Synthesis and Characterization of a Family of Amine-Intercatalated Lamellar Aluminophosphates from Alcoholic System

Qiuming Gao,[†] Jiesheng Chen,[†] Ruren Xu,*[,†] and Yong Yue[‡]

Key Laboratory of Inorganic Hydrothermal Synthesis, Department of Chemistry,
Jilin University, Changchun 130023, China, and Wuhan Institute of Physics,
Academia Sinica, Wuhan 430071, China

Received May 3, 1996. Revised Manuscript Received September 4, 1996[⊗]

A family of lamellar aluminophosphates designated APO-L*n* (L stands for lamellar and *n* = 6, 8, 10, 12, the number of carbon atoms for the occluded template molecules) was synthesized from a mixture of phosphoric acid, aluminum triisopropoxide, ethylene glycol and an unbranched primary alcohol in the presence of an amine as the structure-directing template. The compounds were characterized by X-ray powder diffraction, scanning electron microscopy, MAS NMR spectroscopy, differential thermal, and thermogravimetric analyses. The inorganic layers of APO-L*n* are composed of PO_4, AlO_4, and AlO_6 structural units, and the ratio of the octahedral Al to the tetrahedral Al in the as-synthesized compounds is about 1:1. APO-L*n* exhibit a distinct weight loss when treated at elevated temperatures, and upon dehydration they adsorb a considerable amount of water. Dehydration−rehydration for APO-L*n* materials is reversible with the dehydrated samples containing almost only tetrahedrally coordinated aluminum.

Introduction

Considerable efforts have been devoted to metal phosphates and phosphonates with low dimensionalities (1-D chain and 2-D lamellar structures) as they are potentially applicable in the areas of catalysis, ion exchange, molecular recognition, optics, and electronics.[1−4] A number of lamellar metal phosphates and phosphonates have been discovered,[5−13] and those falling into the category of mesophases have an interlamellar distance of 20−100 Å. Molecule-intercalated inorganic phosphates and metal−phosphonate multilayer films are typical lamellar mesophases; the former possess inorganic layers with organic molecules intercalated between adjacent layers, whereas in the latter the organic groups are chemically bonded to the phosphorus atoms. Organic groups can also be bonded to the O atoms of the phosphate anions which construct the inorganic layers with metal cations. Whereas layered phosphates and phosphonates of divalent and tetravalent metals with a large interlamellar distance have been frequently encountered, lamellar mesophases of trivalent-metal phosphates or phosphonates are rare. The interlamellar distance of most of the layered aluminophosphates and gallophosphates reported previously[10−15] is less than 15 Å, and although their structures and compositions can be varied to a great extent, few of the lamellar aluminophosphates and gallophosphates exhibit significant water adsorption capacities since the layers either are hydrophobic or lack void spaces to accommodate guest molecules. Very recently, Ozin and co-workers[16] described the synthesis of a mesolamellar aluminophosphate denoted MLA from an alcoholic system using tetraethylene glycol as the solvent. This MLA lamellar material has a *d* spacing of 29.42 Å with an Al/P ratio of 1/2. In this paper, we describe the synthesis and characterization of a family of new lamellar aluminophosphate mesophases (APO-L*n*) with an Al/P ratio of 2/1, i.e., the inorganic layer for the materials is a basic aluminophosphate. APO-L*n* contain a considerable amount of water in their as-synthesized forms, and upon dehydration at 100 °C under vacuum they exhibit water adsorption capacities. The water adsorption isotherms are linear within a wide range of experimental relative vapor pressure values.

[†] Jilin University.

[‡] Academia Sinica.

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1996.

(1) Kanazawa, T. *Inorganic Phosphate Materials*; Tokyo, 1989.

(2) Jones, R. H.; Thomas, J. M.; Xu, R.; Huo, Q.; Xu, Y.; Cheetham, A. K.; Bieber, D. *J. Chem. Soc., Chem. Commun.* **1990**, 1170.

(3) Cao, G.; Hong, H.; Mallouk, T. E. *Acc. Chem. Res.* **1992**, *25*, 420.

(4) Ozin, G. A. *Adv. Mater.* **1992**, *4*, 612.

(5) Clearfield A. *Chem. Rew.* **1988**, *88*, 125.

(6) Chen, J.; Natarajan, S.; Wright, P. A.; Jones, R. H.; Thomas, J. M.; Catlow, C. R. A. *J. Solid State Chem.* **1993**, *103*, 519.

(7) Cao, G.; Lynch, V. M.; Yacullo, L. N. *Chem. Mater.* **1993**, *5*, 1000.

(8) Khan, M. I.; Lee, Y. S.; O·connor, C. J.; Haushalter, R. C.; Zubieta, J. *J. Am. Chem. Soc.* **1994**, *116*, 4525.

