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OBSERVATIONS ON THE SYNTHESIS AND STRUCTURE OF WIDE PORE ALUMINUM PHOSPHATE MOLECULAR SIEVES

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The synthesis of wide pore 18-ring aluminum phosphates has been explored using several amines as templates. The systems studied in more detail involve the use of dipentylamine (DPTA), a combination of tributylamine (TBA) and dipentylamine and dipropylamine (DPA). In the latter two systems a thermally unstable phase with an XRD pattern similar to VPI-5 was obtained which has been identified as the H1 phase. In the DPTA system both thermally stable and unstable phases can be formed, depending on the reaction conditions used. By controlling the gel formation in the DPA system $ALPO_4$-8 was synthesized by hydrothermal methods. The products in the first two cases contain significantly higher amounts of the amine than has been reported in the synthesis of VPI-5. The structure of the thermally unstable H1 phase has been solved from X-ray powder data collected using a synchrotron X-ray source and shown to contain 6-coordinate aluminum in the 4-rings.

Keywords: VPI-5, H1, aluminophosphate synthesis and structure.

1. Introduction

The synthesis of large pore aluminum phosphate molecular sieves [1,2] has generated a great deal of interest in their behavior and potential uses [3,4]. We have been interested in this topic from the beginning and used large elliptical or spherical shaped amines in a unsuccessful effort to prepare such wide pore structures [5]. We therefore have undertaken a detailed study of the preparation and behavior of VPI-5 and $AlPO_4$-8 along the lines already disclosed [1,2,6]. In particular we have carried out variations in the synthesis procedure which shed some light on the product stability. For example, Davis, et al. [4] have reported that the VPI-5 prepared with dipropylamine (DPA) is not stable in the mother liquor after approximately 24 h of heating, decomposing at longer heating times. In contrast the VPI-5 prepared in the presence of tributylammonium hydroxide (TBAH) is stable at 150 °C in the mother liquor. In this communication we describe some preliminary findings bearing on phase recognition and stability.

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2. Experimental

Preparation of VPI-5 with dipentylamine (DPTA).

13.8 g of pseudoboehmite (Catapal B-alumina, Vista Chem. Co.) was dispersed in 41.4 ml of distilled, deionized water. To this solution was added a phosphoric acid solution consisting of 23.1 g of concentrated phosphoric acid (Fisher Reagent grade, 85%) diluted with 27.4 ml of distilled, deionized water. The acid solution was added dropwise to the alumina contained in a 250 ml round bottom flask with magnetic stirring. The flask was then placed on a rotary evaporator and heated at 95 °C in a water bath for 25 min. During this time, the flask was rotated but no suction or vacuum was applied. The homogenized gel was then aged at room temperature for 3 h and 15.9 g of dipentylamine added. This mixture was then placed into a stainless steel reaction vessel and heated at 150 ± 2 °C and autogeneous pressure. The vessel required approximately 2 h to reach the reaction temperature and 20 min quenching in cold water to cool to room temperature when the reaction was complete. Reaction times at peak temperature were varied from 4 to 30 h. In each case, the ratio of reactants was DPTA: Al_2O_3: P_2O_5: 40 H_2O. At the completion of the reaction, the filtered solid was washed 3 to 4 times with 100 ml portions of water and dried at 90 °C for 13 h. Reaction times of 18–22 h produced pure VPI-5 whereas shorter (13–18 h) times yielded mixtures of H1 and VPI-5. Pure H1 was produced below 13 h of hydrothermal treatment whereas times longer than 22 h again yielded mixtures.

Preparation of $AlPO_4$-8.

13.8 g of pseudoboehmite was slurried in 41.1 g of water with magnetic stirring for 10–15 min. A phosphoric acid solution containing 23.1 g of 85% H_3PO_4 and 27.4 g of water was added to the psuedoboehmite slurry in increments of 7 ml with a 2 min interval between additions with continuous stirring. This gel was then allowed to age for 10 h at room temperature. Stirring was then commenced once more and 10.1 g of DPA added dropwise. Stirring was continued for an additional 20–30 min and then the contents were transferred to a teflon lined steel vessel and kept at 125 °C for 20–25 hours. The water washed hydrated solid gave an X-ray pattern of an unknown phase. However, on drying the solid phase reverted to the familiar X-ray pattern of $AlPO_4$-8 [6]. For this procedure, the mole ratio of reactants was DPA: Al_2O_3: P_2O_5: 40 H_2O.

