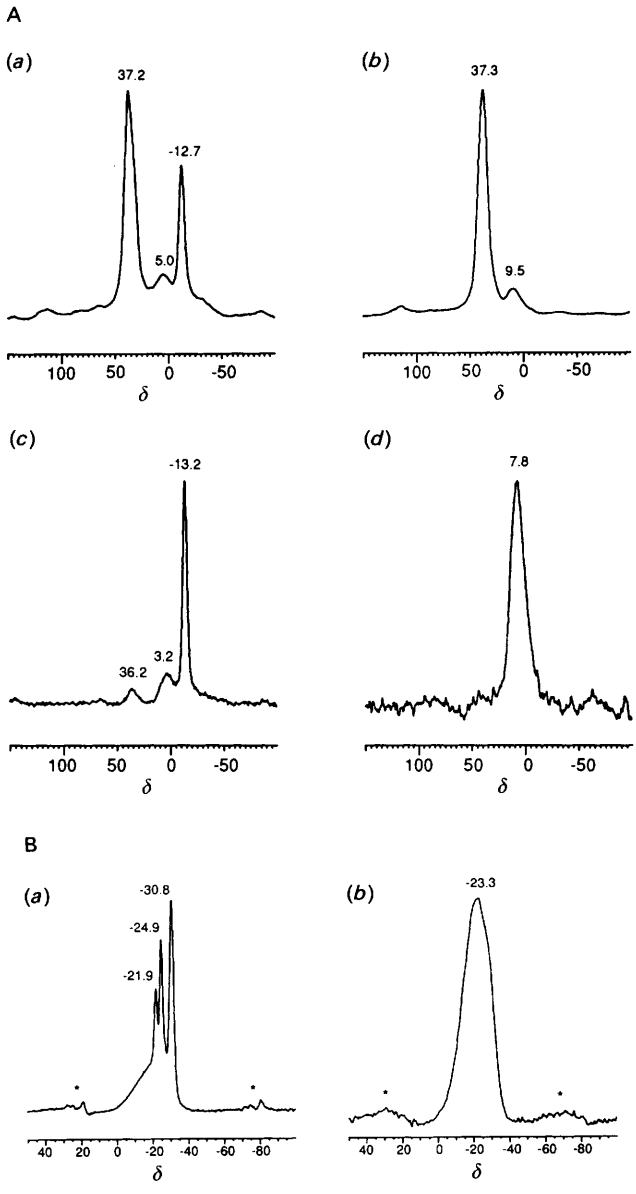

Fig. 5 A, ^{27}Al NMR spectra of (*a*), (*c*) hydrated and (*b*), (*d*) dehydrated $AlPO_4$-8; ^{27}Al MAS NMR, (*a*), (*b*); ^{27}Al CP MAS NMR (*c*), (*d*). B, ^{31}P CP MAS NMR spectra of (*a*) hydrated and (*b*) dehydrated $AlPO_4$-8 (asterisks denote spinning side bands)

VPI-5 *vs.* $AlPO_4$-H1

d'Yvoire synthesized $AlPO_4$-H1 in the presence of other phases such as $AlPO_4$-H2 and/or $AlPO_4$-H3.[22] Only nine X-ray reflections were listed for $AlPO_4$-H1, while many peaks were given for $AlPO_4$-H2 and $AlPO_4$-H3 (see Table 3). Our XRD pattern of pure $AlPO_4$-H2 compares well with the peaks listed by d'Yvoire. However, d'Yvoire's data show three XRD peaks at *d*-spacings of 4.09, 4.06 and 4.04 Å, whereas our XRD pattern reveals only an asymmetric peak in this region. When the pure $AlPO_4$-H2 sample is analysed using synchrotron radiation (high resolution and intensity), the pattern obtained matches exactly the reflections reported by d'Yvoire (see Fig. 1 of ref. 24 and data in Table 3). Table 3 compares the synchrotron X-ray data of the $AlPO_4$-H2 material synthesized in this work with those listed by d'Yvoire. Even though d'Yvoire never synthesized pure $AlPO_4$-H2, it is very impressive that all the peak positions and relative intensities match extremely well between the two sets of data (the exception is that d'Yvoire lists one peak at 3.08 Å, whereas the synchrotron data show a shoulder at 3.087 Å which differs only 0.011 Å from the reflection at 3.076 Å). When the XRD data of the $AlPO_4$-H3 used in this work are compared with d'Yvoire's $AlPO_4$-H3 data, again, all the reflections are in very good agreement (Table 3). If data from VPI-5 are compared with those from $AlPO_4$-H1 (Table 3), the XRD peaks listed for $AlPO_4$-H1 match some of those for

