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High Resolution Transmission Electron Microscopy of Aluminophosphates: Proposed Structure for $AlPO_4$-8

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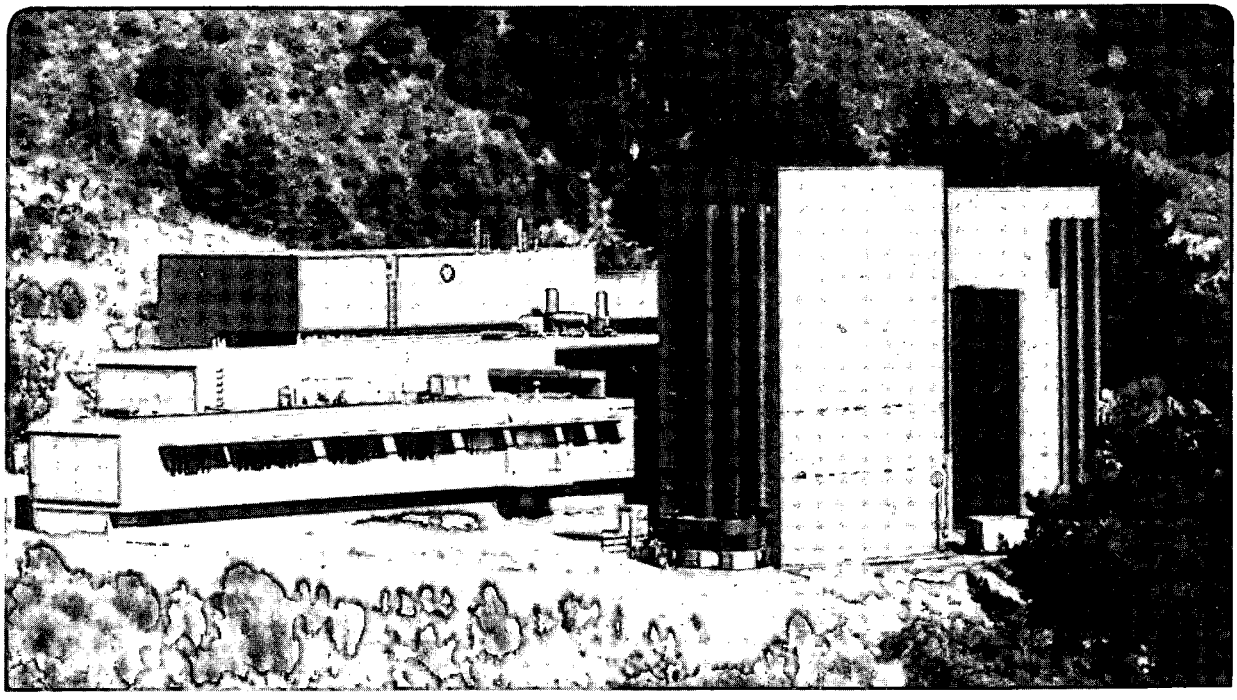

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HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY OF ALUMINOPHOSPHATES: PROPOSED STRUCTURE FOR $AlPO_4$-8

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HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY OF ALUMINOPHOSPHATES; PROPOSED STRUCTURE FOR ALPO4-8

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ABSTRACT

VPI-5 transforms to AlPO4-8 under mild thermal treatment (100 °C, 18 hrs). HRTEM micrographs, oriented normal to the c axis, show extensive defect-free regions in VPI-5, while slip planes normal to the c axis are found in AlPO4-8. Analysis of the HRTEM data, in conjunction with infrared and thermal analysis, adsorption studies and x-ray powder diffraction, has lead to a proposed structure for AlPO4-8. Though the sheets containing the 18 member rings which define the pores in VPI-5 remain intact in AlPO4-8, reduction in the porosity is attributed to blockages created by the movement of these sheets relative to each other.

INTRODUCTION

The first claim in 1987 of an aluminophosphate (VPI-5) with a pore diameter greater than 7 Å regenerated interest in ultra-large pore molecular sieves for which theoretical models have existed since 1969.[1] Large micropore materials are needed, especially in the oil industry, as catalysts which have the high acidity of zeolites, are thermally stable at high temperatures and pressures, and have significant porosity to allow diffusion of heavier feedstocks currently being seen in refineries. Large pore aluminophosphates, modified to possess high acidity, are promising candidates for the next generation of molecular sieve catalysts.