(9) Huo, Q.; Margolese, D. I.; Ciesla, U.; Demuth, D. G.; Feng, P.; Gier, T. E.; Sieger, P.; Firouzi, A.; Chmelka, B. F.; Schuth, F.; Stucky, G. D. *Chem. Mater.* **1994**, *6*, 1176.

(10) Jones, R. H.; Thomas J. M.; Xu, R.; Huo, Q.; Cheetham, A. K.; Powell, A. V. *J. Chem. Soc., Chem. Commun.* **1991**, 1266.

(11) Chippindale, A. M.; Powell, A. V.; Bull, L. M.; Jones, R. H.; Cheetham, A. K.; Thomas, J. M.; Xu, R. *J. Solid State Chem.* **1992**, *96*, 199.

(12) Thomas, J. M.; Jones, R. H.; Xu, R.; Chen, J.; Chippindale, A. M.; Natarajan, S.; Cheetham, A. K. *J. Chem. Soc., Chem. Commun.* **1992**, 929.

(13) Chippindale, A. M.; Natarajan, S.; Thomas, J. M.; Jones, R. H. *J. Solid State Chem.* **1994**, *111*, 18.

(14) Riou, D.; Loiseau, T.; Ferey, G. *J. Solid State Chem.* **1993**, *102*, 4.

(15) Jones, R. H.; Thomas, J. M.; Huo, Q.; Xu, R.; Hursthouse, M. B.; Chen, J. *J. Chem. Soc., Chem. Commun.* **1991**, 1520.

(16) Oliver, S.; Kuperman, A.; Coombs, N.; Lough, A.; Ozin, G. A. *Nature* **1995**, *378*, 47.

S0897-4756(96)00261-X CCC: $14.00

Table 1. Element and Molecule Contents in Weight Percentage for APO-L*n*[a]

sample	C	N	H	Al	P	amine	H_2O	empirical formula
APO-L6	21.46	4.32	6.07	16.02	9.20	29.1	23.2	$2Al_2O_3\cdot P_2O_5\cdot 2.03C_6H_{15}N\cdot 7.07H_2O$
APO-L8	22.66	3.30	6.22	16.91	9.71	30.0	15.6	$2Al_2O_3\cdot P_2O_5\cdot 1.54C_8H_{19}N\cdot 5.51H_2O$
APO-L10	24.00	2.80	6.51	16.14	9.26	31.1	17.0	$2Al_2O_3\cdot P_2O_5\cdot 1.34C_{10}H_{23}N\cdot 5.01H_2O$
APO-L12	28.24	2.75	5.30	15.82	9.08	36.1	13.6	$2Al_2O_3\cdot P_2O_5\cdot 1.32C_{12}H_{27}N\cdot 5.03H_2O$

[a] The C, H, N contents were obtained from elemental analysis; the Al and P contents from chemical analysis whereas those for amines and water molecules from TGA results.

Experimental Section

APO-L*n* were synthesized from a predominantly nonaqueous system in which the mixture of ethylene glycol (EG) and an unbranched primary alcohol (n-$C_mH_{2m+1}OH$, $m = 4, 5, 6, 7, 8$) was used as the medium and an unbranched primary amine (n-$C_nH_{2n+1}NH_2$, $n = 6, 8, 10, 12$) as the template. Typically, aluminum triisopropoxide ((i-PrO)$_3$Al), phosphoric acid (85% H_3PO_4), and the amine were successively added into the solution of an unbranched primary alcohol and ethylene glycol. After stirring for a few hours, a gel with an empirical molar composition of (i-PrO)$_3$Al:1.8H_3PO_4:3.4n-$C_nH_{2n+1}NH_2$:3.4n-$C_mH_{2m+1}OH$:13.8EG:1.7H_2O was formed. The gel was sealed in a Teflon-lined stainless autoclave and heated under autogenous pressure at 180 °C for 8 days. The crystalline product was filtered, washed with water, and dried at ambient temperature.

Elemental analysis was performed on a Perkin-Elmer 240C element analyzer. X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/MAX III A diffractometer with Ni-filtered Cu Kα radiation ($\lambda = 1.5418$ Å). The scanning electron micrographs (SEM) were taken on a Hitachi X-650 electron microscope. Infrared (IR) spectra were obtained on a Nicolet 5DX FTIR spectrometer using KBr pellets. A Perkin-Elmer DTA 1700 differential thermal analyzer was used to conduct the differential thermal analysis (DTA), and a Perkin-Elmer TGA 7 thermogravimetric analyzer for the thermogravimetric analysis (TGA) in N_2 atmosphere. The temperature increasing rate was 20 °C min^{-1}, and the flow rate of N_2 was 50 cm^3 min^{-1}. The adsorption measurements were performed on a Cahn 2000 vacuum electrobalance system. Prior to each measurement, the sample was dehydrated at 100 °C and 10^{-3} Torr.