Table 3 X-Ray powder diffraction data

VPI-5[a]		$AlPO_4$-H1[b]		$AlPO_4$-H2[c]		$AlPO_4$-H2[b]		$AlPO_4$-H3[a]		$AlPO_4$-H3[b]	
d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
16.45	100	16.53	FFF								
9.48	2			8.463	100	8.48	FFF	9.74	23	9.70	F
8.22	27	8.23	f	5.867	15	5.87	m	6.89	96	6.86	FFF
6.17	14	6.16	f	4.960	12	4.96	mf	6.52	78	6.50	FF
5.47	3			4.737	8	4.74	f	5.63	6	5.62	f
4.93	1			4.537	<1	4.55	fff	4.89	37	4.883	F
4.74	14			4.237	3	4.25	f	4.85	37	4.842	F
4.10	19			4.095	24	4.09	m	4.72	<1		
4.06	36			4.071	71	4.06	FF	4.35	4	4.341	ff
3.97	12	3.97	f	4.044	7	4.04	ff	4.26	100	4.251	FFF
3.94	21	3.93	m	3.917	<1			3.98	3	3.973	ff
3.77	20			3.752	29	3.75	F	3.62	10	3.611	mf
3.73	4			3.668	30	3.66	F	3.45	8	3.445	f
3.64	7			3.637	6	3.64	f	3.40	42	3.393	mF
3.59	6							3.38	5	3.375	f
3.42	2							3.25	<1		
3.39	1							3.23	<1		
3.28	30	3.28	m	3.239	21	3.24	m			3.071	f
3.16	8			3.147	5	3.14	f	3.07	53	3.061	FF
3.08	15			3.087[d]	14	3.08	F	3.05	23	3.048	mF
3.03	6			3.076	31			2.94	14	2.933	m
2.95	15	2.944	f	3.011	5	3.01	f	2.90	15	2.893	m
2.90	5			2.932	3	2.933	ff	2.78	11	2.779	mf
2.89	5			2.877	5	2.875	f	2.68	39	2.679	mF
2.77	4	2.762	fff	2.818	13	2.819	mf	2.61	3	2.602	f
2.74	13	2.736	f	2.696	14	2.697	mf	2.57	4	2.570	ff
2.63	3			2.664	4	2.666	ff			2.564	f
2,50	3			2.585	1	2.581	fff	2.50	1	2.492	ff
2.39	1			2.535	1	2.533	fff	2.44	1	2.441	fff
2.35	5			2.483	2	2.482	ff	2.42	4	2.423	f
2.28	1			2.454	4	2.453	f			2.413	ff
2.26	1			2.381	1			2.36	6	2.362	mf
2.21	1			2.371	1	2.373	ff	2.35	1	2.353	fff
2.20	2			2.355	4	2.352	f	2.22	3	2.223	ff

[a] X-Ray diffraction data from this work. [b] Data from ref. 22 (F = strong; m = medium; f = weak). [c] Synchrotron X-ray diffraction data from this work. [d] Shoulder.

VPI-5. However, many peaks found for VPI-5 are not listed for $AlPO_4$-H1, even though some of the reflections, *e.g.* at 9.48, 5.47, 3.59 and 3.42 Å, do not overlap with the peaks for $AlPO_4$-H2 for $AlPO_4$-H3 (phases co-crystallized with $AlPO_4$-H1 in d'Yvoire's work). It is therefore difficult to justify that $AlPO_4$-H1 and VPI-5 are the same phase, since it is hard to rationalize why d'Yvoire would miss these reflections if he had synthesized VPI-5, because he recorded perfect X-ray data for $AlPO_4$-H2 and $AlPO_4$-H3.