The aluminophosphate VPI-5 is reported to be the first molecular sieve to contain an 18 member ring structure.[2] The adsorption data indicates that VPI-5 possesses a free pore diameter of 12 to 13 Å which is the largest of any reported molecular sieve. Analysis of the x-ray powder diffraction data indicates that the symmetry of VPI-5 is hexagonal with unit cell dimensions of a = 18.989 Å, c = 8.113 Å and space group P63cm (P6/mmm) and fits a proposed structure with a unidimensional channel system defined by an 18T-atom ring as shown in Figure 1. This is one model which fits the x-ray powder diffraction data, and HRTEM images of the material could confirm the structure.

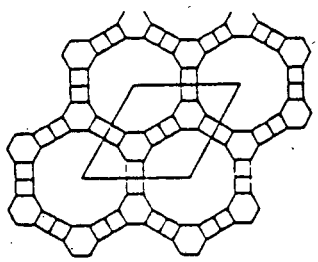

Figure 1: Framework [001] projection of VPI-5

Although VPI-5 is claimed to be stable to 800 °C [2] we have observed that it undergoes a very reproducible low temperature solid state transformation to AlPO4-8. AlPO4-8 is an intriguing material for several reasons. Such a transformation while in the crystal state is rather remarkable and we are interested in understanding its mechanism. Before this can be done the crystal structure of AlPO4-8 must be determined. Although it was patented in 1982 , its structure remains unsolved.[3] The x-ray powder diffraction patterns of VPI-5 and AlPO4-8 are very similar except for the presence of several extra lines in the AlPO4-8 pattern. In particular, the peaks which are indicative of the 18 member ring in VPI-5 (d = 16.44 Å) are still present in AlPO4-8

indicative of the 18 member ring in VPI-5 (d = 16.44 Å) are still present in $AlPO_4$-8 (d = 16.7Å). The x-ray powder diffraction patterns of VPI-5 and $AlPO_4$-8 are shown in Figure 2 and the diffraction data summarized in Table I. For molecular sieves, adsorption data is used to identify pore dimensions, however the $AlPO_4$-8 adsorption data is conflicting.[3-6] There is no indication that $AlPO_4$-8 has the large molecule adsorption capacities of VPI-5, and pore diameters between 4 and 10 Å have been claimed. Although the adsorption data suggests that $AlPO_4$-8 and VPI-5 are very different materials, the low temperature conversion and the great similarity in x-ray powder diffraction data suggests that the structure of $AlPO_4$-8 is only a minor alteration of the VPI-5 structure.

