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Pillaring of Layered Tetravalent Metal Phosphates and Oxides Using (3-Aminopropyl)trimethoxysilane

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(3-Aminopropyl)trimethoxysilane, $(CH_3O)_3Si(CH_2)_3NH_2$, has been intercalated into a series of tetravalent metal phosphates of the general formula $M(HPO_4)_2{\cdot}H_2O$ (M = Zr, Ti, Sn) and a potassium tetratitanate, $K_2Ti_4O_9{\cdot}xH_2O$, to give a new range of compounds with greatly expanded interlayer distances. Calcination of these intercalates in air led to the formation of nonporous and microporous silica-pillared materials with interlayer distances between 11 and 21 Å and BET surface areas ranging from 29 to 232 $m^2\ g^{-1}$.

Introduction

Pillaring of layered compounds has been a topic for extensive research over the past 15 years.[1] Clays which are two-dimensional silicate structures with a negative layer charge produced by substitution defects can be pillared with positively charged inorganic polymers or organic molecules. Temperature stable porous materials have been synthesized using polymeric inorganic cations. It is hoped that these new materials would possess pores larger than those found in zeolites and would then have the ability to crack larger organic molecules. One of the more widely used inorganic polymers is the aluminum Keggin ion which has a formula of $Al_{13}O_4(OH)_{24}(H_2O)_{12}{}^{7+}$. Its extensive use can be attributed to its stability and its ease of synthesis as well as being the most thoroughly characterized polymeric cation.

However, clays were not the only materials to be pillared. New layered materials such as the tetravalent metal phosphates and oxides underwent investigation,[2–8] but due to the high charge density of these lamellar phosphates and oxides, the interlamellar region is usually effectively "stuffed" with the pillaring species resulting in materials with relatively low surface areas. Recently though, high surface area pillared α-tin phosphate has been synthesized[4,5] by means of chromium pillars. The present investigation is aimed at overcoming the problem of the high charge density by intercalating an organosilane into the interlamellar region and utilizing the relatively bulky organic groups to effectively space the silica pillars. Subsequent calcination would lead to the loss of the organic spacer resulting in an open, porous, cross-linked structure. An initial attempt in this direction was previously made by Li et al.[9] and Lewis et al.[10] though little information on the porosity of the compounds synthesized was given. More complete details on the silica pillaring of 4-valent phosphates was reported by Roziere et al.[11]

Landis and co-workers[12] have reported pillaring the disodium trititanate using tetraethyl orthosilicate (TEOS). The titanate was first preswelled using an alkylammonium ion or amine and then reacted with TEOS. Because the height or size of the polymer appears to be dependent upon the preswelling distance of the layers, the silicate polymer is believed to have formed in situ in the gallery region. In this study we used the dipotassium tetratitanate, whose structure was solved by Tournoux et al.,[13] as the layered host instead of the disodium trititanate.

Experimental Section

Metal Phosphates. The layered phosphates were prepared according to standard literature methods.[14–17] The titanium phosphate (TiP) and zirconium phosphate (ZrP) gels initially obtained were refluxed for 48 h in 4.5 and 9 M phosphoric acid respectively to obtain crystalline products. In the crystalline state the compounds have the α structure[18] and are designated α-MeP. To indicate which sample was used, we add the concentration of acid and time of reflux as in α-ZrP (9:48). The α-tin phosphate (α-SnP) was refluxed for an additional 48 h following the initial precipitation. Two methods as detailed below were used to intercalate (3-aminopropyl)trimethoxysilane (AMPS) into the phosphate host.

Direct Intercalation. The metal phosphate (2 g) was refluxed with a solution of 8 g of AMPS in 300 mL of deionized

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water or ethanol or a mixture of the two for 18 h. The solid product was then filtered, washed with deionized water and/or ethanol, and dried at 65 °C prior to analysis. This method is similar to the method developed by Roziere and will be used in comparison with the method below.[11]

Intercalation into Colloidal Phosphate Dispersions. A sufficient amount of *n*-propylamine was added slowly to 2 g of the phosphate in 75 mL of deionized water to form a 50% amine-exchanged phase. This mixture was diluted further with deionized water (200–250 mL) and subsequently placed in an ultrasonic bath for 1 h to completely disperse the phosphate lamellae. A more complete description of these colloidal dispersions has been given by Alberti et al.[19] AMPS (8 g) was added to 50–100 mL of deionized water and heated to reflux. Then the AMPS solution was added to the already refluxing colloidal suspension of half-exchanged propylamine metal phosphate phase and refluxing continued for an additional 18 h. The solid product was separated by centrifugation, washed with deionized water, and dried at 65 °C.

Pillaring of the phosphates was achieved by calcination of the precursor amine intercalates at 500 °C in air for 18 h. This treatment effectively removed the organic groups present resulting in the formation of silica pillars within the interlamellar region.

Synthesis of the Tetratitanate and Its Pillaring. The potassium tetratitanate was synthesized using a solid state method developed by Izawa et al.[20] The potassium was then exchanged for protons by mixing the solid with a 2.9 M HCl solution and kept at 65 °C for 2 days. The resulting product was collected and then reacted with a 6.0 M propylamine solution for 5 days at 65 °C to obtain an intercalated product. Propylamine titanate (0.70 g) was mixed with 10 mL of AMPS and 60 mL of deionized water, and the mixture was then refluxed for 24 h. The product was separated by filtration and washed five times with deionized water and then calcined at 340 °C for 24 h to obtain the pillared material.

Instrumentation and Elemental Analysis. CHN analyses were carried out by Desert Analytics, Tucson, AZ. Elemental analyses were obtained by dissolving a known mass of the compound in hydrofluoric acid (α-ZrP and α-TiP) or fusing with sodium peroxide (α-SnP) and analyzing the resultant solutions using ICP-AES spectrophotometry. (Actual ICP-AES analysis was performed by the ICP analysis laboratory, Department of Horticulture, Texas A&M University.) The titanate was fused with sodium peroxide and extracted with HCl and H_2SO_4. The analysis was carried out using DCP-AES instead of ICP spectrometry. Surface area measurements were obtained with a Quantachrome Autosorb 6 unit using nitrogen adsorption–desorption at 77 K. X-ray powder diffraction patterns were obtained on a Scintag PAD V diffractometer using nickel-filtered Cu Kα radiation. Thermogravimetric analyses were obtained using a DuPont Thermal Analyst 2000 under a flowing air/O_2 atmosphere usually at a rate of 10 °C/min.