Preparation of H1.

In a slight variant of the above procedure for preparing $AlPO_4$-8, we obtained the unstable form of VPI-5 which has now been identified as the H1 phase reported by d'Yvoire [7]. The changes in the procedure involve the addition of the phosphoric acid solution 4 ml at a time at 2 min intervals and a longer period of aging. Both phases, $AlPO_4$-8 and H1 were found to be almost free of the amine used in the synthesis as indicated by the weight losses in the TGA curves (1.2 and

0.1%, respectively). The H1 phase has also been prepared using a combination of two amines. The preparation and quantities of the gel follow the same procedure as indicated before. Once the gel is aged between 3 to 10 hours, 20.97 g of tributylamine (TBA) is added dropwise with magnetic stirring followed by the addition of 3.18 g of dipentylamine (DPTA). Stirring was continued for an additional 20–30 min and then the contents were transferred to a teflon lined steel vessel and kept at 130 °C for 20–24 hours. The water washed dried solid gave an X-ray pattern similar to the pattern of the thermally stable VPI-5 with some differences in intensities for the X-ray peaks in the region of 21–24° 2θ (CuKα radiation). For this procedure, the mole ratio of reactants was (1.12 TBA, 0.2 DPTA): Al_2O_3: P_2O_5: 40 H_2O. The use of the amine mixture helped to prevent the appearance of other aluminum phosphate phases in the products. A typical TGA for one of the samples indicated a total weight loss of 22.9% up to 800 °C, with 14.2% due to loss of amine. Further analysis by mass spectrometry gave a ratio of DPTA: TBA = 1.02. ICP analysis for aluminum and phosphorus yielded a P/Al mole ratio of 0.93 in this case. Elemental analysis (Galbraith Laboratories, Inc.) gave 1.11% N and 4.3% C and confirmed the presence of the organic templates contained in the aluminum phosphate channels (vide infra).

Instrumental.

X-ray diffraction patterns were recorded with a Scintag PAD II powder unit with CuKα (Ni filtered) radiation. The scan speed was 1°/min at 40 kV and 20 mA. In some cases the patterns were obtained by step scanning at 0.05° per step and 10 sec count time with a Si (NBS-640) standard for accurate d-spacing determination. Thermal analysis was carried out with a DuPont Thermal Analyst 2000 unit at heating rates of 4 to 10 °/min under N_2. Elemental analysis was carried out either by Galbraith Laboratories or internally by AA and inductively coupled plasma arc methods.

3. Results and discussion

The X-ray powder diffraction patterns for VPI-5 and H1 (as made) are shown in fig. 1. At first glance they appear very similar. The one for the thermally stable phase of VPI-5 is almost identical to the $AlPO_4$-54 pattern [8]. During the preparation of this manuscript we became aware of a report describing the synthesis of d'Yvoire's H1 phase [9]. Our thermally unstable VPI-5 powder pattern agrees very well with the one given in this report and therefore will be designated as H1. The X-ray powder patterns of H1 and VPI-5 differ in the region of 20–24° in 2θ. In the H1 phase there are three major reflections in this angular span as follows: 4.10 Å, 3.97 Å, 3.77 Å. However, at higher resolution the first two of these reflections are actually shown to be doublets with $d = 4.11$ Å, 4.07 Å and 3.99 Å, 3.95 Å. In the case of VPI-5 the reflections are not doublets