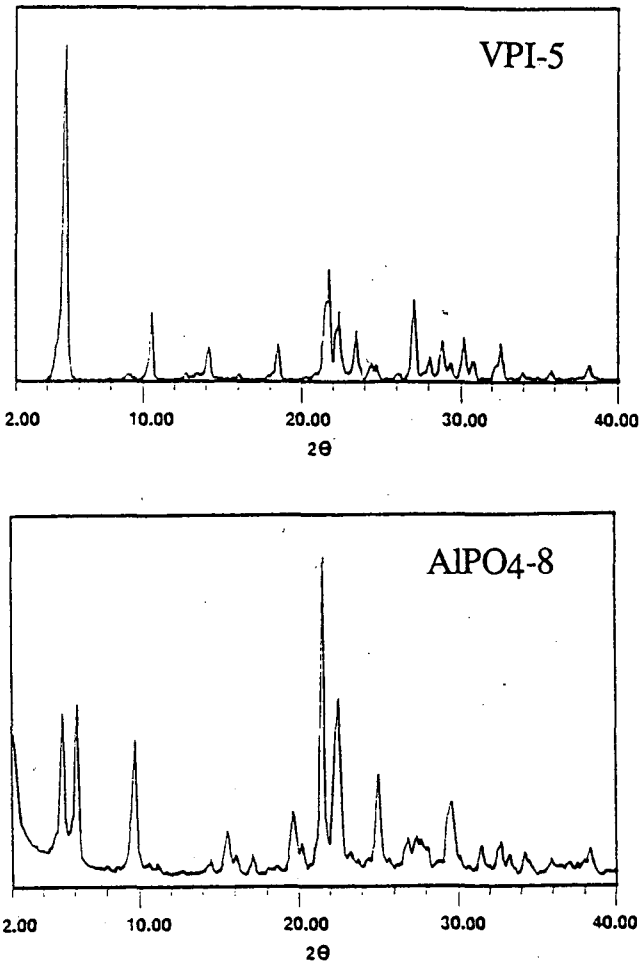

Figure 2: X-ray powder diffraction patterns of VPI-5 and $AlPO_4$-8

Table I: X-ray powder diffraction data for $AlPO_4$-8 and VPI-5

$AlPO_4$-8		VPI-5	
d (Å)	I/I_o(%)	d (Å)	I/I_o(%)
16.7	80	16.43	100
13.6	100	9.49	2
8.84	17	8.23	14
8.19	2	6.21	6
6.07	4	5.48	2
5.56	16	4.75	6
4.72	2	4.08	20
4.48	8	4.05	22
4.40	12	3.97	14
4.19	82	3.94	15
4.08	18	3.77	10
3.97	39	3.64	4
3.92	Shoulder	3.41	2
3.77	3	3.28	16
3.68	11	3.17	5
3.58	11	3.08	7
3.29	2	3.03	4
3.16	5	2.95	8
2.85	4	2.90	5
2.72	3	2.74	7
2.62	1	2.63	2
2.52	3	2.50	3
2.37	9	2.35	3

EXPERIMENTAL PROCEDURE

The chemicals used for synthesis were pseudoboehmite (CATAPAL), 85 % phosphoric acid (FISHER), di-n-propylamine, DPA (KODAK) and deionized water. VPI-5 was crystallized in 3 hrs at 145 °C from a gel with molar composition Al_2O_3:P_2O_5:DPA:40H_2O. $AlPO_4$-8 was formed by heating VPI-5 at 100 °C over night. The x-ray powder diffraction data was collected on a Rigaku x-ray powder diffractometer with CuK alpha radiation. The morphology was studied by scanning electron microscopy (SEM) on a Cambridge Stereoscan 150 at 10 KeV.

Crushed and dispersed specimens of VPI-5 and $AlPO_4$-8 were prepared on 400 mesh Cu grids. The HRTEM micrographs were obtained on a JEOL 200CX at 200 KeV. $AlPO_4$-8 and VPI-5 were extremely beam sensitive and it was very difficult to obtain high resolution images. These materials damaged so rapidly that it was not possible to adjust specimen orientation or obtain through focal series before crystallographic information was lost. Low dose imaging techniques were used. Focus and astigmatism was adjusted on one area of the sample, then, to

minimize beam damage, the beam was defocused and the sample was translated to a new area. The new area was imaged with a very low beam intensity, requiring a long exposure time. By working essentially "in the dark" most of the images were badly out of focus and could not be used, however a few interpretable high resolution micrographs of AlPO4-8 and VPI-5 were obtained. Diffraction data could later be obtained from optical diffractometry of the micrographs.

RESULTS

The SEM micrographs, shown in Figure 3, indicate that $AlPO_4$-8 is a single phase material and not a physical mixture of VPI-5 and an unidentified dense phase, as has been claimed by other researchers.[6]