During the course of this study, several other aluminophosphate materials were obtained, which, surprisingly, also possess XRD peaks coincidently matching some of those for VPI-5. Sample(DBA) was synthesized using a reactive aluminophosphate gel containing dibutylamine. The XRD pattern of this sample is shown in Fig. 6. At first glance, sample(DBA) seems to contain $AlPO_4$-H2 and VPI-5, or $AlPO_4$-H1 and $AlPO_4$-H2 (similar to the results given by d'Yvoire for syntheses in the absence of amines). This phase may be related by VPI-5, but it has some distinct features from VPI-5. First of all, the reflections at $2\theta \approx 22.5°$ are very weak compared with those in the XRD patterns of VPI-5 (Fig. 1) and the physical mixture of VPI-5 and $AlPO_4$-H2 [Fig. 6, sample(mix1)]. Secondly, notice that in the ^{31}P MAS NMR spectra of VPI-5 and $AlPO_4$-H2, the peaks overlap with one another, whereas in ^{27}Al NMR, the tetrahedral Al resonance for VPI-5 appears as a sharp peak at 40.5 ppm, while the one for $AlPO_4$-H2 shows a broad resonance at 36.5 ppm. Fig. 7 shows the ^{31}P and ^{27}Al MAS NMR spectra of sample(DBA), sample(mix1) and sample(mix2). The ^{31}P NMR spectra are not able to distinguish between these samples conclusively. However, the ^{27}Al NMR spectrum for sample(DBA) shows only one tetrahedral Al signal at 36.7 ppm, whereas the spectra for sample(mix1) and sample(mix2) clearly exhibit distinct tetrahedral Al peaks for VPI-5 (40.5 ppm) and for $AlPO_4$-H2 (36.5 ppm). Thus, although sample(DBA) has some X-ray reflections similar to VPI-5, it does not show the characteristic ^{27}Al NMR resonance for VPI-5. Also, sample (DBA) has an extremely low adsorption

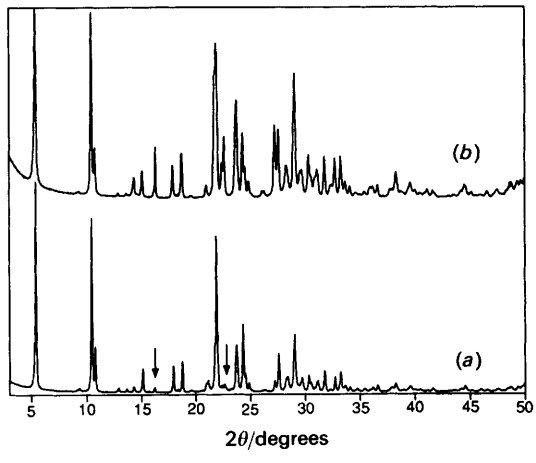

Fig. 6 XRD patterns of (*a*) sample(DBA) and (*b*) sample(mix1)