Results and Discussion

X-ray powder diffraction patterns confirmed the phase purity and crystallinity of the initial metal phosphates. As expected, the least crystalline starting material was the α-SnP.[21] Thermogravimetric analysis showed weight losses in conformity with the expected composition, $M(HPO_4)_2 \cdot H_2O$, M = Ti, Zr, Sn.

Titanium Phosphate. Attempts at direct intercalation of the AMPS into the α-TiP (4.5:48) in aqueous solution were unsuccessful as little or no reaction occurred. By increasing the time of reflux to 48 h, an amorphous product with a very broad X-ray diffraction (XRD) peak at approximately 13.4 Å was obtained. It was also noted that a solid precipitate formed in the filtrate upon addition of acetone. This product was also amorphous. It was believed that the layered structure of the α-TiP was being destroyed by hydrolysis in the basic aqueous solution. The solvent was then changed to ethanol in hopes of eliminating the possible dissolution problem of the layered host. However, upon investigation of the final product, unreacted α-TiP was the only phase present. The α-TiP was then allowed to react with the AMPS in a 50% mixture of ethanol and deionzed water. The solid was collected by filtration and air dried. This product was predominately unreacted α-TiP with perhaps 10% of the amine intercalate (as shown by reflections at 36.4 and 15.7 Å in the X-ray pattern). Since the amount of recovered solid was only half the expected yield, a quantity of ethanol was added to the filtrate to recover a second solid. This product was amorphous and contained both titanium and phosphorus and may represent a hydrolyzed basic phosphate complexed by the aminosilane.

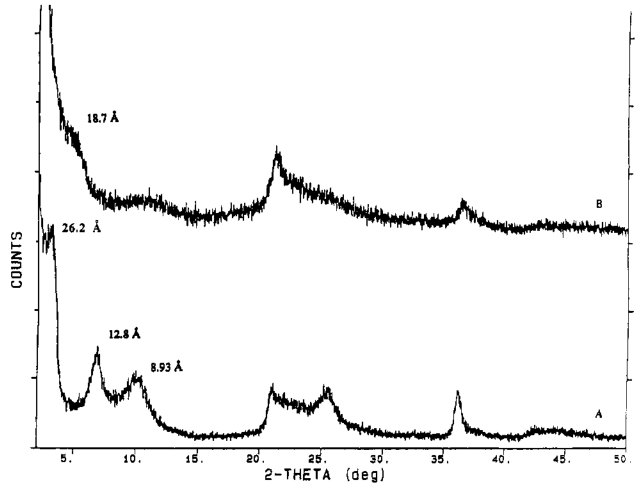

Figure 1. XRD powder patterns of AMPS intercalated directly into α-SnP (A) before calcination and (B) after calcination at 500 °C.

After the unsuccessful attempts at pillaring α-TiP in a direct manner, intercalation of the AMPS was tried using the colloidal phosphate dispersion. An XRD of the propylamine α-TiP with AMPS solid yielded a single phase of low crystallinity similar to the amorphous phase recovered previously from the filtrate. A highly crystalline α-TiP, that would be less likely to undergo hydrolysis, may withstand the reaction conditions in a more robust fashion. However all attempts thus far have proven unsuccessful with the α-TiP (4.5:48).

Tin Phosphate. α-SnP showed similar characteristics to α-TiP when the intercalation of AMPS was attempted in aqueous solutions. The results of the reactions showed partial dissolution of the host phosphate and a loss of the layered structure. By contrast, the use of an ethanolic medium achieved complete intercalation of AMPS into the α-SnP (sample II-8) to form a single-phase intercalate with a *d* spacing of approximately 26.2 Å as seen in Figure 1A. Intercalation of the AMPS into the colloidal dispersion of α-SnP prepared with propylamine in aqueous solution proved unsuccessful.

It can be seen from the elemental analysis (Table 1) that the use of ethanolic media resulted in minor

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Table 1. Elemental Analyses of the Phosphate AMPS Intercalates

metal phosphate	% M	% P	% Si	% C	% H	% N	M:P:Si
α-ZrP II-4A	15.52	10.39	14.50	7.49	4.17	5.47	1:2.0:3.1
α-ZrP I-5	17.31	10.28	10.47	13.69	3.76	5.30	1:1.8:2.0
α-SnP II-8	20.61	10.32	9.28	14.02	3.65	5.16	1:1.9:1.9

hydrolysis of the α-SnP as the P/Sn ratio was only slightly less than 2. Analysis of the untreated α-SnP showed the expected P/Sn ratio of 2. A simplified formula for the α-SnP intercalation compound is $Sn(HPO_4)_2[(HO)_3Si(CH_2)_3NH_2]_2$ indicating that a saturated phase was obtained. That is, one amine molecule was intercalated for each available proton. This formula is not strictly accurate due to the small amount of hydrolysis which has taken place, and the fact that the elemental analysis indicates that the ratio of nitrogen to silicon is greater than one (N/Si = 1.11). In addition, the ratio of carbon to silicon is greater than 3 (C/Si = 3.53). These results are an indication that some of the propylamino groups may hydrolyze off of the silane and then be incorporated into the interlayer region. This phenomenon will be discussed in more detail in the Discussion. Added to this is the fact that the interlayer spacing before calcination is 26.2 Å, a value also observed by Roziere et al.[11] To achieve such a high value for the interplanar spacing, a highly polymerized silicon species is required.

To help construct a rational formula for the intercalated product, we also carried out a thermal analysis by TGA methods. The weight loss curve is shown in Figure 2A. The total weight loss is 28.24%, and on the assumption that no phosphorus is lost the final composition would be $SnO_{0.08}(P_2O_7)_{0.96}{\cdot}1.9SiO_2$. This composition accounts for the hydrolysis of some tin phosphate during the intercalation process as shown by the elemental analysis data in Table 1. The formula weight for this composition is 401.12, so that the formula weight required for the intercalated tin phosphate is 558.97. A reasonable formula which can then be constructed is $Sn(OH)_{0.16}(HPO_4)_{1.92}[NH_2(CH_2)_3SiO_{1.5}]_{1.9}(CH_3CH_2CH_2NH_2)_{0.2}{\cdot}2H_2O$ (FW = 563.07) for which we calculate 21.08% Sn, 10.56% P, 9.47% Si, 13.42% C, 5.22% N, 3.80% H, and 28.76% total weight loss. This formula assumes that a certain amount of propylamine from the hydrolysis reaction of the silane in solution is incorporated into the interlamellar space of the tin phosphate. A supposition of this nature is required to account for the higher mole ratios of carbon and nitrogen relative to silicon than is required if only the hydrolyzed aminosilane was intercalated. Since the interlayer spacing increased by more than 16 Å, we assume that the silane has hydrolyzed off the majority of its methoxyl groups and exists in a polymerized state between the tin phosphate layers. Furthermore, the distribution of oxo and hydroxo groups in the polymer is unknown. Therefore, we have indicated the distribution in a noncommittal manner, with all oxo groups in brackets and the correct amount of water as determined from the TGA curve as water of hydration.