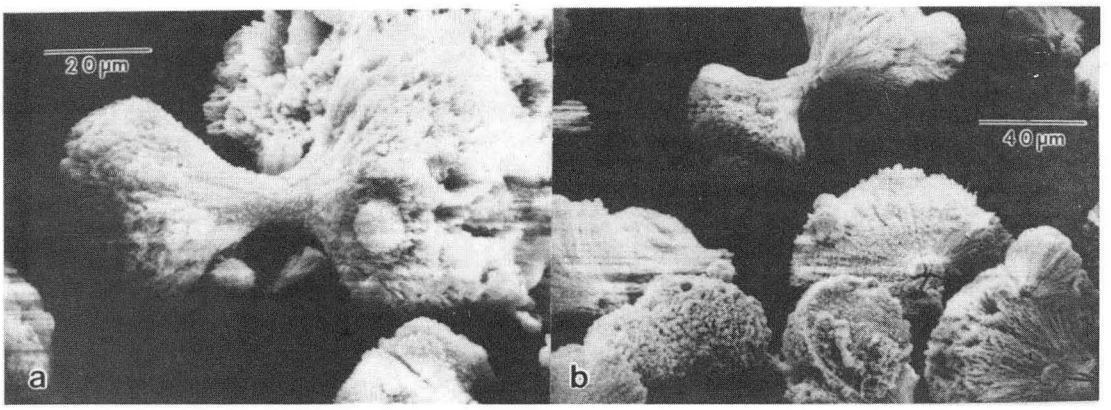

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Figure 3: SEM micrographs of a) VPI-5 and b) $AlPO_4$-8.

Consideration of the atomic structure of VPI- 5 based on the proposed model [7] aids the interpretation of the high resolution micrographs. Figure 4 is a model of VPI-5 from two directions perpendicular to the pores ([1 1 0] and [1 -1 0] orientations). The large channels of VPI-5 are lined exclusively with six member rings which produce a regular stacking arrangement with a periodicity of 4.05 Å seen in any orientation perpendicular to the c axis. In addition the large pores produce variations in density with a periodicity of 16.4 Å perpendicular to the c direction, clearly illustrated in the [110] orientation.

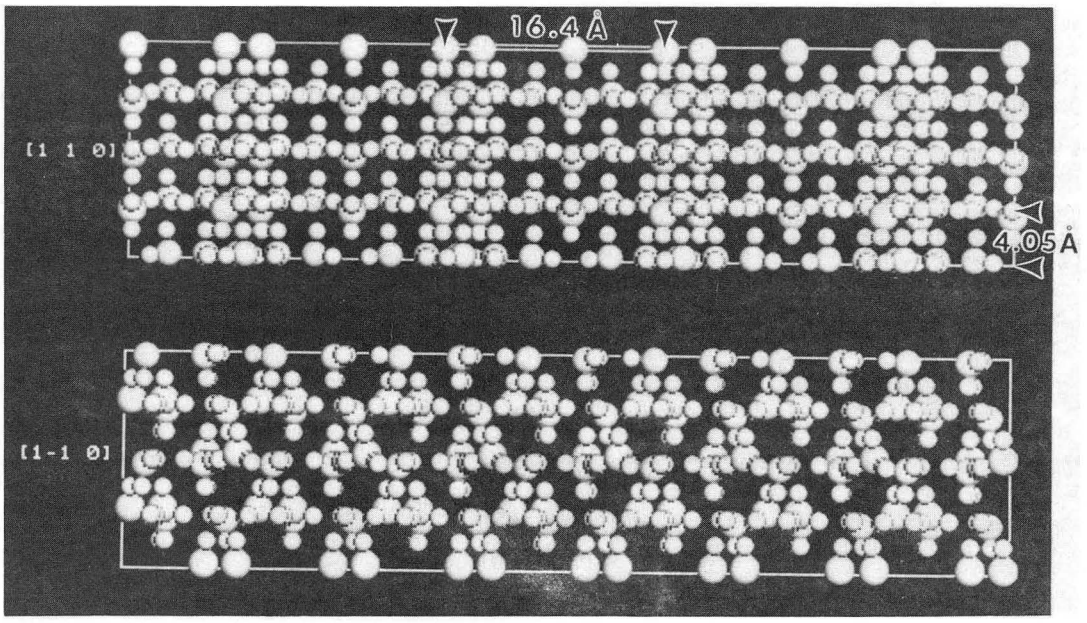

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Figure 4: Models of VPI-5 in the [1 1 0] and [1 -1 0] orientations.

VPI-5 and $AlPO_4$-8 form needle shaped crystals which generally lie flat on the grid. Fringes with spacings of 16.4 Å parallel to the long axis of the crystal were frequently observed and analysis of diffraction confirmed that this orientation is normal to the c axis.

TEM micrographs indicate that extensive defect-free regions exist in VPI-5, as shown in Figure 5.