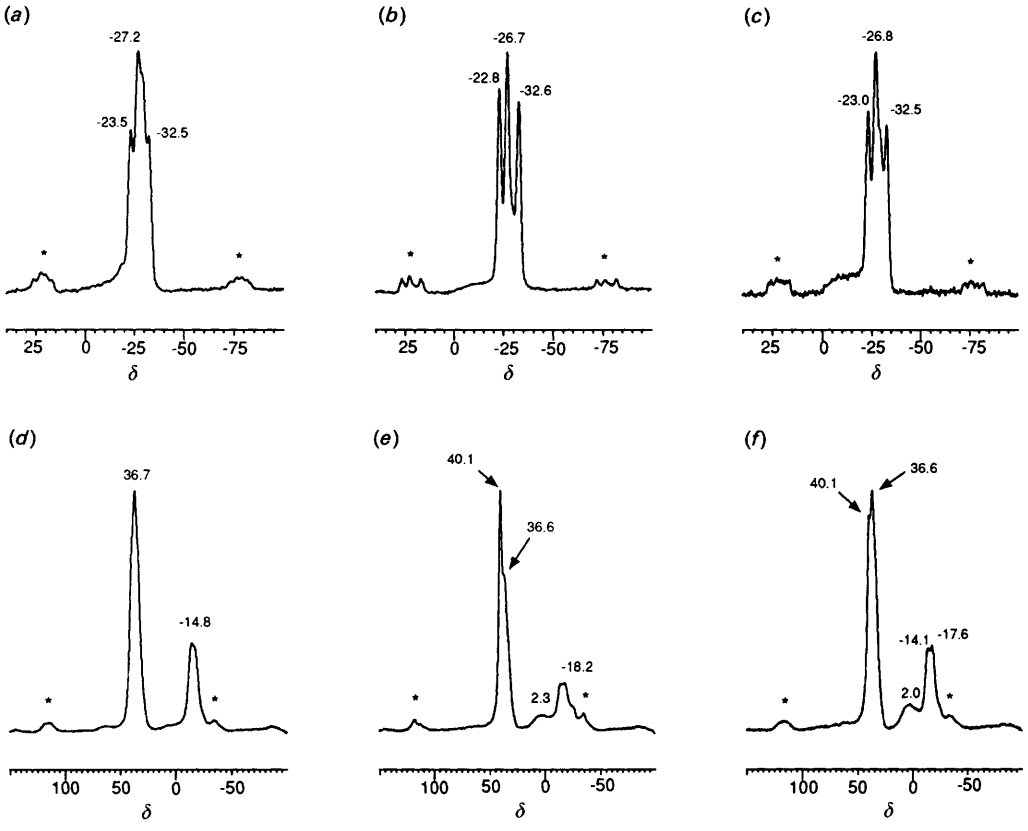

Fig. 7 (*a*)–(*c*) ^{31}P and (*d*)–(*f*) ^{27}Al MAS NMR spectra of sample (DBA), (*a*), (*d*) sample(mix1) (*b*), (*e*) and sample(mix2) (*c*), (*f*) (asterisks denote spinning side bands)

capacity for N_2 at 77 K (0.022 $cm^3\ g^{-1}$), while VPI-5 adsorbs N_2 up to 0.249 $cm^3\ g^{-1}$ under the same conditions.[2]

Another aluminophosphate material was synthesized,[40] and denoted here as $AlPO_4$(unknown). Again some of the XRD reflections for the $AlPO_4$(unknown) are very close to those for VPI-5 (Fig. 8). However, the properties of this material are very different from those of VPI-5. $AlPO_4$(unknown) contains *ca.* 10 wt.% of water and 30 wt.% of organics (cyclohexylamine). Although the ^{31}P and ^{27}Al MAS NMR spectra of this sample (Fig. 9) show several peaks that are at positions similar to those for VPI-5, the ^{31}P resonances at −12.3, −14.2 and −19.4 ppm are indicative of a considerable amount of P atoms associated with hydroxy groups and organic species in the material. Additionally, there are unresolved resonances for tetrahedral and octahedral aluminium species in the ^{27}Al NMR spectrum. This very crystalline material is most likely a layer-like $AlPO_4$ compound.

At this time, the nature of d'Yvoire's material $AlPO_4$-H1 remains unclear. We have provided sufficient evidence to show that aluminophosphates can crystallize in many forms and that wrong conclusions about these materials can be drawn if a sufficient number of different physicochemical properties are not investigated. For example, we have synthesized a material according to the procedure reported by Duncan *et al.*[5] (who claimed that such material is pure $AlPO_4$-H1) and found out that the XRD pattern of this material matches extremely well with that of VPI-5. Clearly,