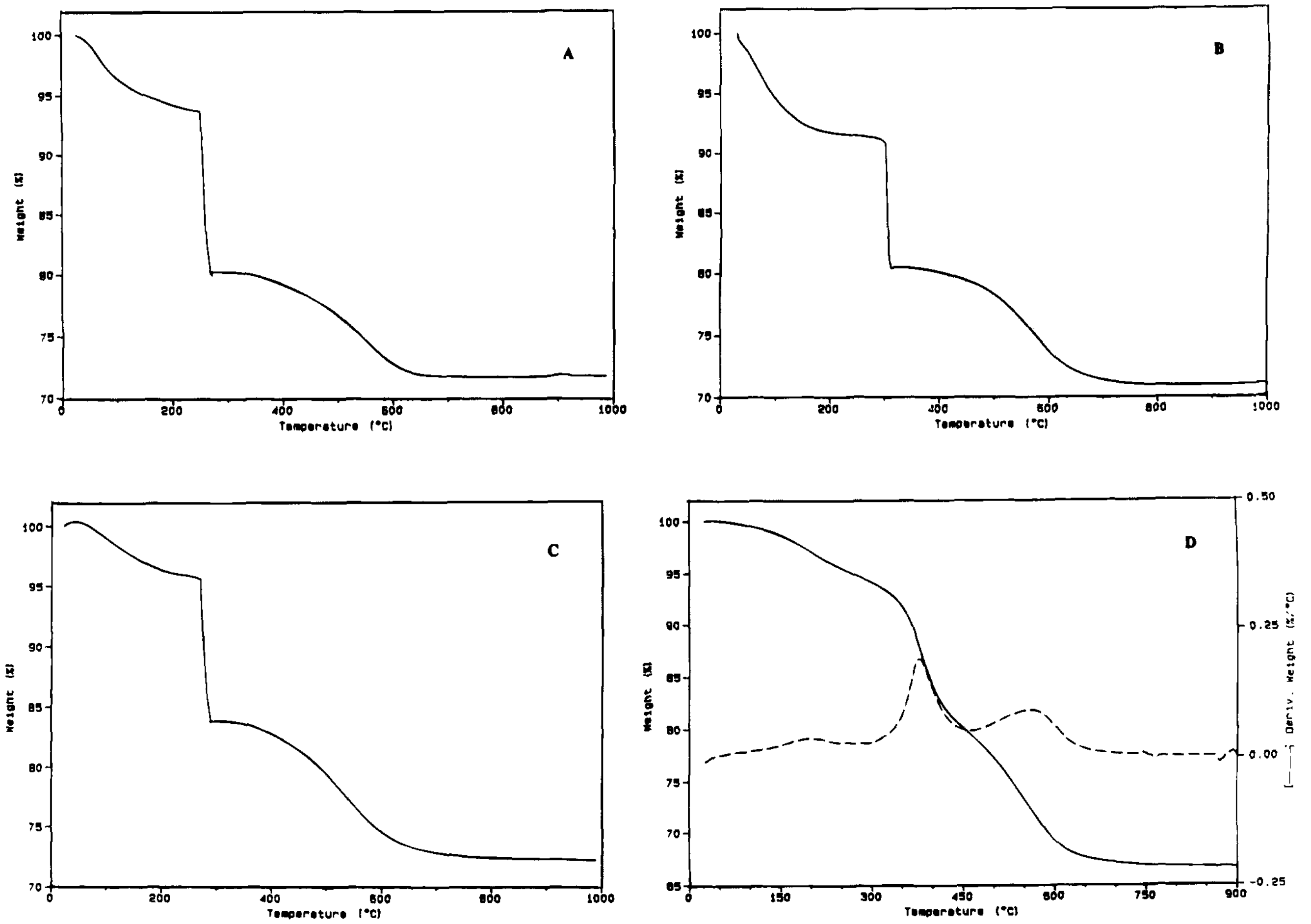

Figure 2. TGA curves of intercalated silane products for (A) α-SnP (sample II-8), (B) α-ZrP (sample I-5) prepared by direct intercalation of AMPS, (C) α-ZrP (sample II-4A) containing two phases and (D) α-ZrP (sample II-6) intercalated as a colloidal dispersion.

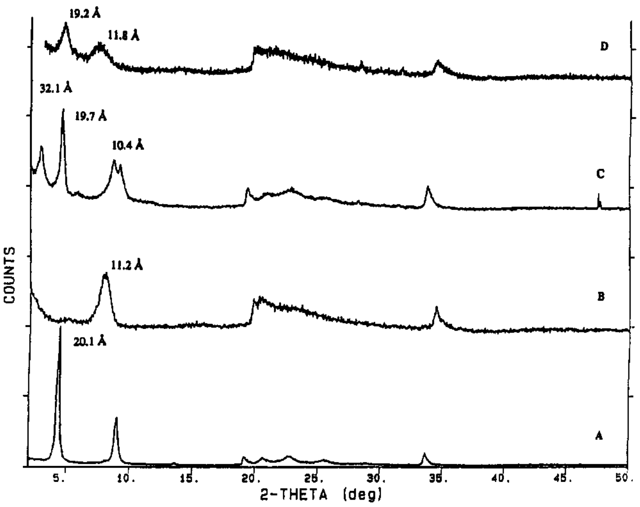

Figure 3. XRD powder patterns of the direct intercalation of AMPS into samples (A) I-5, (B) I-5 after calcination at 500 °C, (C) II-4A, and (D) II-4A after calcination at 500 °C.

Calcination of the intercalated α-SnP at 500 °C gives a weak XRD reflection at approximately 18.7 Å as seen in Figure 1B. This large change in *d* spacing results from the removal of the propylamine groups attached to the Si atom and some water. The BET surface area of this "pillared" material is 132 m^2/g but with very few micropores evident. This relatively high surface area is probably due to the small particle size of the product caused by calcination as well as mesopores resulting from the defects incurred through pillaring and calcination.