^{27}Al, ^{13}C, and ^{31}P magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded on a Bruker MSL-400 spectrometer with a magnetic field strength of 9.4 T. The spinning rates were 10, 5, and 6 kHz, respectively. For ^{27}Al spectra, single-pulse excitation technique was applied and the spectra were obtained at 104.3 MHz. Other parameters were pulse width, 0.5 μs; recycle delay, 10 s; number of transients, 1000. Al(NO$_3$)$_3$ aqueous solution was used as external reference. For ^{13}C and ^{31}P spectra, the cross-polarization technique was applied and the contact time was 5.0 ms with scan number 1000 and recycle delay 14 s. The chemical shifts were relative to $SiMe_4$ and H_3PO_4 (85 wt %), respectively.

Results and Discussion

Formation of APO-L*n*. The use of a mixed solvent is very important for the synthesis of APO-L*n*. If ethylene glycol and unbranched primary alcohols are used independently as the solvent, APO-L*n* is not obtainable. On the other hand, it seems that the polarity of the cosolvent (unbranched primary alcohols) also plays an important role for the formation of APO-L*n* as suggested by the fact that the compounds form readily in the presence of both ethylene glycol and a larger unbranched primary alcohol such as *n*-butanol, *n*-pentanol, *n*-hexanol, *n*-heptanol, or *n*-octanol as the medium, whereas only an amorphous phase exists in the product when a shorter unbranched primary alcohol (methanol, ethanol, or *n*-propanol) is used with ethylene glycol.

The preferable source of phosphorus is orthophosphoric acid which has a good solubility in alcoholic solvents. In an alcoholic medium, an ester of phosphoric acid does not react with aluminum triisopropoxide and inorganic phosphates are difficult to dissolve, and as a result, they are not suitable phosphorus sources. The most reactive source of aluminum is aluminum triisopropoxide, and the 2-propanol evolved from it does not affect the nature of the alcoholic medium. Pseudoboehmite, an excellent aluminum source for preparation of microporous aluminophosphates in aqueous media, and other inorganic aluminum sources, such as aluminum sulfate and sodium aluminate has a very small solubility in the alcohol systems.

Crystallization temperature is also an important factor for the synthesis of APO-L*n*. A temperature of 200 °C or above results in a large amount of $AlPO_4$–tridymite in the product without appearance of APO-L*n*, whereas when the temperature is below 160 °C, only amorphous material exists in the product.

Composition of APO-L*n*. The results of chemical, element and thermogravimetric analyses for as-synthesized APO-L*n* samples are listed in Table 1, together with the empirical formulas calculated on the basis of these analysis results. It is interesting that the Al:P ratio for APO-L*n* is 2:1, in contrast with the previously reported aluminophosphates synthesized from an alcoholic system which invariably have an Al:P ratio greater than 1. Aluminophosphates with Al:P ratio greater than unity fall into the basic category and are represented by a series of minerals.[17] It is also worthwhile to note that the content of the amine molecule intercalated in APO-L*n* decreases with its chain length. However, the amine/P molar ratios for APO-L10 and for APO-L12 are almost the same, implying that with a longer alkyl chain, the effect of chain length on the intercalation amount is less distinct.

Structure of APO-L*n*. The X-ray powder diffraction pattern (Figure 1) of each APO-L*n* shows only three peaks. The absence of reflection peaks at higher angles is a typical feature for inorganic–organic composite mesophases which lack long-range order within the inorganic structure regions. As for the lamellar silicate mesophase,[9,18,19] the three peaks for APO-L*n* are attributable to the (001), (002), and (003) reflections of the lamellar structures. The materials synthesized using *n*-hexylamine, *n*-octylamine, *n*-decylamine, and *n*-dodecylamine, respectively, as the template have different *d* spacings (22.50, 26.53, 30.68, and 34.70 Å),

---

(17) Kniep, R. *Angew. Chem., Int Ed. Engl.* **1986**, *25*, 525.

(18) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(19) Huo, Q.; Margolese D. J.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schuth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317.

