Lamellar Mesostructured Aluminophosphates: Intercalation of *n*-Alkylamines into Layered Aluminophosphate by Ultrasonic Method

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A family of lamellar mesostructured aluminophosphates, denoted Mu-4-L*n* (L stands for lamellar, $n =$ 4, 8, 12, 16, the number of carbon atoms for *n*-alkyl chain) has been prepared through intercalating *n*-alkylamines into the layered aluminophosphate $[(C_2H_5)_2NH_2]_4[Al_8P_{10}O_{40}H_2]\cdot[H_2O]_{2.5}$ (Mu-4) using an ultrasonic method. The intercalation compounds are characterized by XRD, IR, TG, NMR, as well as compositional analyses. The results show that the intact sheet structure of Mu-4 retains while the *n*-alkylamines are intercalated into the layers. A linear relationship is observed between the interlayer distance and the number of carbon atoms in *n*-alkyl chains. A possible arrangement of the *n*-alkylamines in the interlayer space has been proposed using computer simulations.

Introduction

Since the discovery of aluminophosphate molecular sieves $AlPO_4$-*n* (*n* denotes the structure type) by Union Carbide Corp. in 1982[1] great interest has been aroused to microporous aluminophosphates because of their potential applications in the areas of catalysis, adsorption, separation, and host−guest assembly chemistry.[2,3] The number of crystalline aluminophosphates has continuously increased over the past decades. A variety of aluminophosphates has been prepared with three-dimensional (3D) open-framework, 2D layer, and 1D chain structures.[4] The family of aluminophosphates exhibits rich structural chemistry, among which the members of 2D layered materials show diverse stoichiometries, sheet structures, and sheet stacking sequences. Typically, the 2D layered compounds consist of macroanionic sheets built up from alternation of Al-centered polyhedra (AlO_4, AlO_5, AlO_6) and P-centered $P(O_b)_n(O_t)_{4-n}$ tetrahedra (b, bridging; t, terminal; $n = 1-4$). The protonated organic amine molecules or complex cations, acting as the structure-directing agents, reside in the interlayer region. In contrast to $AlPO_4$-*n* with an Al/P ratio of unity, these anionic aluminophosphate sheets show various Al /P ratios of less than unity, such as 1/2, 2/3, 3/4, 4/5, and 13/18. The inorganic network is composed of porous sheets with 4.6-, 4.8-, 4.6.8-, and 4.6.12-nets (4, 6, 8, and 12 stand for *n*-membered rings). These inorganic sheets stack in various stacking sequences, such as AAAA, ABAB, ABCABC, ABCDABCD,[5] ABCDEFABCDEF, etc. It would be interesting to develop these 2D layered materials to the lamellar mesostructured materials with well-defined porous sheet structures and further to pillared microporous−mesoporous materials. Thus far, a number of lamellar mesostructured aluminophosphates have been prepared using supramolecular templates, such as neutral long-chain amine (primary and tertiary amine),[6−11]anionic surfactant with a phosphate headgroup,[12−14] and cationic ammonium surfactant.[15−21] However, these materials are typically noncrystalline, periodically ordered, but amorphous with respect to their short-range atomic structure. Within these materials templates form tilted organic bilayers between the inorganic layers. Crystalline lamellar mesostructured aluminophosphates can be prepared using long-chain alkylene diamine, which exhibit a three-dimensional periodicity on the atomic scale.[22−24] Different from the single-headgroup surfactants, the double-headgroup surfactants form monolayers rather than bilayers in the

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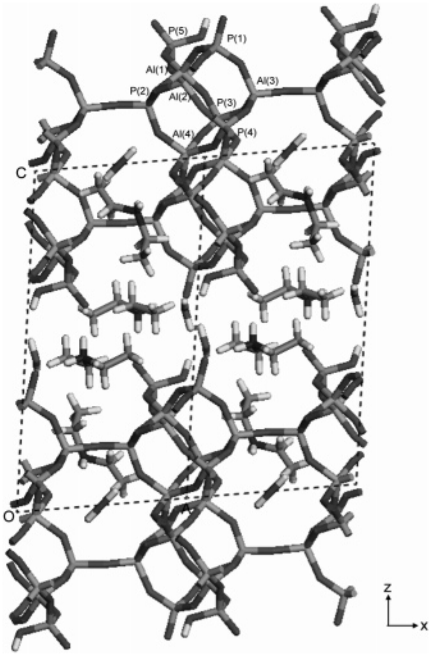