Zirconium Phosphate. Unlike the α-TiP and α-SnP, complete intercalation of AMPS into α-ZrP was achieved in aqueous solution (sample I-5) giving a single phase with a typical *d* spacing of 20.1 Å (Figure 3A). Calcination at 500 °C leads to a phase with an 11.2-Å interlayer spacing (Figure 3B). However, one synthesis (II-4A) gave a product consisting of two phases one with a *d* spacing of 32.1 Å in addition to the latter phase with its reflection at 19.7 Å in this (Figure 3C). Although the preparation method was identical to the standard method, the higher *d* spacing observed suggests that more extensive polymerization of a portion of the AMPS occurred in solution resulting in a biphasic product. Not surprisingly, calcination of this precursor at 500 °C gave a mixed phase pillared phosphate as seen in Figure 3D with d-spacings of 19.2 and 11.8 Å. The *d* spacing of 11.8 Å is undoubtedly of a phase similar to the one obtained with sample in I-5 (11.2-Å interlayer spacing). The reflection at 19.2 Å is then derived from the calcination of the 32.1-Å phase. Only partial intercalation of AMPS into α-ZrP was achieved in ethanolic solution.

From the elemental analysis of I-5, which can be found in Table 1, a general formula of $Zr(HPO_4)_{1.77}(OH)_{0.46}[O_{1.5}Si(CH_2)_3NH_2]_2{\cdot}2.36H_2O$ can be derived. The calculated values for this formula are 17.31% Zr, 10.29% P, 10.54% Si, 13.52% C, 5.26% N, 4.34% H, and 7.98% H_2O. The mole ratio of phosphorus to zirconium is 1.77 indicative of about 11% hydrolysis of phosphate groups resulting from the long reflux time in a slightly basic solution. This extent of hydrolysis exceeds that obtained for α-SnP which is normally the more hydrolyzable compound. However, the intercalation of the tin phosphate was carried out in ethanol, greatly reducing the tendency for hydrolysis. The proposed formula disagrees slightly with the weight loss observed in the TGA trace (Figure 2B). A total weight loss of 30.56% is calculated from the formula. However, the TGA trace shows a total weight loss of only 29.04%. It was believed that a rapid combustion reaction may be occurring during the heating process as evidenced by the sharp weight loss at 289 °C thus producing the errors in the total weight loss. Reexamination of the TGA using a slower heating rate of 5 °C/min instead of the usual 10 °C/min in the temperature range between 240 and 350 °C shows that the sharp weight loss due to the combustion of organic material becomes smoother being extended over a larger temperature range, with an attendant overall weight loss increase of 2%. The slower heating rate allows for a more complete combustion of the organic material and better agreement with the calculated formula. A similar formula for sample II-4A is not proposed due to the presence of two phases. However, the XRD powder patterns in Figure 2C and D suggests that one phase is similar to that represented by the formula given above for sample I-5 and the other is a new phase with a more extended interlayer spacing of 32.1 Å. This sample also contained about 50% more silica than I-5. After calcination the XRD pattern (Figure 3D) contained a reflection at 11.8 Å as expected from comparison with sample I-5 and another reflection at 19.2 Å. This latter reflection must arise from loss of organic by the 32.1-Å intercalate.

The BET surface areas for samples I-5 and II-4A are 29 and 81.7 m^2/g, respectively. After calcination of I-5 at 500 °C, the *d* spacing was 11.2 Å (Figure 3B). By subtracting the *d* spacing of the dehydrated α-ZrP, which is 6.3 Å, from the *d* spacing of the pillared material, the pore height would be 4.9 Å. This small value and the fact that the sample contained a high level of silica would explain the low surface area. The higher surface area of 81.7 m^2/g for sample II-4A is attributed to the presence of the phase with the larger *d* spacing of 19.2 Å after calcination.

In contrast to the materials described thus far, a microporous material was obtained by intercalation of AMPS into a colloidal dispersion of half exchanged n-propylamine α-ZrP dispersion (sample II-6). The XRD powder patterns of the intercalated material before and after calcination is shown in Figure 4A,B. The powder pattern of the intercalate (Figure 4A) is reminiscent of that shown in Figure 3C but with somewhat reduced *d* spacings. However, on heating to 500 °C only a single phase with interlayer spacing of 21.5 Å was obtained. It would appear that a biphasic product formed as evidenced by the X-ray peaks at 29.6 and 17.2 Å. The later peak is thought to be that of a propylamine exchanged ZrP or a smaller silane polymer intercalated α-ZrP phase. Interestingly, there is no evidence in the XRD powder pattern, Figure 4B, of the calcined material of a dehydrated α-ZrP phase or a zirconium pyrophosphate phase as would be expected if the peak at 17.2 Å was due to a ZrP/*n*-propylamine phase and dehydrated as such. If the peak was attributed to a silane pillar intercalate, then an XRD pattern similar to that obtained with sample II-4A would be expected on calcination (Figure 3D). In fact, the calcined sample shows evidence for the presence of only one phase (*d* = 21.5 Å). Further studies on this system were conducted, and

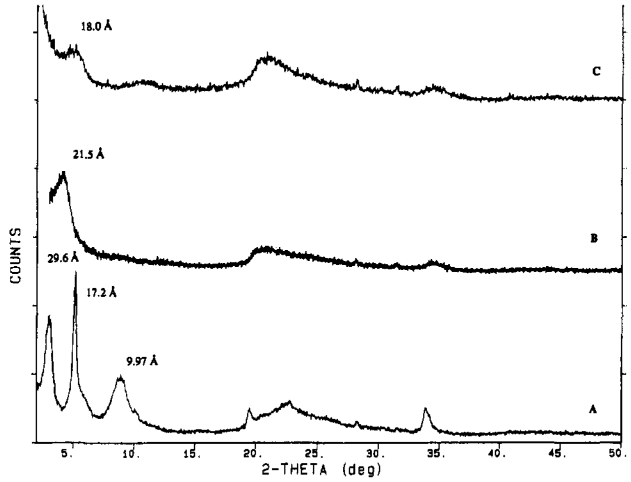

Figure 4. XRD powder pattern of (A) the α-ZrP/AMPS intercalate formed via the dispersed α-ZrP/propylamine phase and (B) the silica pillared α-ZrP via the *n*-propylamine phase after calcination at 500 °C, and (C) after calcination at 750 °C.