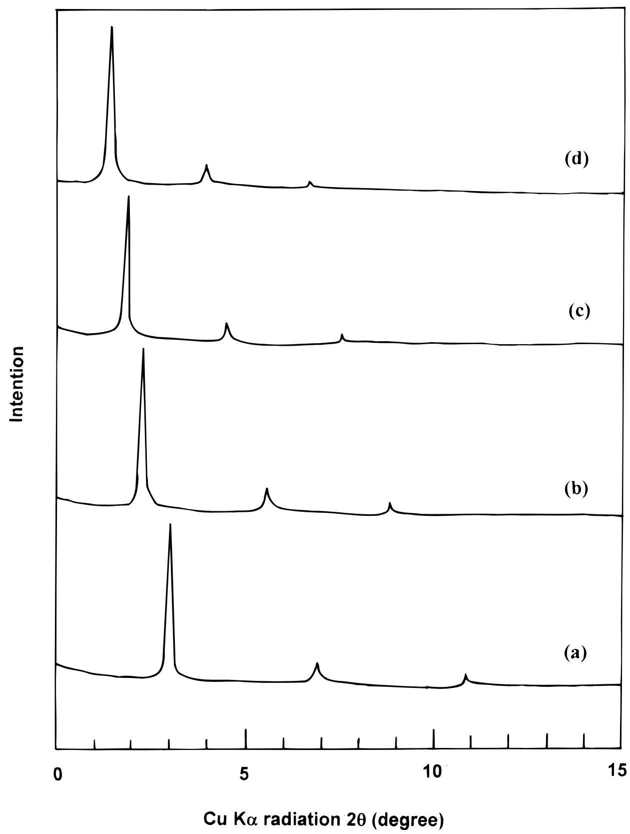

Figure 1. X-ray powder diffraction patterns for (a) APO-L6, (b) APO-L8, (c) APO-L10, and (d) APO-L12.

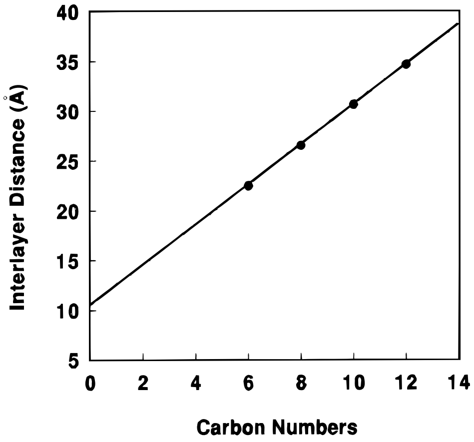

Figure 2. Plot of interlayer distance versus number of carbon atoms in the *n*-alkyl chain for APO-L*n*.

characteristic of layered structures with variable interlamellar distances.

The infrared spectra for APO-L*n* appear very similar to one another, indicating that the materials possess similar structural features. It is reasonable to assume that the inorganic layers for different APO-L*n* samples are more or less the same—they all lack long-range order in their structure as described above.

The plot of interlayer *d* spacing for APO-L*n* versus the number of methylene groups in the *n*-alkylamine is linear (Figure 2) with a slope of 2.04 Å/CH_2. Since the distance between two adjacent carbon atoms can be expressed as 1.27 Å/CH_2[20] in an all-trans trans-extended

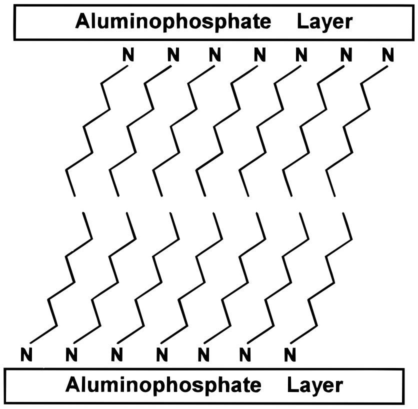

Figure 3. Schematic representation of the structure for APO-L6.

alkyl chain, the *n*-alkyl chains must be arranged as double layers in the interlamellar region, with a tilt angle[7,21] of $\sin^{-1}$ [2.04/(2 × 1.27)], i.e., 53.4° for APO-L*n*. The intercept of the line on the ordinate in Figure 2, which is about 10.3 Å, represents the thickness of the inorganic layer for APO-L*n*. This value is similar to that for the wall thickness of the mesoporous material MCM-41 and the layer thickness of the surfactant-containing lamellar silicates.[18,19] It must be emphasized that the interlamellar distances of APO-L*n* are shorter than that (ca. 40 Å) of the surfactant-containing lamellar silicate,[18,19] owing to the length of the unbranched fatty chain of the template in APO-L*n* being shorter than that of the surfactant in the lamellar silicate. On the other hand, the interlamellar distances of APO-L*n* are close to that for the MLA material[16] but considerably greater than those (ca. 15 Å) of the lamellar aluminophosphates[10−14] reported earlier, where the templates used are amines with short chains. Figure 3 is a schematic representation of the structure of APO-L6 in which the double layers of the hexylamine molecules are sandwiched by the aluminophosphate layers. The other three APO-L*n* presumably adopt a similar structure model with their organic double layers consisting of octylamine, decylamine, and dodecylamine molecules, respectively.