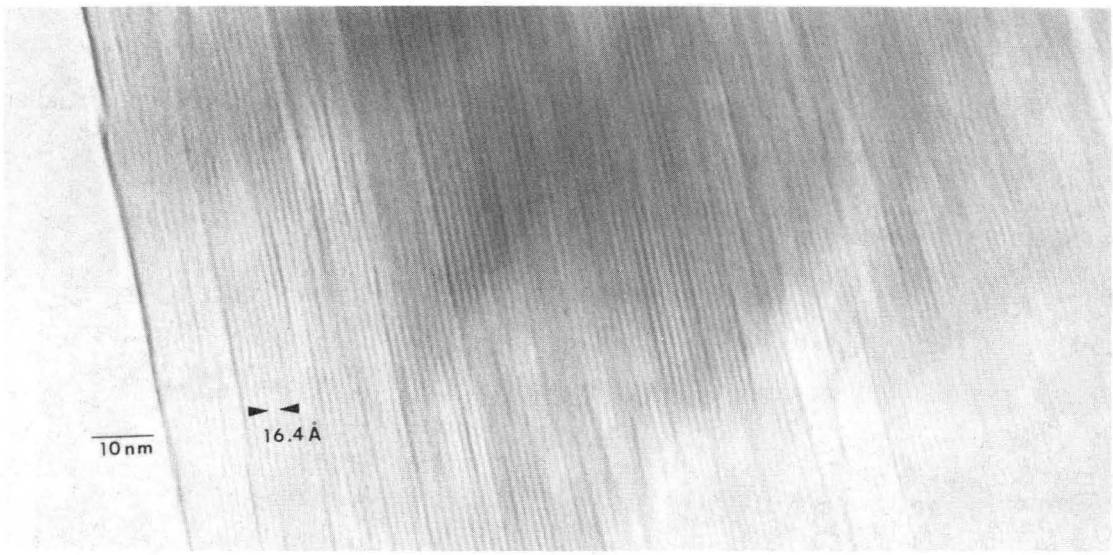

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Figure 5: TEM micrograph of VPI-5

A HRTEM micrograph of AlPO4-8, shown in Figure 6, revealed a very different situation. An extensive number of slip planes normal to the c axis were observed in AlPO4-8.