Figure 1. Structure of Mu-4 along [010] showing the inorganic layer and the location of the organic species (water molecules not shown).

interlayer space. It is stated that this kind of monolayer organic amine leads to better “structural communication” between two adjacent inorganic layers and thus to a higher degree of periodic order on the atomic scale.[25]

It is well known that various layered compounds have the capability to accommodate organic ions and molecules to form intercalation compounds.[26,27] Intercalation chemistry is a subject of considerable interest because of its applications in many fields such as heterogeneous catalysis, nonlinear optics, solid-state protonic conductors, and specific adsorbents. While much progress has been achieved in the intercalation chemistry of clays,[28] zirconium phosphates,[29] vanadium phosphates,[30] and transition metal oxides,[31] etc., reports on the intercalation of aluminophosphates are rare. Recently, Huang and co-workers reported the delamination and alkylamine intercalation of layered aluminophosphates; however, breaking of the Al−O−P bonds in the layers during the delaminating process resulted in degradation of the crystalline layers.[32,33]

Here we describe the first *n*-alkylamine-intercalated layered aluminophosphates with rigidity of the porous sheets. The host material is a double-layered aluminophosphate $[(C_2H_5)_2NH_2]_4[Al_8P_{10}O_{40}H_2]\cdot[H_2O]_{2.5}$ (Mu-4) reported by Vidal et al.[34] Mu-4 crystallizes in a triclinic system with space group *P*-1, $a = 8.632(4)$ Å, $b = 9.267(7)$ Å, $c = 17.461(10)$ Å, $\alpha = 86.66(5)°$, $\beta = 82.20(4)°$, and $\gamma = 89.28(5)°$. The structure of Mu-4, as seen in Figure 1, consists of anionic double layers essentially built from double four-ring (D4R) units connected through four-, six-, and eight-membered rings. The water molecules and protonated diethylamine molecules locate in the interlayer region. Meanwhile, another type of diethylamine molecule protrude into the 8-MR present in the layers. Each asymmetric unit contains four unique Al atoms in tetrahedral and distorted trigonal-bipyramidal coordinations ($Al(1)O_4$, $Al(2)O_4$, $Al(3)O_4$, $AlO(4)O_5$) and five unique P atoms in tetrahedral coordination ($P(1)O_{3b}O_{1t}$, $P(2)O_{4b}$, $P(3)O_{4b}$, $P(4)O_{4b}$, $P(5)O_{2b}O_{2t}$).

Using an ultrasonic technique a series of intercalation compounds with different interlayer distances has been prepared. Furthermore, intercalation and deintercalation are reversible. The advantage of the ultrasonic method lies in that the intercalation compounds can be quickly prepared in a short time. This work provides access to a new area of aluminophosphate intercalation chemistry.

Experimental Section

Synthesis of Mu-4. Mu-4 was prepared using a procedure similar to that described in ref 34. The difference lies in that diethylamine was used as the template and triethylene glycol as the solvent in this work. The typical synthesis procedure was as follows: 1.0 g of finely ground aluminum triisopropoxide was first dispersed in 10 mL of triethylene glycol with stirring, followed the addition of 3.0 mL of diethylamine. Finally, 2.3 mL of phosphoric acid (85 wt % in water) was added dropwise to the above mixture with stirring. The reaction mixture was stirred until it was homogeneous and then sealed in a Teflon-lined stainless steel autoclave and heated under autogenous pressure at 180 °C for 8 days. The product with a platelike shape was separated by filtration, washed with deionized water, and dried in air at ambient temperature.

Intercalation of *n*-Alkylamines. A 1 g amount of *n*-alkylamine ($C_nH_{2n+1}NH_2$, $n = 4, 8, 12, 16$) was first dissolved in 40 mL of solvent followed by addition of 0.2 g of Mu-4. The mixture was treated in an ultrasonic bath for 30 min (Ultrasonic Crusher Machine, Scientz Co., Ltd, 400 W/20 kHz) or stirred at room temperature for a few days. The product was filtrated, washed with methanol, and air-dried. The intercalation compounds were designated Mu-4-L*n*, where L stands for lamellar and *n* represents the number of carbon atoms in *n*-alkylamines ($n = 4, 8, 12, 16$). Various parameters that influence the preparation of the intercalation compounds were studied and will be discussed in the Results and Discussion.

Characterizations. X-ray powder diffraction (XRD) patterns of the products were recorded on a Simens D5005 diffractometer with Cu Kα radiation ($\lambda = 1.5148$ Å). The interlayer distances of intercalation compounds were determined based on [001] reflections.