The scanning electron micrographs (Figure 4) show that APO-L*n* crystals appear as thin plates with diameters of 10−20 μm, characteristic of layered materials. The shape of the plates is irregular, different from that of the structure-known lamellar aluminophosphates which normally exhibit well-defined three-dimensional morphologies.

In the ^{31}P MAS NMR spectrum of the reaction gel for APO-L6 (Figure 5), only one peak at −8.2 ppm is observed, suggesting the presence of phosphorus atoms in a reasonably uniform tetrahedral coordination environment.[22−24] The ^{31}P MAS NMR spectrum for the as-synthesized APO-L6 sample also exhibits one peak, but the maximum of the peak shifts slightly to −7.8 ppm. The difference between the spectrum of the gel and that for the as-synthesized APO-L6 indicates that

---

[20] Kitaigorodskii, A. I. *Molecular Crystals and Molecules*; Academic Press: New York, 1973; p 48.

[21] Cao, G.; Mallouk, T. E. *Inorg. Chem.* **1991**, *30*, 1434.

[22] Tapp, N. J.; Milestone, N. B.; Bibby, D. M. *Zeolites* **1988**, *8*, 183.

[23] Nakashiro, K.; Ono, Y.; Nakata, S.; Moyimura, Y. *Zeolites* **1993**, *13*, 561.

[24] Maistrian, L.; Gabelica, Z.; Derouane, E. G.; Vogt, E. T. C.; van Oene J. *Zeolites* **1991**, *11*, 583.

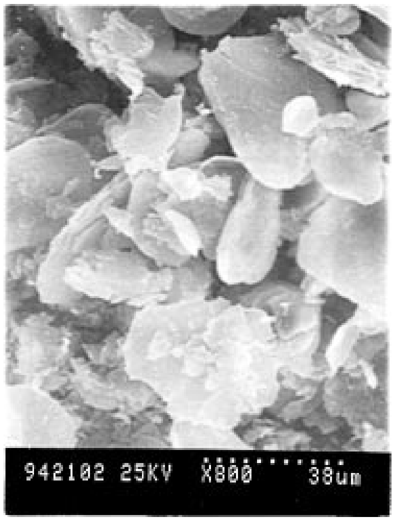

Figure 4. Scanning electron micrographs for APO-L6 crystals.

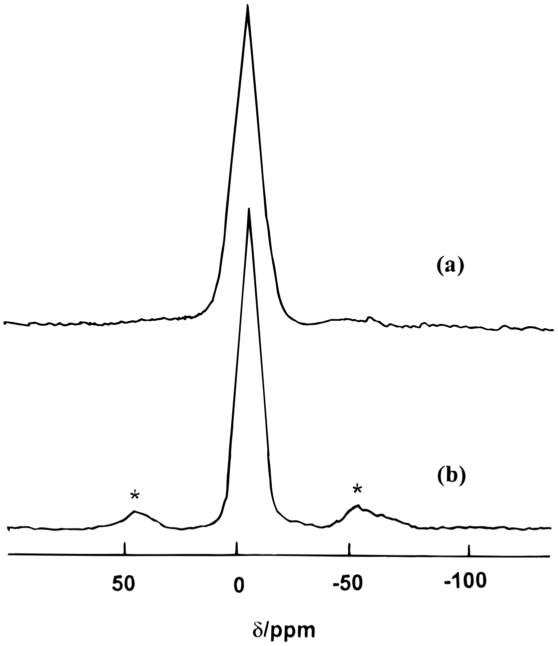

Figure 5. ^{31}P MAS NMR spectra of (a) the as-synthesized APO-L6 and (b) the reaction gel with sidebands marked by asterisks.

the local environment of the P atoms is changed, to a certain degree, when the gel is transformed to the lamellar material. The ^{27}Al MAS NMR spectrum of the reaction gel for APO-L6 (Figure 6) exhibits one signal at 4.3 ppm, characteristic of aluminum atoms in an octahedral coordination of O atoms.[24–26] On the other hand, the ^{27}Al MAS NMR spectrum of the as-synthesized APO-L6 sample shows a peak centered at 45.4 ppm, attributable to Al in a tetrahedral symmetry, and another one at −8.1 ppm assigned to Al in an octahedral symmetry. It is interesting to note that the areas of the two peaks are more or less equal, suggesting that the molar ratio of the octahedral Al to the tetrahedral Al is approximately 1:1. The ^{31}P and ^{27}Al spectra for the as-synthesized samples of APO-L8, APO-L10 and APO-L12 correspond very well with those for APO-L6, further revealing the similarity of the inorganic layer among the four samples.