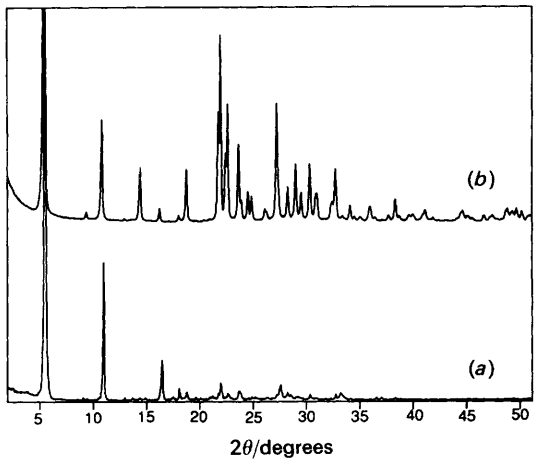

Fig. 8 XRD patterns of an $AlPO_4$(unknown) phase (*a*) and VPI-5 (*b*)

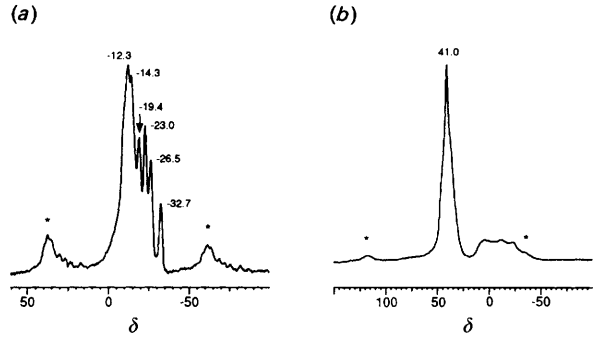

Fig. 9 (*a*) ^{31}P and (*b*) ^{27}Al MAS NMR spectra of the $AlPO_4$(unknown) material (asterisks denote spinning side bands)

claims of $AlPO_4$-H1 syntheses[5,6,23] are unwarranted at this time. Additionally, there is no evidence to support any claim that VPI-5 and $AlPO_4$-H1 are the same material.

Conclusions

VPI-5 and $AlPO_4$-H2 are constructed from the same type of hydrated chain building unit which places limitations on the ability for silicon substitution in their frameworks. At elevated temperatures, VPI-5 and $AlPO_4$-H2 irreversibly transform to $AlPO_4$-8 and $AlPO_4$-tridymite, respectively, *via* similar bond rearrangements. Hydrated VPI-5 and $AlPO_4$-H2 reveal unusual ^{31}P NMR spectra that cannot fully be explained on the basis of crystallographic data. Several aluminophosphate materials having XRD reflections similar to some of those for VPI-5 are synthesized. These materials reveal quite different physicochemical properties. Strong evidence is provided to suggest that previous claims that VPI-5 and $AlPO_4$-H1 are the same phase are unwarranted.