Elemental analyses were conducted on a Perkin-Elmer 2400 elemental analyzer. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. The infrared (IR) spectra were recorded on a BRUKER VECTOR22

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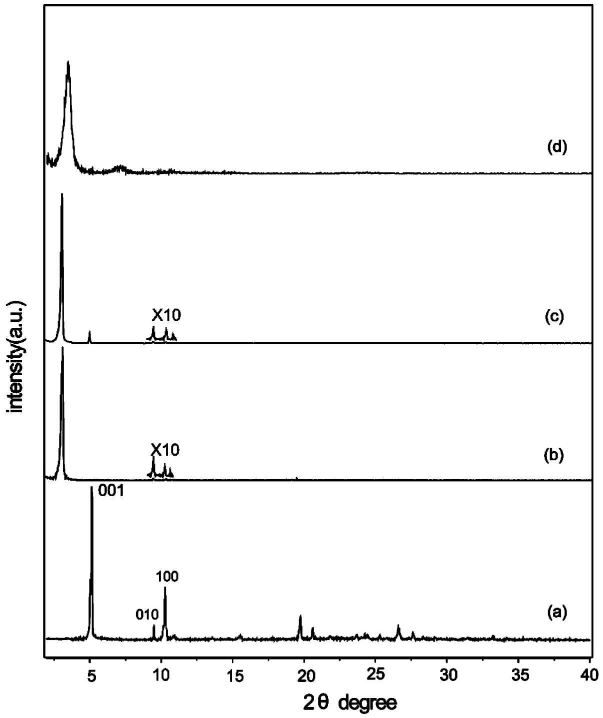

Figure 2. Powder XRD patterns of Mu-4 (a) and products obtained from reaction of Mu-4 with *n*-octylamine in methanol (b), ethanol (c), and water (d).

Spectrometer with the KBr-disk technique. A NETZSCH STA 449C unit was used to carry out the TGA and DTA analyses in air with a heating rate of 10 °C/min. Solid-state NMR experiments were performed on a Varian Infinity Plus-400 spectrometer operating at frequencies of 104.20, 161.88, and 100.52 MHz for ^{27}Al, ^{31}P, and ^{13}C, respectively. Chemical shifts were referenced to an external standard of $Al(NO_3)_3$ for ^{27}Al, 85% H_3PO_4 for ^{31}P, and tetramethylsilane for ^{13}C, respectively. SEM photographs were taken on a SHIMADZU SSX-550 microscope. Transmission electron microscopy (TEM) images were taken on a JEOL-JEM 3010 microscope with an acceleration voltage of 300 kV.

Molecular simulations were carried out using the Cerius^2 software package.[35]

Results and Discussion

Intercalation Reaction. The influence of solvent, length of alkyl chain, and intercalation method on the preparation of *n*-alkylamine intercalated Mu-4 was studied.

Effect of Solvent. Taking the intercalation of *n*-octylamine in Mu-4 as an example, Figure 2 shows the XRD patterns of intercalated products obtained in methanol, ethanol, and water. The product obtained in methanol indicates a well-crystalline structure. The strong [001] reflection at $d = 1.73$ nm of Mu-4 shifts to one at $d = 2.82$ nm, indicating an increase of basal spacing of Mu-4 and formation of *n*-octylamine-intercalated compound. The reflections, which are assigned as [010] and [100] in the XRD pattern of Mu-4, remain. The intercalation reaction in ethanol shows a similar result. Except for the strong reflection peak at $d = 2.82$ nm, a peak at $d = 1.73$ nm due to the original [001] reflection of Mu-4 can also be observed in the XRD pattern. The single phase of completely intercalated products cannot be obtained using ethanol as the solvent, even if the reaction time is prolonged and the power of the ultrasonic wave is enhanced. On the other hand, reaction in water gives a quite different result. Only a broader [001] reflection at $d = 2.44$ nm can be observed, and the others reflections disappear. This indicates that the crystalline layers are degraded, as in the case described in refs 13 and 14. ICP analysis gives an Al:P ratio of 1:1, which is different from the original Al:P ratio of 4:5 in Mu-4, further confirming degradation of the sheet structure.