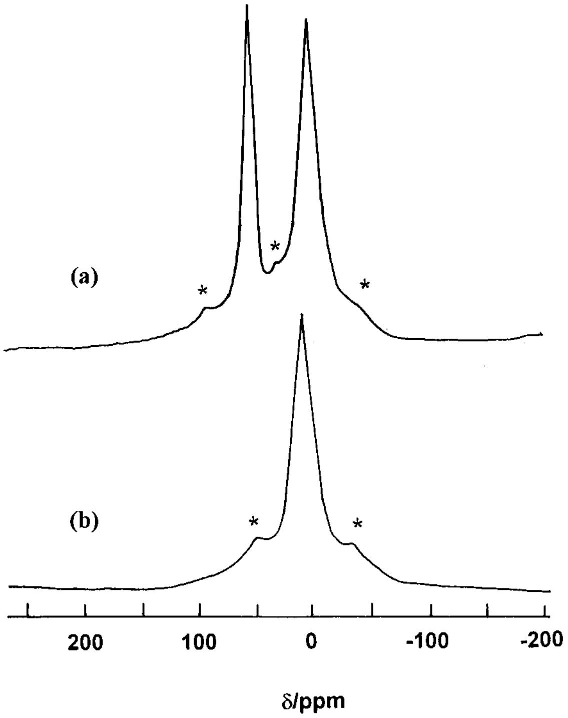

Figure 6. ^{27}Al MAS NMR spectra of (a) the as-synthesized APO-L6 and (b) the reaction gel with sidebands marked by asterisks.

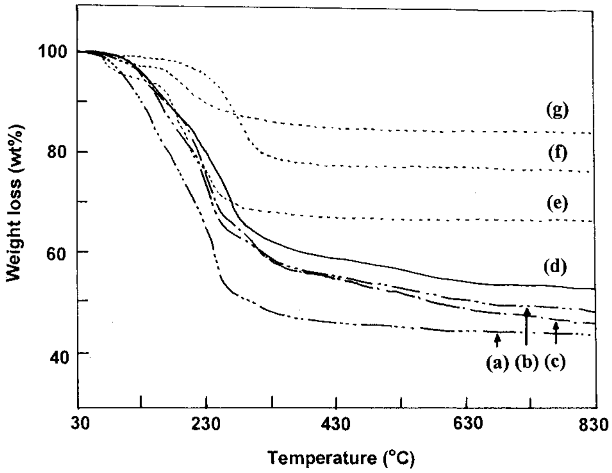

Figure 7. TGA curves for (a) APO-L6, (b) APO-L8, (c) APO-L10, (d) APO-L12, (e) JDF-20, (f) $AlPO_4$-17, and (g) $AlPO_4$-41.

APO-L*n* samples all exhibit a ^{13}C MAS NMR spectrum essentially identical with that for the corresponding free template molecule, that is, the unbranched primary amine used as the structure-directing agent. This is in agreement with the fact that the *n*-alkylamines remain intact after being intercalated between the inorganic layers.

Thermal Properties. Thermogravimetric analysis (Figure 7) shows that there are weight losses of 23.2, 15.6, 17.0, and 13.6 wt % from 100 to 180 °C and of 29.1, 30.0, 31.1, and 36.1 wt % from 180 to 430 °C for APO-L6, APO-L8, APO-L10, and APO-L12, respectively. The low-temperature weight losses are associated with the removal of water molecules and the high-temperature ones to the decomposition of the templates. Correspondingly, two endothermic peaks at 100−120 and

---

(25) Stein, A.; Wehrle, B; Jansen, M. *Zeolites* **1993**, *13*, 291.

(26) Davis, M. E.; Montes, C.; Hathaway, P. E.; Arhancet, J. P.; Hasha, D. L.; Garces J. *J. Am. Chem. Soc.* **1989**, *111*, 3919.

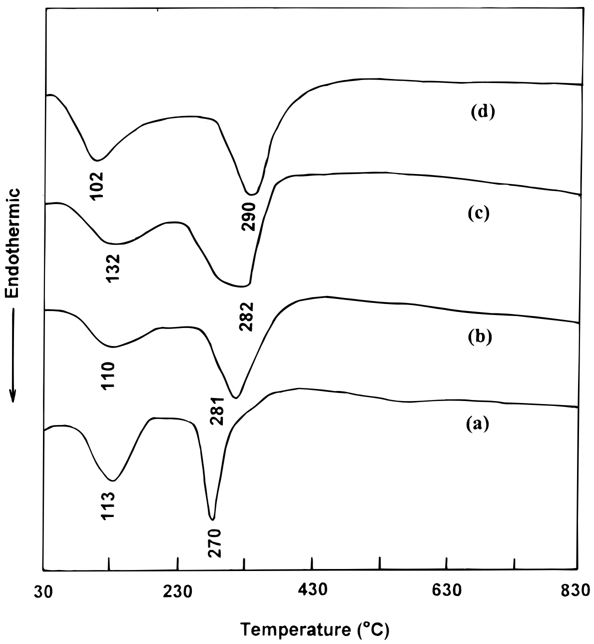

Figure 8. DTA curves for (a) APO-L6, (b) APO-L8, (c) APO-L10, and (d) APO-L12.