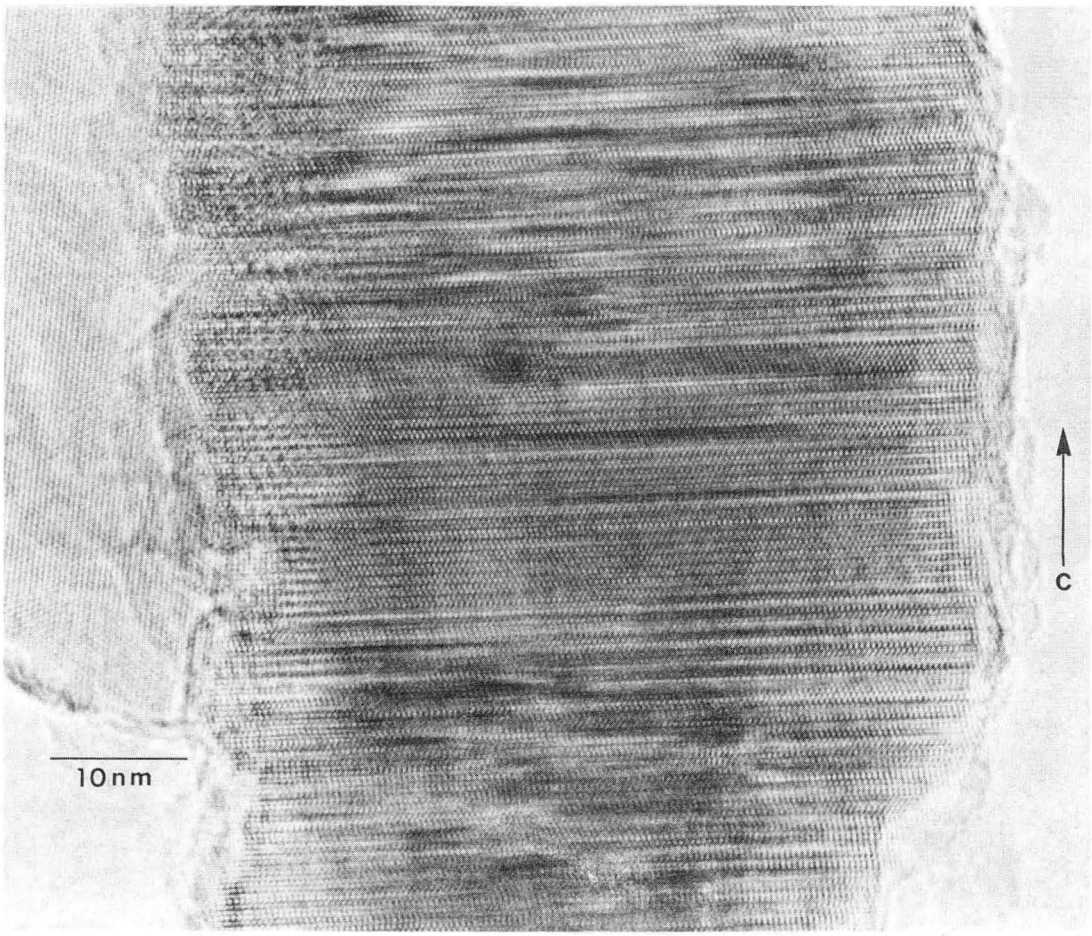

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Figure 6: HRTEM micrograph of AlPO4-8

Proposed structure

Two proposed structures are shown in Figure 7. The layer of 4-ring-4-ring-6-rings which defines the pore has slipped relative to each other. The presence of such slip planes block the pores but do not destroy the 18 member ring, explaining the loss in adsorption capacity. By examining the micrograph it is clear why it would be difficult to solve the structure of $AlPO_4$-8 with x-ray powder diffraction, the complicated layering does not correspond to a regular unit cell. The proposed model satisfactorily accounts for both the slip planes observed in the micrograph and the low angle spacing found in the powder diffraction pattern. Such a model , however, results in the generation of non-"framework" bonding T- O units. Such species may be coordinatively satisfied through complexation with water. The accuracy of the original VPI-5 model must also be considered.

An alternative model for the VPI-5 structure is presently under investigation. High resolution imaging of VPI-5 and $AlPO_4$-8 is continuing.[8] Modelling of the rearrangement to simulate the high resolution images and match the x-ray powder diffraction peaks in $AlPO_4$-8 is under development .

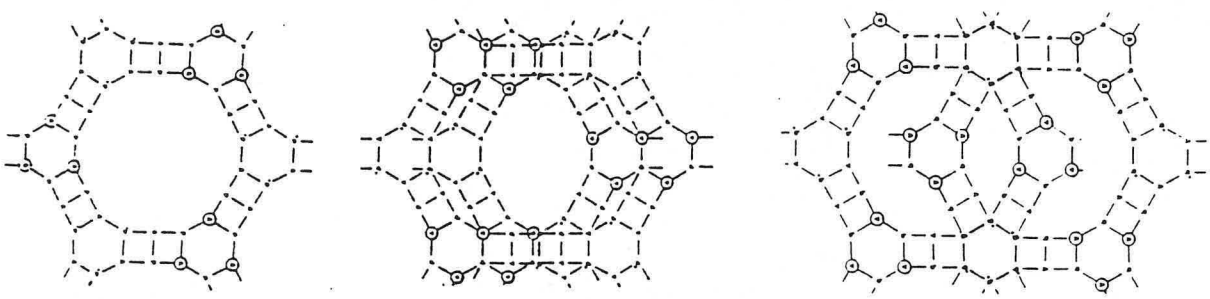

Figure 7: Structure model of VPI-5 and two possibilities for $AlPO_4$-8

SUMMARY

TEM micrographs of VPI-5 and $AlPO_4$-8 have been obtained. Analysis of these images in conjunction with known thermal stability, adsorption and x-ray powder diffraction data has lead to a proposed structure for $AlPO_4$-8. In addition the thermal rearrangement VPI-5 undergoes is understood and it may be possible to develop ways of stabilizing the material.

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