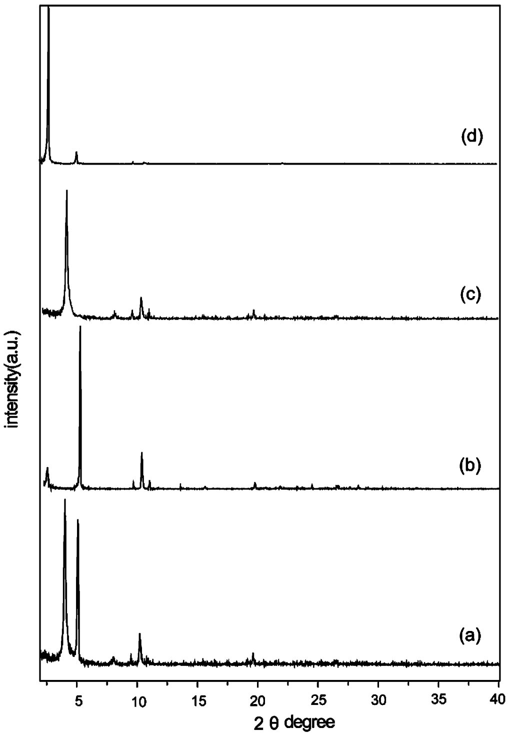

Figure 3. Powder XRD patterns of reaction products of *n*-alkylamine ($C_nH_{2n+1}NH_2$, $n = 4$, 16) with Mu-4 (a and b) and Mu-4-L8 (c and d).

Effect of the Length of Alkyl Chain. For $n = 8$ and 12 the *n*-alkylamine completely intercalated products can be prepared with Mu-4 as the host. However, for $n = 4$ and 16 intercalation was not complete since the [001] reflection of Mu-4 at $d = 1.73$ nm is always observed in XRD patterns. The reason might lie in that *n*-butylamine has a similar size to diethylamine residing in the interlayer region of Mu-4 while *n*-hexadecylamine is too large for the limited interlayer distance. The completely intercalated products of Mu-4-L4 and Mu-4-L16 could be obtained using Mu-4-L8 instead of Mu-4 as the host, and the procedure of intercalation is the same as that described above. This demonstrates that the intercalation products have the capability for re-intercalation of other either smaller or larger molecules. Furthermore, Mu-4-L8 can be prepared using Mu-4-L4 as the host. This indicates that the mesostructured lamellar phase has a reversible intercalation and deintercalation property. Figure 3 shows the XRD patterns of intercalation compounds of *n*-alkylamine ($C_nH_{2n+1}NH_2$, $n = 4$ and 16) with Mu-4 and Mu-4-L8, respectively.

Stirring Method. For comparison, the intercalation reaction is also carried out by conventional stirring method. Taking the intercalation of *n*-octylamine as an example, it takes at least 3 days to obtain the completely intercalated products.

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(35) *Cerius*^{2}; Molecular Simulations/Biosym Corp., San Diego, 1995.

Table 1. Element and Molecular Contents (wt %) of Mu-4-L*n*

sample	Al	P	C	H	N	H_2O	amine	empirical formula
Mu-4-L4	13.40	19.12	12.40	4.04	3.61	7.0	20.2	$[Al_4P_5O_{20}H]\cdot[C_4H_9NH_3]_2\cdot3H_2O$
Mu-4-L8	11.20	16.42	24.17	6.04	3.46	3.5	30.7	$[Al_4P_5O_{20}H]\cdot[C_8H_{17}NH_3]_2\cdot2H_2O$
Mu-4-L1 2	9.91	14.56	30.78	7.37	3.02	3.0	38.2	$[Al_4P_5O_{20}H]\cdot[C_{12}H_{25}NH_3]_2\cdot2H_2O$
Mu-4-L1 6	9.47	13.60	33.68	7.10	2.46	6.5	41.5	$[Al_4P_5O_{20}H]\cdot[C_{16}H_{33}NH_3]_2\cdot4H_2O$

In contrast, employing ultrasonic treatment, intercalation can be completed within 30 min at ambient temperature. Therefore, the ultrasonic method provides a rapid and efficient method to prepare the intercalated compounds. A possible explanation for the accelerated intercalation reaction rate might be the *microstreaming effect*, known as sonochemistry. It is known that when a solid−liquid mixture is treated ultrasonically the cavitation bubbles formed in the rarefaction cycle undergo unsymmetric collapse near the solid surface, which causes 'in-rush' of the liquid into the solid. This effect is called 'microjet formation' or 'microstreaming', wherein the velocity of the in-rushing liquid is as high as 100 m/s. This is the reason ultrasound is more effective for cleaning.[36,37]