280–300 °C, respectively, are observed on the DTA curves for the four compounds (Figure 8). The temperature for the desorption of water is marginally higher than that of the boiling point of water, indicating that the interaction between the water molecules and the aluminophosphate layers is not very strong. The decomposition temperature of the templates is high enough for the material to stand the removal of the water without structure destruction. One sees that the template-decomposition temperatures are quite close for all the four APO-L*n*, suggesting that the interaction between the inorganic layer and the template has more or less the same strength from sample to sample. The total weight loss for all APO-L*n* is over 50%, greater than that (less than 40%) for the known lamellar aluminophosphates containing a template and for as-synthesized aluminophosphate molecular sieves, such as $AlPO_4$-41[27] with a one-dimensional medium-pore framework, $AlPO_4$-17[28] with a cage-containing framework and JDF-20,[29,30] an aluminophosphate possessing 20-membered ring channels.

On the basis of X-ray diffraction patterns, APO-L*n* are stable up to 250 °C, a temperature high enough for the water molecules to be desorbed from the layer structures as suggested by the DTA-TGA curves described above. The XRD patterns of the APO-L*n* samples treated at 250 °C are essentially the same as those of the corresponding as-synthesized materials, indicating that the water molecules adsorbed within the compounds have no observable effect on the interlayer distances of APO-L*n*. A treatment temperature above 300 °C leads to distinct decrease in crystallinity of APO-L*n* samples, and when heated at 350 °C, the materials become amorphous. Further increase of the treatment temperature results in a series of phase transitions. The products formed from APO-L*n* after thermal treatments at various temperatures are as follows: $AlPO_4$-tridymite mixed with amorphous material (350–400 °C); $AlPO_4$-tridymite and γ-alumina (450–850 °C); $AlPO_4$-tridymite, δ- and θ-aluminas (1000 °C); $AlPO_4$-tridymite, δ-, θ-, and α-aluminas (1100 °C).

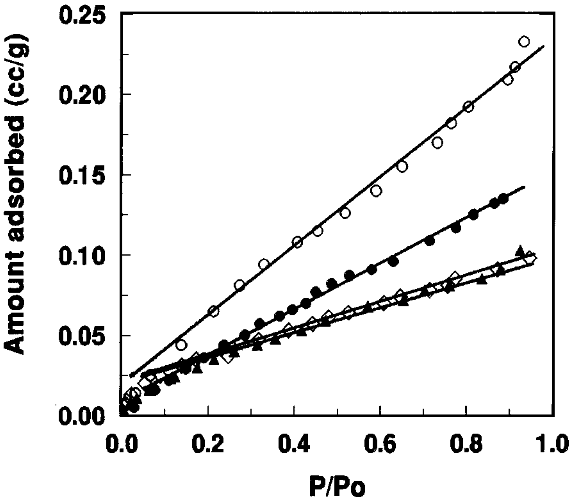

Figure 9. Water-adsorption isotherms at 293 K for (○) APO-L6, (△) APO-L8, (◇) APO-L10, and (●) APO-L12.

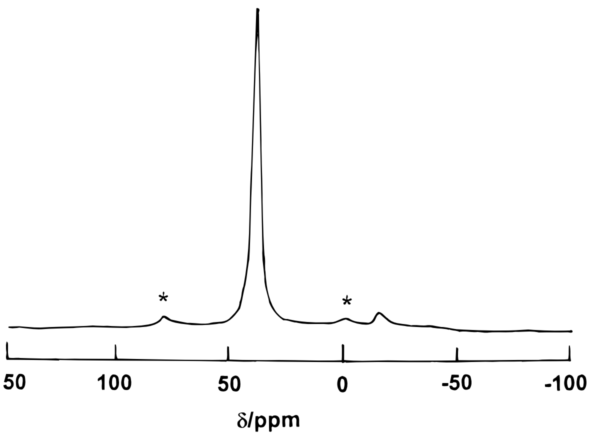

Figure 10. ^{27}Al MAS NMR spectrum of APO-L6 after dehydration at 100 °C and 10^{-3} Torr for 2 h.