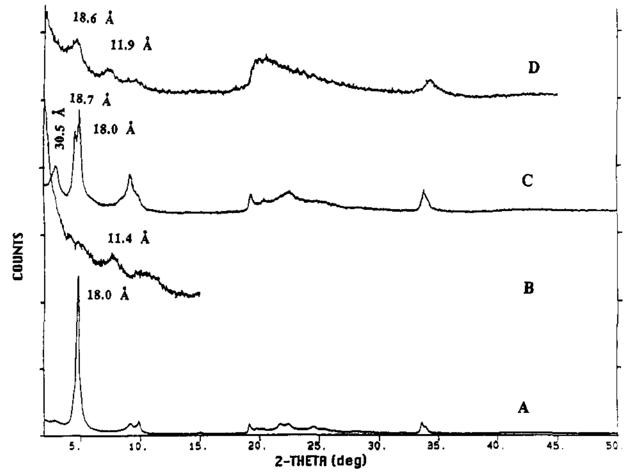

Figure 5. XRD pattern of (A) an α-ZrP/AMPS intercalate formed via the dispersed α-ZrP/propylamine phase with little to no 30-Å phase, (B) A after calcination at 500 °C, (C) α-ZrP/AMPS intercalate formed via the dispersed α-ZrP/propylamine phase with higher concentration of the 30-Å phase, and (D) C after calcination at 500 °C.

the results show that by varying the amount of water present in the initial half exchanged propylamine ZrP gel, one can control the intensity of the 17.2-Å reflection. However, experiments thus far have only shown an ability to increase the intensity of the 17.2-Å peak compared to that of the 29.6-Å peak.

By varying the conditions of preparation it was possible to obtain AMPS intercalated phases with (001) reflections as low as 17.9 Å. Calcination of one of these samples yielded a product with an 8.4-Å reflection. This low *d* spacing may indicate formation of a single SiO_2 layer between the phosphate layers. A similar sample with an 18.0-Å interlayer spacing is shown in Figure 5A. Calcination yielded the pattern shown in Figure 5B which may be an intergrowth of the 11.4-Å phase with the 8.4-Å phase. All of these combined features are exhibited by the X-ray pattern shown in Figure 5C,D. Three intercalated phases are present with interlayer spacings of 30.5, 18.7, and 18.0 Å. On calcination, the microporous phase with an 18.6 Å formed along with reflections at 11.4 and 8.4 Å for the other phases. Only when the peak at 29−31 Å is present in large amount, as shown in Figure 4A was a single phase obtained on calcination. We tentatively conclude that the reflection at 17.2 Å is due to a propylamine intercalate and, as will be explained in the Discussion, this absence of a second phase in sample II-6 results from diffusion of the propylamine and counterdiffusion of the larger silane intercalated species between the layers leading to a uniform distribution within the interlamellar region and consequently to a single phase on calcination. A similar process involving the diffusion of amines and Na^+ in α-ZrP has previously been observed.[22−24]

Table 2. Elemental Analyses of the α-ZrP/AMPS Intercalate Formed via the Dispersed α-ZrP/Propylamine Phase

metal phosphate	% Zr	% P	% Si	% C	% H	% N	Zr:P:Si
α-ZrP II-6	14.04	8.26	15.42	18.55	4.65	6.90	1:1.75:3.61

Elemental analysis of sample II-6 is given in Table 2. This sample has the highest ratio of Si to Zr of the three zirconium phosphate preparations. It is also evident from the ratio of organic to Si (C/Si = 2.81, Si/N = 1.11) that the silicon exists in a more highly polymerized form than previously obtained. Furthermore, a significant portion of the crystals are in the form of the propylamine intercalate. Since the Si/N ratio is 1.11, there must be less than one organic propylamine group per silicon atom. A formula which accounts for all of these requirements is the following; $Zr(OH)_{0.50}(HPO_4)_{1.75}(CH_3CH_2CH_2NH_2)_{0.531}[(NH_2(CH_2)_3)_6Si_8O_{12}(OH)_2]_{0.451}$ with calculated values of 13.93% Zr, 8.19% P, 15.30% Si, 17.62% C, 6.85% N, and 4.50% H. The formula presented here gives no indication of how much of the silane is intercalated as Si_8 octamers and as Si_8 groups in a double layer configuration (Figure 9).

The weight loss curve for sample II-6 is shown in Figure 2D. The first weight loss is due to about 1% surface water followed by loss of propylamine (4.74%) in the temperature range 135−330 °C. At higher temperatures (330−600 °C) the propylamine groups are lost (24%) from the aminosilane with a probable cross-linking of the pillars and layers as indicated in eq 1.

$$-P-OH + NH_2(CH_2)_3Si-O \rightarrow -P-O-Si-O + CH_3CH_2CH_2NH_2 \quad (1)$$

$$-SiOH + NH_2(CH_2)_3Si-O \rightarrow -Si-O-Si- + CH_3CH_2CH_2NH_2 \quad (2)$$

Loss of propylamine from the aminosilane accompanied by further polymerization (eq 2) may also be occurring in this temperature range. Evidence for the cross-linking reaction is derived from ^{31}P NMR spectra (Figure 6). The silicon polymer intercalated zirconium phosphate exhibits a single resonance peak at −14.8 ppm due to the layer HPO_4^{2-} groups interacting with adjacent amino groups which shifts the ^{31}P peak slightly

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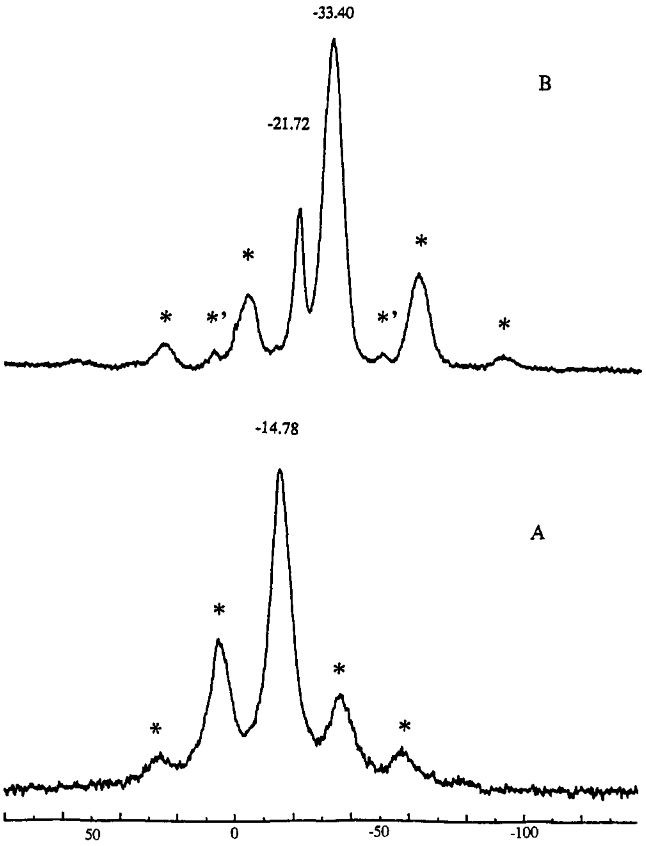

Figure 6. Solid-state MAS NMR for ^{31}P in (A) uncalcined sample II-6 and (B) calcined at 750 °C. Peaks marked with an asterisk are spinning sidebands.

down field.[25] After heating at 500 °C, a temperature that is near the midpoint of the amine weight loss in the TGA curve, two ^{31}P resonance's are observed, one at −21.7 ppm and the other at −33.4 ppm. The former peak is similar to that of the phosphorus in α-ZrP[26] or in layered zirconium phosphate−phosphonate mixed derivatives.[27] The resonance at −33 ppm is thought to result from the cross-linking reaction and represents phosphorus linked through oxygen to silicon. These results are similar to those reported by Li et al.,[9] who also demonstrated from IR data that all the organic groups were volatilized out at 450 °C. The final weight loss results from condensation of 0.25 mol of water of the layer hydroxyl groups and 0.92 mol of water from the silicate hydroxyl groups and amounts to 1.94%. The total weight loss is thus 31.38% compared to an observed value of 33.26%.