Composition of Mu-4-L*n*. Phosphorus and aluminum contents of Mu-4-L*n* ($n = 4, 8, 12, 16$) were determined by ICP analysis. The Al/P ratio for Mu-4-L*n* is 4 /5, consistent with Mu-4, which implies that the Al−O−P connectivity might be retained after intercalation of *n*-alkylamine. C, H, and N contents were determined by elemental analysis, giving C:N molar ratios of Mu-4-L*n* as n:1 ($n = 4, 8, 12, 16$), consistent with those of *n*-alkylamines. Thermogravimetric analysis shows that there are weight losses of 7.0, 3.5, 3.0, and 6.5 wt % from 50 to 150 °C and 20.2, 30.7, 38.2, and 41.5 wt % from 150 to 650 °C for Mu-4-L4, Mu-4-L8, Mu-4-L12, and Mu-4-L16, respectively. The low-temperature weight losses are associated with removal of water molecules accompanied with an endothermic effect and the high-temperature ones to decomposition of templates with an evident exothermic effect. The results of compositional and thermogravimetric analysis for Mu-4-L*n* are listed in Table 1 together with the empirical formulas of Mu-4-L*n* calculated on the basis of these analysis results. As with Mu-4, each $[Al_4P_5O_{20}H]^{2-}$ associates with two moles of protonated *n*-alkylamine molecules. This indicates that the original diethylamine molecules occluded in the interlayer region of Mu-4 have been completely replaced by the *n*-alkylamine molecules in Mu-4-L*n*.

Characterization of Mu-4-L*n*. Figure 4 shows the XRD patterns of Mu-4 and its intercalation products with *n*-alkylamines. After intercalation the [001] reflection of Mu-4 disappears and a new set of [001] reflections appears. The basal space of the intercalation products with *n*-alkylamines increases with an increase of the number of carbon atoms in the *n*-alkyl chain: 2.22 nm for $n_c = 4$, 2.82 nm for $n_c = 8$, 3.30 nm for $n_c = 12$, and 3.97 nm for $n_c = 16$, indicating formation of lamellar mesostructured compounds.

Formation of a lamellar solid is also evident from the TEM image of Mu-4-L12 (Figure 5). It shows a parallel stacking of layers with a basal space of 3.1 nm, corresponding to the basal spacing of 3.3 nm obtained from XRD analysis. Close examination of the TEM image of Mu-4-L12 shows that its layer thickness is ∼1.3 nm with an interlayer separation ≈ 1.8 nm. This layer thickness is very close to that for Mu-4 of 1.4 nm, which further confirms that the inorganic sheets are kept intact after intercalation.

The SEM images show that the crystal morphology can be kept after intercalation of *n*-alkylamines into the Mu-4

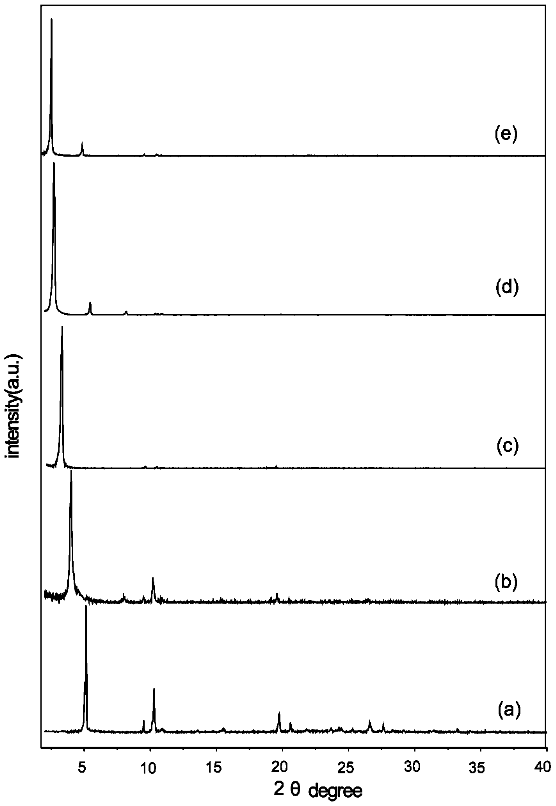

Figure 4. Powder XRD patterns of Mu-4 (a), Mu-4-L4 (b), Mu-4-L8 (c), Mu-4-L12 (d), and Mu-4-L16 (e).