Isothermal Water Adsorption and Nature of Adsorbed Water. The water-adsorption isotherms at 293 K for dehydrated APO-L*n* are shown in Figure 9. It can be seen that the isotherms each appear more or less as a straight line within a wide range of the experimental relative pressure values. The amount of adsorbed water is nearly the same as that of the desorbed water, indicating that the dehydration–rehydration for APO-L*n* materials is reversible. The water-adsorption behavior for APO-L*n* is rather similar to the Langmuir type with a relatively low adsorption pressure.

The ^{27}Al MAS NMR spectrum (Figure 10) of the APO-L6 sample dehydrated at 373 K and 10^{-3} Torr shows a strong signal at 38.9 ppm and a very weak one at −15.0 ppm. The former is attributable to tetrahedral Al, whereas the latter to octahedral Al. This implies that almost all the Al atoms in dehydrated APO-L6 are in a tetrahedral symmetry. Obviously, the six-coordinated Al atoms in the as-synthesized APO-L6 are converted

---

(27) Gao, Q.; Chen, J.; Li, S.; Xu, R. *Microporous Mater.* **1996**, *7*, 219.

(28) Gao, Q.; Li, S.; Xu, R. *J. Chem. Soc., Chem. Commun.* **1994**, 1465.

(29) Huo, Q.; Xu, R.; Li, S.; Ma, Z.; Thomas, J. M.; Jones, R. H.; Chippindale, A. M. *J. Chem. Soc., Chem. Commun.* **1992**, 875.

(30) Jones, R. H.; Thomas, J. M.; Chen, J.; Xu, R.; Huo, Q.; Li, S.; Ma, Z.; Chippindale, A. M. *J. Solid State Chem.* **1993**, *102*, 204.

into four-coordinated ones after dehydration. No conversion of octahedral Al to tetrahedral Al without structural destruction, to our knowledge, has been observed for basic aluminophosphate (Al/P > 1) materials.[17] The presence of six-coordinated Al in the as-synthesized APO-L6 must be due to adsorbed water molecules as extra ligands coordinating to them. XRD patterns and ^{31}P MAS NMR spectra of the as-synthesized samples are basically the same as those with dehydration or rehydration showing that the dehydration−rehydration process does not affect the distances between the adjacent layers, P atoms' tetrahedral environments, and the environments of templates. In other words, the dehydration−rehydration process occurs on the voids among the adjacent inorganic layers and the organic templates and the coordinated places nearest to Al atoms, because the XRD has only three peaks related to the distances of the adjacent layers, whereas the environments of 2-dimensional layers are not affected; d_{001} and ^{31}P MAS NMR spectra are not changed in the above process.

The other three members of APO-L*n* behave similarly, in sharp contrast to the lack of coordinating water molecules in the previously reported layered aluminophosphates with smaller interlamellar distances.[10−14] On the other hand, the presence of six-coordinated Al atoms is very common[31−33] for hydrated−detemplated aluminophosphate molecular sieves, in which the adsorbed water can be reversibly desorbed by evacuation and/or thermal treatment.

Conclusions

By using a mixture of ethylene glycol and an unbranched primary alcohol as the solvent and an unbranched long-chain primary amine as the structure-directing template, a family of new lamellar aluminophosphates (designated APO-L*n*) with essentially identical inorganic layers but different intercalated amine molecules can be directly synthesized. The inorganic layers of the as-synthesized materials are composed of AlO_4, AlO_6, and PO_4 structural units with an Al:P ratio of 2:1, and the presence of the AlO_6 units is due to coordination of adsorbed water molecules to the Al atoms as extra ligands. The adsorbed water in the materials can be removed without structural destruction provided that the treatment temperature is below 250 °C. Removal of adsorbed water also results in conversion of the AlO_6 units to AlO_4 ones. The dehydrated ALPO-L*n* exhibit a considerable water adsorption capacity whereas the adsorption isotherms are linear within a wide range of experimental relative vapor pressure.

Acknowledgment. We are grateful to the National Natural Science Foundation of China and the Ph.D. Studentship Foundation of the State Education Commission of China for financial support.

CM9602611

---

(31) Martens, J. A.; Feijen, E.; Lievens, J. L.; Crobet, P. J.; Jacobs, P. A. *J. Phys. Chem.* **1991**, *95*, 10025.

(32) Fyfe, C. A.; Grondey, H.; Muller, K. T.; Wong-Moon, K. C.; Morkus, T. *J. Am. Chem. Soc.* **1992**, *114*, 5876.

(33) Wu, Y.; Lewis, D.; Frye, J. S.; Palmer, A.; Wind, R. A. *J. Magn. Reson.* **1992**, *100*, 425.