The surface area of sample II-6, as determined from BET N_2 adsorption−desorption isotherm was 232 m^2/g with 70% (deBoer *t*-plot method) of the surface area arising from micropores. The isotherm is shown in Figure 7 and shows features of both a microporous and mesoporous solid with a large hysterisis indicative of slitlike pores. The volume was found to be 0.261 cm^3/g for all pores and 0.081 cm^3/g for the pores with diameter less than 20 Å. For this sample the isotherm did not close. Redetermination of the isotherm at longer equilibration times failed to correct this situation and may suggest some chemisorption.[28] This point will be investigated further.

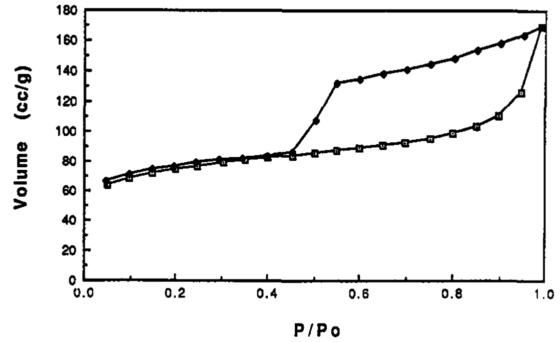

Figure 7. Adsorption−desorption isotherm of silica-pillared α-ZrP, sample II-6.

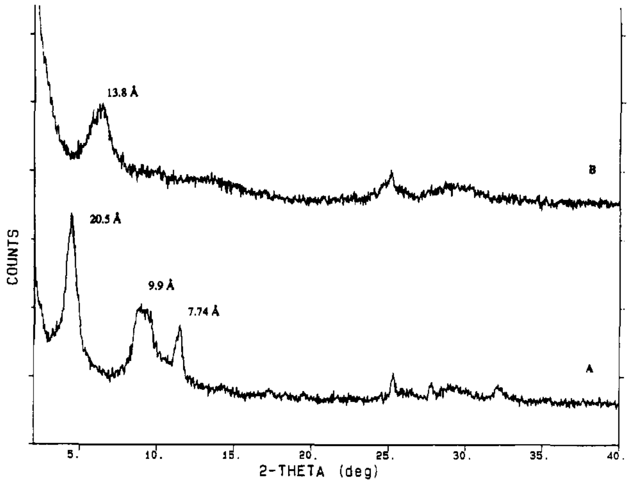

Figure 8. XRD powder patterns of (A) the titanate/AMPS intercalate and (B) the silica pillared titanate after calcination at 340 °C.

Pillaring of the Layered Tetratitanate. The layered titanates in general tend to be difficult to pillar directly thus making a preswelling step necessary. Intercalated propylamine tetratitanate was found to form a colloidal suspension in water while the larger alkylamines did not produce this phenomenon. Therefore, a suspension of the colloidal tetratitanate was treated with AMPS to yield a product with the X-ray pattern shown in Figure 8A. The peak at 20.5 Å indicates uptake of the AMPS by the titanate. The second broad reflection centered at 9.9 Å in the XRD pattern is thought to be a combination peak due to the (002) plane of the intercalate and the (001) plane of the protonated tetratitanate. The peaks at ~10 and 7.74 Å, present in the X-ray pattern of the propylamine intercalate, supports this conclusion. However, since the 001 reflection for the propylamine phase, at 16.4 Å, is not present in the X-ray pattern, which indicates the absence of this phase, the remaining non 00*l* reflections must arise from the titanate layers themselves. Calcination of the sample at 340 °C for 24 h yielded the pattern shown in Figure 8B. The reflection at 13.8 Å undoubtedly represents the (001) plane of the silica pillared titanate. A small reflection at 3.53 Å is attributable to the presence of some residual anatase from the original synthesis of $K_2Ti_4O_9$. Interestingly, the

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Table 3. Elemental Analyses of the Tetratitanate/AMPS Intercalate

titanate sample	% Ti	% Si	% C	% H	% N	Si:Ti
II-32	45.4	3.27	5.06	2.04	1.87	1:8.14

reflections at 9.9 and 7.74 Å are no longer present which would be expected if the peaks were due to the proton form of the tetratitanate. $H_2Ti_4O_9$ would form an amorphous or fairly noncrystalline form of $BTiO_2$ at this temperature.

The gallery height of the pillared tetratitanate is estimated by subtracting the layer thickness from the 13.9-Å interlayer distance. To obtain the layer thickness the ionic diameter of K^+ ion (2.66 Å) was subtracted from the interlayer distance for $K_2Ti_4O_9$ (8.70 Å) which gives a layer thickness of 6.04 Å. Thus the gallery height is 7.86 Å on the assumption that the structure and β angle of the pillared phase are not too different from that of the original tetratitanate. This height is in accord with the size of the $[Si_8O_{12}]^{8+}$ cube.

Elemental analysis of the pillared but uncalcined tetratitanate is given in Table 3. On the basis of these reuslts and a TGA weight loss of 15.84%, the following formula was arrived at: $H_2Ti_4O_9[NH_2(CH_2)_3Si(OH)_3]_{0.5}[CH_3CH_2CH_2NH_2]_{0.075}\cdot 0.4H_2O$. Calculated values for this formula are: 45.85% Ti, 3.36% Si, 4.95% C, 1.93% N, and 2.06% H, weight loss 16.31%. The surface area of sample II-32 was found to be 42.1 m^2/g by the BET N_2 adsorption–desorption method. Although this value is much larger than that of the original tetratitanate crystals, the isotherm was representative of a nonporous material.