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References

1 M. E. Davis, C. Saldarriaga, C. Montes, J. Garces and C. Crowder, *Nature (London)*, 1988, **331**, 698.
2 M. E. Davis, C. Saldarriaga, C. Montes, J. Garces and C. Crowder, *Zeolites*, 1988, **8**, 362.
3 M. E. Davis, C. Montes, P. E. Hathaway, J. P. Arhancet, D. L. Hasha and J. M. Garces, *J. Am. Chem. Soc.*, 1989, **111**, 3919.
4 M. E. Davis, C. Montes, P. E. Hathaway and J. M. Garces, *Stud. Surf. Sci. Catal.*, 1989, **49**, 199.
5 B. Duncan, R. Szostak, K. Sorby and J. G. Ulan, *Catal. Lett.*, 1990, **7**, 367.
6 B. Duncan, M. Stöcker, D. Gwinup, R. Szostak and K. Vinje, *Bull. Soc. Chim. Fr.*, 1992, **129**, 98.
7 J. A. Martens, I. Balakrishnan, P. J. Grobet and P. A. Jacobs, *Stud. Surf. Sci. Catal.*, 1991, **69**, 135.
8 H. Gauffriez, L. Delmotte and J. L. Guth, *Zeolites*, 1992, **12**, 121.
9 J. A. Martens, H. Geerts, L. Leplat, G. Vanbutsele, P. J. Grobet and P. A. Jacobs, *Catal. Lett.*, 1992, **12**, 367.
10 J. A. Martens, M. Mertens, P. J. Grobet and P. A. Jacobs, *Stud. Surf. Sci. Catal.*, 1988, **37**, 97.
11 L. Sierra de Saldarriaga, C. Saldarriaga and M. E. Davis, *J. Am. Chem. Soc.*, 1987, **109**, 2686.
12 E. M. Flanigen, R. L. Patton and S. T. Wilson, *Stud. Surf. Sci. Catal.*, 1988, **37**, 13.
13 R. M. Dessau, J. L. Schlenker and J. B. Higgins, *Zeolites*, 1990, **10**, 522.
14 J. W. Richardson Jr. and E. T. C. Vogt, *Zeolites*, 1992, **12**, 13.
15 M. E. Davis, P. E. Hathaway and C. Montes, *Zeolites*, 1989, **9**, 436.
16 E. T. C. Vogt and J. W. Richardson Jr., *J. Solid State Chem.*, 1990, **87**, 469.
17 M. J. Annen, D. Young, M. E. Davis, O. B. Cavin and C. R. Hubbard, *J. Phys. Chem.*, 1991, **95**, 1380.
18 P. J. Grobet, J. A. Martens, I. Balakrishnan, M. Mertens and P. A. Jacobs, *Appl. Catal.*, 1989, **56**, L21.
19 L. B. McCusker, Ch. Baerlocher, E. Jahn and M. Bülow, *Zeolites*, 1991, **11**, 308.
20 J. P. van Braam Houckgeest, B. Kraushaar-Czarnetzki, R. J. Dogterom and A. de Groot, *J. Chem. Soc., Chem. Commun.*, 1991, 666.
21 L. Maistriau, Z. Gabelica, E. G. Derouane, E. T. C. Vogt and J. van Oene, *Zeolites*, 1991, **11**, 583.
22 F. d'Yvoire, *Bull. Soc. Chim. Fr.*, 1961, 1762.
23 J. O. Perez, N. K. McGuire and A. Clearfield, *Catal. Lett.*, 1991, **8**, 145.
24 H-X. Li and M. E. Davis, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 951.
25 M. E. Davis, C. Montes and J. M. Garces, *ACS Symp. Ser.*, 1989, **398**, 291.
26 M. E. Davis and D. Young, *Stud. Surf. Sci. Catal.*, 1991, **60**, 53.
27 J. J. Pluth and J. V. Smith, *Nature (London)*, 1985, **318**, 165.
28 D. W. Breck, *Zeolite Molecular Sieves*, Wiley, New York, 1974, p. 29.
29 G. Brown, *The X-Ray Identification and Crystal Structures of Clay Minerals*, Mineralogical Society, London, 1961.
30 M. E. Davis, *Ind. Eng. Chem. Res.*, 1991, **30**, 1675.
31 X. Liu, H. He and J. Klinowski, *J. Phys. Chem.*, 1991, **95**, 9924.
32 K. Sorby, R. Szostak, J. G. Ulan and R. Gronsky, *Catal. Lett.*, 1990, **6**, 209.
33 D. Müller, E. Jahn, G. Ladwig and U. Haubenreisser, *Chem. Phys. Lett.*, 1984, **109**, 332.
34 D. Müller, E. Jahn, B. Fahlke, G. Ladwig and U. Haubenreisser, *Zeolites*, 1985, **5**, 53.
35 E. B. Keller, W. M. Meier and R. M. Kirchner, *Solid State Ionics*, 1990, **43**, 93.
36 W. Kolodziejski, H. He and J. Klinowski, *Chem. Phys. Lett.*, 1992, **191**, 117.
37 P. J. Grobet, A. Samoson, H. Geerts, J. A. Martens and P. A. Jacobs, *J. Phys. Chem.*, 1991, **95**, 9620.
38 D. Goldfarb, H-X. Li and M. E. Davis, *J. Am. Chem. Soc.*, 1992, **114**, 3690.
39 J. O. Perez, P. J. Chu and A. Clearfield, *J. Phys. Chem.*, 1991, **95**, 9994.
40 D. Young and M. E. Davis, unpublished results.

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