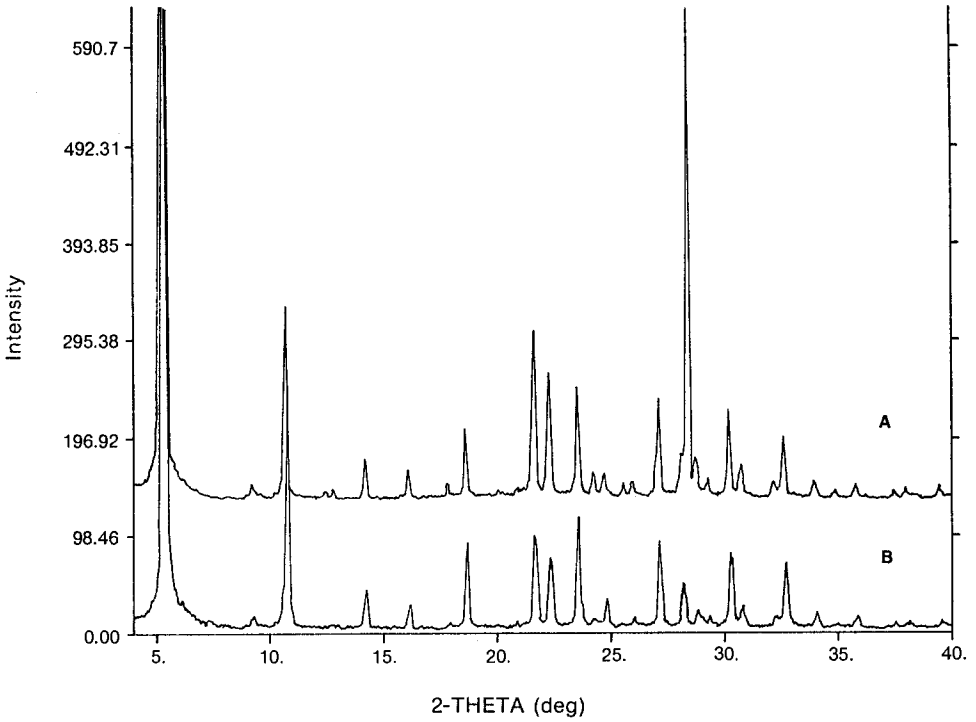

Fig. 1. X-ray diffraction powder patterns of (A) VPI-5 and (B) H1. The very large peak at $2\theta = 28.47°$ is due to the added silicon standard.

and furthermore the intensities of the reflections in this region of 2θ are different for the two phases.

Another point of difference between the two phases is their composition. The VPI-5 phase contained 4.5% H_2O and 14.1% DPTA as well as a ratio of Al to P close to one. On the assumption that the ratio of aluminum to phosphorus in the product is strictly one, the analysis leads to a formula of $AlPO_4 \cdot 0.375H_2O \cdot 0.133$ DPTA with 18 such units per unit cell. In contrast the aluminum to phosphorus ratio for three different preparations of H1 averaged 1.1 A typical complete analysis gave Al, 17.85%; P, 17.66%; Al/P = 1.16, H_2O(TGA), 8.6%; C, 4.3%; N, 0.87%. The carbon content requires that 0.079 moles of amine be present, however the nitrogen content requires almost twice this amount. However, the weight loss (TGA) curve showed a loss of 8.6% water from slightly above room temperature to a plateau at 165 °C. A further weight loss of 14.47% was complete at 450 °C. This latter weight loss is attributed to the removal of the amines which amounts to a value equivalent to 0.12 moles of amine. Using this value we arrive at the formula $H_{0.14}Al_{1.07}P_{0.93}O_4 \cdot 0.75H_2O \cdot 0.12$ (TBA + DPTA).

It should be emphasized at this point that the preparations of both VPI-5 and H1 using dipropylamine as template contained very little amine. This is in accord

with the report of Davis et al. [1,2,4]. However, whenever the larger amines were used a considerable amount of amine resided in the tunnels even though the washing procedure was the same for all preparations.