Discussion

It is necessary to place the results of this study in the context of earlier work on this subject. Three pillared α-zirconium phosphate samples were prepared. The first one described was obtained by direct interaction of AMPS with α-ZrP under refluxing conditions to obtain a product with 20.1 Å (sample I-5) and a Si:Zr ratio of 2. On calcination, the interlayer distance was reduced to 11.5 Å. This product is comparable to those prepared by Li et al.[9] and Roziere et al.[11] In the former study the aminosilane and α-ZrP were refluxed together for 72 h, but only 0.94 mol of silane were intercalated. The interlayer spacing of the intercalated solid was 22.07 Å. This low uptake of amino silane may have resulted from the presence of considerable excess phosphoric acid in their α-ZrP. On heating to 600 °C the *d* spacing was reduced to 13.18 Å. Although no surface area was given, porosity was demonstrated by hexane uptake.

Roziere and co-workers[11] carried out the intercalation reaction at room temperature and achieved a maximum loading of 1.58 Si per Zr, about 50% more than reported by Li et al. Interestingly the interlayer separations obtained (17.69 and 18.31 Å) were smaller than that of the more lightly intercalated product (22.07 Å) of Li. According to Roziere this layer separation is in accord with the intercalation of a cubic octamer which is 11.2 Å long. Since the thickness of an α-ZrP layer is 6.6 Å, their observed increase in layer spacing matches well the sum of layer + intercalated species distance. The surface area of one face of the cube with propylamine sidearms was estimated to be 125 Å^{2,11} and on thermal removal would bond to four P–OH groups (24 Å^2 each) or 96 Å^2. Thus, they rationalize a situation in which a maximum of 0.768 cubes/8 phosphate groups represents the maximum uptake (0.79 Si/P observed) of AMPS.

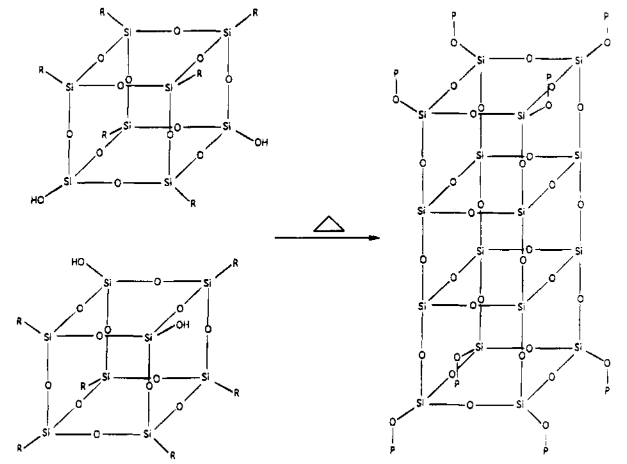

Figure 9. Schematic representation of a double layer of partially hydrolyzed silicon octamer.

Thermal removal of the organic groups should leave behind $[Si_8O_{12}]$ units of cubic structure linked through P–O–Si groups to the layers. Such cubes would consist of Si–O–Si linkages on all 12 edges of length equal to two Si–O bonds plus two Si–O–P linkages to the layers.

Assuming a bond distance of 1.67 Å for each tetrahedral Si–O bond would make a cube length 3.34 Å. However, if we take the middle oxygen layer (Figure 9) as the widest point we would add ~2 oxygen radii ($r_{O^{2-}}$ = 1.36 Å) to the cube length of 3.34 or 6.06 Å. In α-ZrP the phosphate groups are arranged approximately at the corners of parallelograms 5.3 Å apart.[18] Each Si_8O_{12} cube would be bonded to four phosphates on the top layer and four on the bottom layer. Thus the silicate cubes would have to occupy every other parallelogram with approximately 3.5 Å between the cubic pillars. However, since only 79% occupancy was attained, this distance would be increased by an angstrom on average. Apparently such spaces are still too small for N_2 to penetrate so that this product was found to be nonporous.

Our porous high surface area pillared zirconium phosphate (sample II-6) had a silicon–phosphorus ratio of 2.06. This value far exceeds the limiting value proposed by Roziere et al. of 0.768. However, the limit was arrived at by assuming that all of the silicon was present as the octamer $[NH_2(CH_2)_3SiO_{1.5}]_8$. Our intercalated phase had an interlayer spacing of 29.6 Å which indicates that a more highly polymerized species exists between the layers. We assume at this point that this species is a double layer of the cubic octamer in which one-quarter of the propylamine groups have been replaced by hydroxyls as pictured in Figure 9. The reaction for this hydrolysis step is represented as

$$NH_2(CH_2)_2CH_2{-}Si(OH)_3 + H_2O \rightarrow NH_2(CH_2)_2CH_3 + Si(OH)_4$$

The enthalpy for the above reaction can be approximated by using the C–H bond dissociation for propane

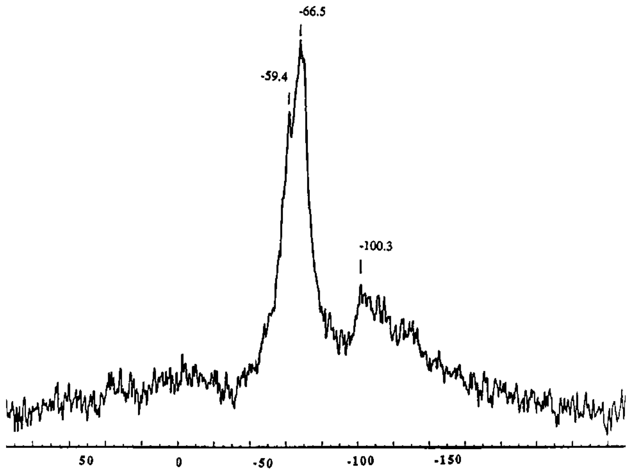

Figure 10. Solid-state MAS NMR for ^{29}Si in AMPS intercalated into α-ZrP (sample II-6) before calcination.

(98 kcal/mol),[29] the H−OH bond dissociation for water (119 kcal/mol),[30] the C−Si bond dissociation (75 kcal/mol),[31] and a conservative value of 101 kcal/mol for the bond dissociation of Si−O.[32] By using the appropriate signs for bond formation, an estimated enthalpy for the reaction is −5 kcal/mol which suggest that the hydrolysis reaction is feasible. The entropy would appear to be positive by inspection and thus the probability of the proposed hydrolysis reaction is aided by the reaction temperaure used in the synthesis of the pillared material. The propylamine generated by the reaction is now available for intercalation into the α-MP layers. Subtracting the α-ZrP layer thickness, 6.6 Å from 29.6 Å leaves 23 Å as the long dimension of the double cube stack. This is just twice the 11.2-Å size of a single octamer. On heating to expel the organic portion a triple layered polymer, as pictured in Figure 9 would form. This structure would have a length of 6 Si−O bonds (1.67 Å each) plus two oxide ion radii of 1.36 Å each or 12.74 Å. Adding the layer thickness to this yields a total interlayer separation of 19.34 Å compared to an observed value of 21.5 Å. According to this scheme twice as much silicon per phosphorus atom can be intercalated as predicted for a single stack of octamers. However, even in this highly polymerized state 0.225 mol of such pillars is required to account for the composition of the intercalated phase. This value is larger than the 0.198 mol in Roziere's preparation and therefore should also be nonporous. The only way out of this dilemma is to assume there are less pillars by bringing together more silicon atoms. For example, for pentagonal-shaped pillars 20 Si would be present requiring 0.185 mol of pillars and for hexagonal shaped ones (24 Si) 0.154 mol would be required.

Evidence that not every silicon atom is attached to a propylamine group prior to calcination is available from NMR spectra. Figure 10 is the MAS NMR spectrum of sample II-6 before calcination. There are two prominent resonances, one at −66.5 ppm and the other at −59.4 ppm. These resonance's have been assigned to Q^2 and Q^3, respectively by Li et al.,[9] which represents Si with two and three Si near neighbors, respectively. We assign the larger peak at −66.5 ppm to Q^3 silicon also, but attached to the amine whereas the smaller peak may indicate those silicons which have lost the amine. However, there is at least one more peak at −100.3 ppm and perhaps a second one in the vicinity of 112 ppm. These same resonance's appear in the spectrum of the sample calcined at 450 °C.[9] Thus, they indicate the formation of a silica like structure even before calcination and with hydroxyl groups attached as shown by cross-polarization ^{1}H−^{29}Si enhancement of the peak by Li et al.[9] Thus, our conclusion is that a well developed cluster of 22−24 silicon atoms forms during the refluxing stage. These clusters, having amino groups on the top and bottom face, bring the colloidally dispersed layers together in such a way that a two phase solid forms. This phenomenon is a common occurrence with α-ZrP.[22−24] For example, when Na^+ is exchanged for the α-ZrP protons, the first stage of exchange takes place by conversion of the protonated phase $Zr(HPO_4)_2{\cdot}H_2O$ to the half-exchanged phase, $Zr(NaPO_4)(HPO_4){\cdot}5H_2O$.[33] Both solid phases are present until the conversion is complete. If, at an intermediate stage of exchange, the solid is recovered and heated to 250 °C new phases form.[22] At 10% of exchange a single pure phase of composition $ZrNa_{0.2}H_{1.8}(PO_4)_2$ was formed and at a Na^+ content of 40% of the total exchange capacity the phase formed was $ZrNa_{0.8}H_{1.2}(PO_4)_2$. There was no trace of either the original α-ZrP or the half-exchanged phase. A similar result was obtained on partial intercalation of amines, where on heating the two phase system of α-ZrP and amine intercalate formed a single amine containing phase.[23,24] Diffusion of ions or intercalate molecules occurs from the outside inward so that a single crystal may contain one species along the outer periphery and a second one in the central portion of the crystal.[34] In the case of amine intercalation reactions equilibrium may be reached slowly. Therefore if the solid phosphate host is recovered before equilibrium is reached, two phases may be obtained. On heating, the amine then distributes itself uniformly within the solid. In the present study we believe such a two-phase system was obtained with AMPS and propylamine present in the same crystal, but on heating, the propylamine is volatilized out and the aminosilicate cluster distributes itself relatively uniformly throughout the solid.

Titration of a calcined sample similar to II-6 yielded an exchanged capacity of 0.58 mequiv of Na^+/g. This translates to 0.282 mol of HPO_4 on the assumption that on heating II-6 to 500 °C the formula is $Zr(OH)_{0.5}(HPO_4)_{1.75}(Si_8O_{16})_{0.451}$ (FW = 485.4). The remaining 1.498 monohydrogen phosphate groups are presumably tied up in bonding to the silicate pillars or are otherwised blocked by them from exchanging. This value is in keeping with the relative peak areas in Figure 6. We make the assumption that each pillar interacts with eight phosphate groups, or 0.187 mol of pillars. Then it would be required that slightly in excess of 19 silicon atoms are present in each pillar rather than 16 as pictured in Figure 9. The area occupied by the free HPO_4 groups, counting those displaced by hydroxyl

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groups is (on HPO_4^- occupies 24 Å^2 of surface[18])

$$\frac{0.531 \text{ mol} \times 24 \text{ Å}^2 \times 6.025 \times 10^{23}}{10^{20} \text{ Å}^2/\text{m}^2 \times 485.4 \text{ g/mol}} = 158 \text{ m}^2/\text{g}$$

This value is less than the observed value of 232 m^2/g and leaves 74 m^2/g for the surface on the pillars. This value is about half what is calculated on the assumption that the pillars have the shape shown in Figure 9.

When the refluxing procedure was attempted with colloidally dispersed α-SnP, extensive hydrolysis occurred. This result stands in contrast to the results obtained by Roziere et al.[11] They were able to intercalate a double stacked octasilicate polymer to achieve an interlayer spacing of 26.9 Å by allowing the reaction to occur over a 5-day period at room temperature. On calcination this spacing was reduced to 17.95 Å. These spacings are very close to those obtained in this study for both α-ZrP and α-SnP and indicates that the large silica cluster can form in solution at room or reflux temperatures. In this case the product was microporous whereas our silica pillared α-SnP was disordered and mesoporous.

Conclusions

This work has shown that it is possible to obtain pillared lamellar phosphates by the heat treatment of the corresponding AMPS intercalate. As would be expected, α-ZrP forms the best characterized pillared compound with α-SnP being somewhat susceptible to hydrolysis due to the basicity of aqueous solutions of AMPS and temperature at which the reactions are carried out. The pillared α-ZrP produced from the direct intercalation of AMPS appears to be similar to that described by Klinowski et al.[9] Predispersion of α-ZrP using *n*-propylamine led to an increase in the *d* spacing and the formation of a microporous pillared product. This was due to increased hydrolysis of the AMPS leading to the formation of larger polymeric species within the interlamellar region. This procedure was found to be unsuitable for α-TiP and α-SnP due to hydrolysis problems. It has not proved possible to successively pillar α-TiP in this study. Similar problems were previously encountered by Roziere et al.[11]

The method used for the tetratitanate showed results similar to direct intercalation of AMPS into α-ZrP. No substantial amount of hydrolysis or polymerization of the silane appears to have occurred in the interlamellar region thus a nonporous material was the result. Further studies are required in order to develop a better process for obtaining a microporous material. Additional studies are being conducted to investigate the nature of the intercalated polymer attained using the colloidal dispersion method and to understand the hydrolysis of AMPS in aqueous solutions.

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