Removal of the amine thermally above 300 ° C resulted in the transformation of the H1 phase to $AlPO_4$-8. The excess aluminum could not be removed from either the H1 phase or the converted $AlPO_4$-8 phase by extensive washing. Furthermore, the supernatant liquid from the preparation of H1 contained four times more phosphate than aluminum and the subsequent washings contained phosphate but no aluminum. We therefore conclude that the high aluminum content is real and the excess Al atoms may be situated in either the framework or the tunnels. Furthermore it was found that even the thermally stable VPI-5 deteriorates when slurried in water for long periods of time. For example, 25 mg of VPI-5 was added to 25 ml of water and stirred magnetically for 5 h. The filtrate was found to contain 16.8 μg of phosphate but only 1.5 μg of Al. When a similar stirred mixture was allowed to stand overnight, even more phosphate (42 μg) was dissolved and the pH dropped from an initial value of 9.67 to 8.20. The resultant solid had an Al : P ratio of 1.075 and consisted of a mixture of about 30% $AlPO_4$-8 together with the original VPI-5 hydrate.

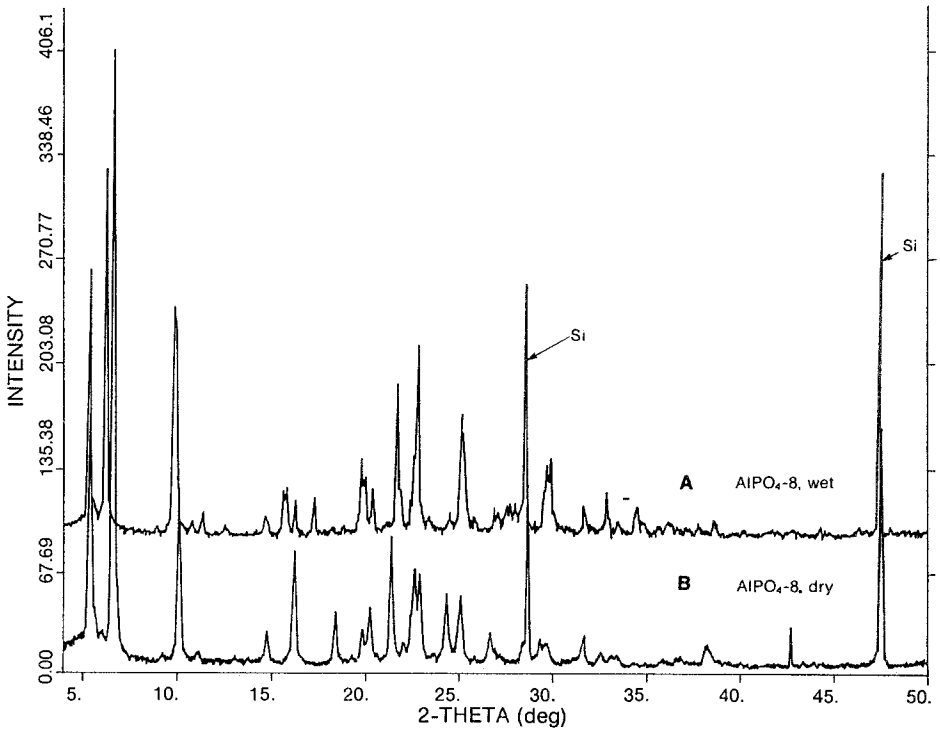

Fig. 2. X-ray diffraction powder patterns of (A) hydrated $AlPO_4$-8 obtained from hydrothermal synthesis and (B) dehydrated at 50 ° C in vacuo.

The X-ray diffraction pattern of the dehydrated $AlPO_4$-8 prepared at 50 °C in vacuo and kept in an anhydrous state is compared (fig. 2) to the highly hydrated $AlPO_4$-8 which was obtained by direct hydrothermal synthesis, in fig. 2. It is seen that the (200) reflection remains almost constant at 16.5 Å but the next reflection is at 14.5 Å for the hydrated phase and 13.3 Å for the dehydrated phase. Other differences are evident in the region of 20–25° in 2θ. Furthermore, the synthesis of $AlPO_4$-8 by the hydrothermal procedure also yields products with Al > P. To help clarify some of these issues we have obtained X-ray and neutron powder diffraction data for VPI-5, H1 and $AlPO_4$-8 and structure determinations of both the hydrated on dehydrated phases are in progress. At this stage of our work we report on the structure of the H1 phase which was prepared using a mixture of tributylamine (80%) and DPTA (20%). X-ray powder diffraction data for this solid were obtained at the National Synchrotron Light Source on beam line X7A. Data was collected from 4 to 70° 2θ at a wavelength of 1.33087 (Å). The unit cell is hexagonal, with the dimensions $a = 18.9690(2)$ (Å), $c = 8.1159(1)$ (Å). The space group is $P6_3cm$, and there are 18 $AlPO_4$ units per unit cell. These parameters agree with those reported for VPI-5 by Davis, et al. [2]. The starting aluminum and phosphorus positions were generated by symmetry and the size of the unit cell. The structural parameters were refined using the Rietveld method of full-profile analysis contained in the GSAS program package [10] and the oxygen

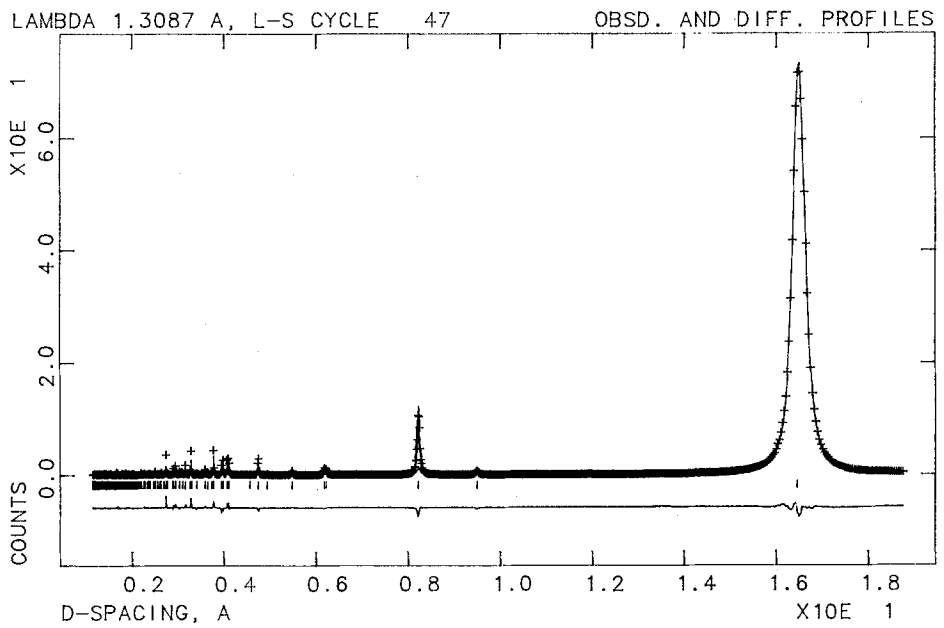

Fig. 3. Plots of X-ray intensity versus *d*-spacing for H1. Observed data are represented by crosses and the calculated values by the solid lines, with the difference plot below as one solid line below. Vertical strokes indicate calculated Bragg-peak positions.

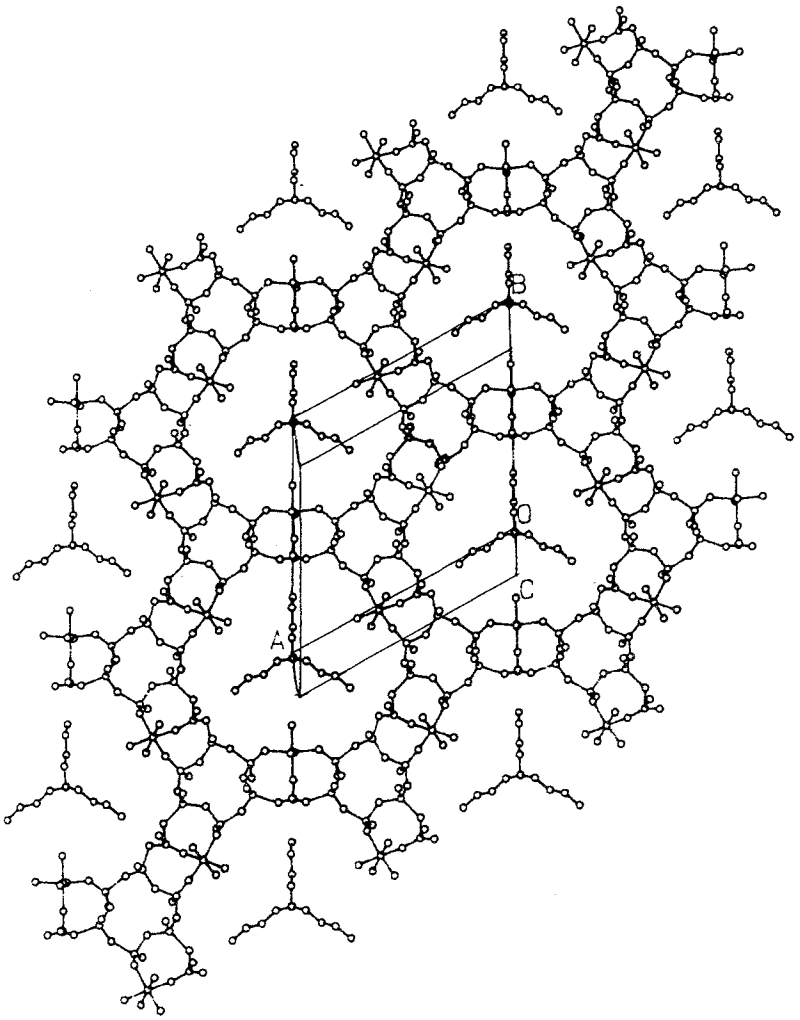

Fig. 4. A schematic drawing of the structure of H1 as determined from synchrotron X-ray powder data showing the presence of the template and 6-coordinate aluminum in the double 4-rings.

atoms found by difference syntheses. The refinement is still in progress and at a later stage the data will be merged with neutron diffraction data in an attempt to locate the excess aluminum. At this stage of the refinement Rp is 0.128, Rwp = 0.207, and $\chi^2 = 22.4$. The difference profiles are shown in fig. 3. However, some interesting results are apparent at this stage of the refinement.

The structure viewed down the C-axis is shown in fig. 4. It is clearly seen that TBA is contained within the tunnels with the nitrogen atom being located on a 3-fold axis and the butyl chains occupying special positions along the edges of the unit cell and along the lines where $x = y$. It was not possible at this stage of the refinement to distinguish the ordered tributylamine from the disordered di-

pentylamine due to thermal vibration. For clarity only the tributylamine is shown. A second feature to note is that two water molecules are bonded to the aluminum atom which is exclusively in the 4-rings. This bonding makes the coordination about this aluminum atom octahedral, as opposed to the aluminum atoms in the 6-rings, which are tetrahedral. In this respect it differs from the fully hydrated structure of VPI-5 determined by Rudolf and Crowder which showed no six coordinate aluminum [11]. Octahedral coordination of the aluminum atoms in the 4-rings also differs with the hypothesis put forth by Grobert et al. [12] that in VPI-5 the aluminum atoms in alternate 6-rings are six coordinate. Whether this difference results from the presence of the amine template which blocks the approach of water to the 6-rings or is a real preference resulting from the presence of possible excess aluminum in the framework is under investigation by a combined diffraction and NMR study.

4. Conclusions

1. Two very similar 18-ring aluminum phosphate molecular sieves, termed VPI-5 and H1, have been synthesized by control of gel viscosity and choice of amine additive.
2. H1 converts to $AlPO_4$-8 upon heating to at least 170 °C in vacuum or 300 °C in air whereas VPI-5 does not.
3. $AlPO_4$-8 may also be synthesized by hydrothermal means by proper control of gel viscosity and choice of amine additive.
4. The H1 phase exhibits 6-coordination of the Al atoms in the 4-rings and contains an excess of aluminum over phosphorus whereas VPI-5 has a ratio Al : P of one and may prefer 6-coordination of Al in alternate 6-rings.
5. The differences cited in 4 between VPI-5 and H1 may be responsible for their different thermal behavior.

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