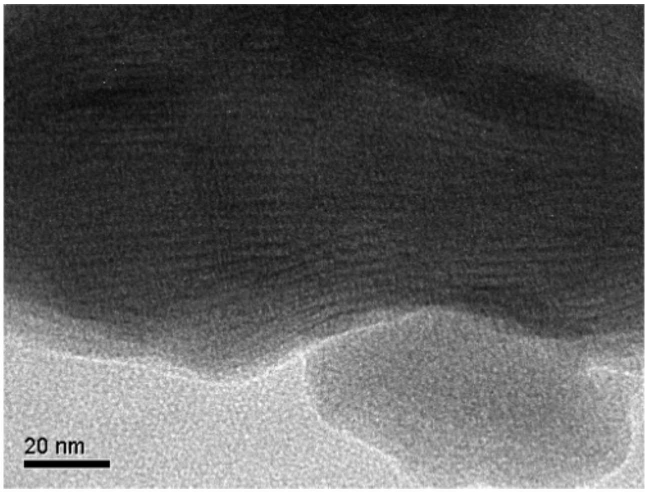

Figure 5. TEM image of Mu-4-L12.

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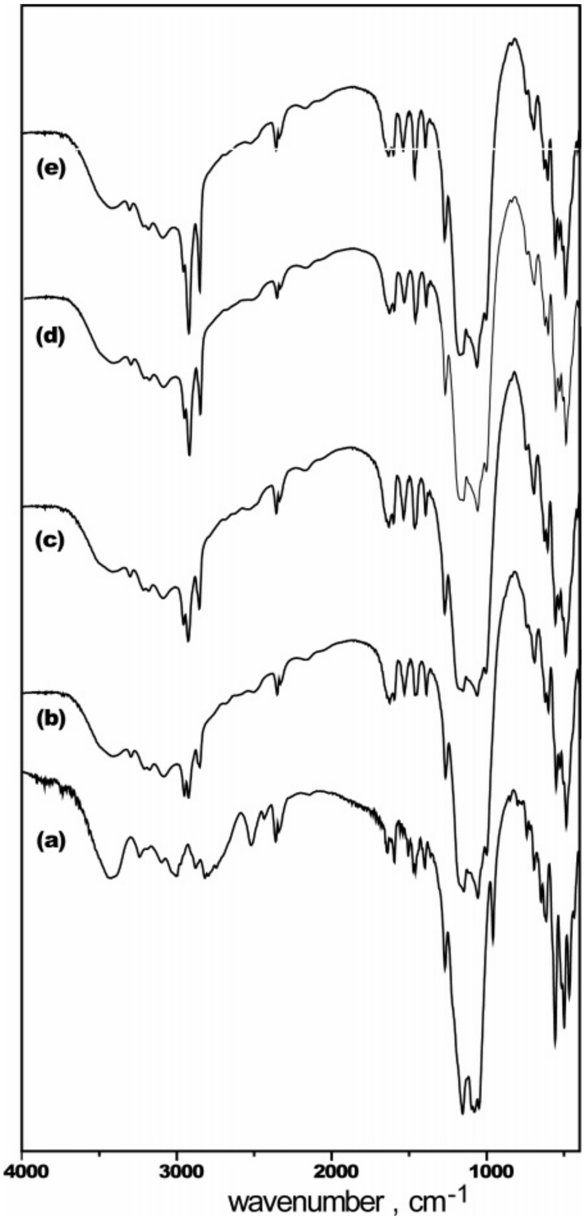

Figure 6. IR spectra of Mu-4 and Mu-4-Ln ($n = 4, 8, 12, 16$).

by ultrasonic wave treatment. The warped shape of the intercalated thick platelets might be caused by mechanical stress due to interlayer expansion.

Figure 6 shows that the IR spectra of Mu-4-Ln ($n = 4$, 8, 12, 16) are very similar. It is well known that the positions of the antisymmetric stretching band (2920 cm^{-1}) and the symmetric stretching band (2850 cm^{-1}) of CH_2 groups (abbreviated υas (CH_2) and υs (CH_2), respectively) in n-alkyl chains are sensitive to chain conformation and that these two bands shift to lower wavenumbers if disorder (kinkand gauche-blocks) is introduced into the n-alkyl chains.[38-41] Each IR spectrum of Mu-4-Ln exhibits the υas (CH_2) band at 2919 cm^{-1} and the υs (CH_2) band at 2852 cm^{-1}, indicating that the n-alkyl chains possess an ordered all-trans conformation in the interlayer space.

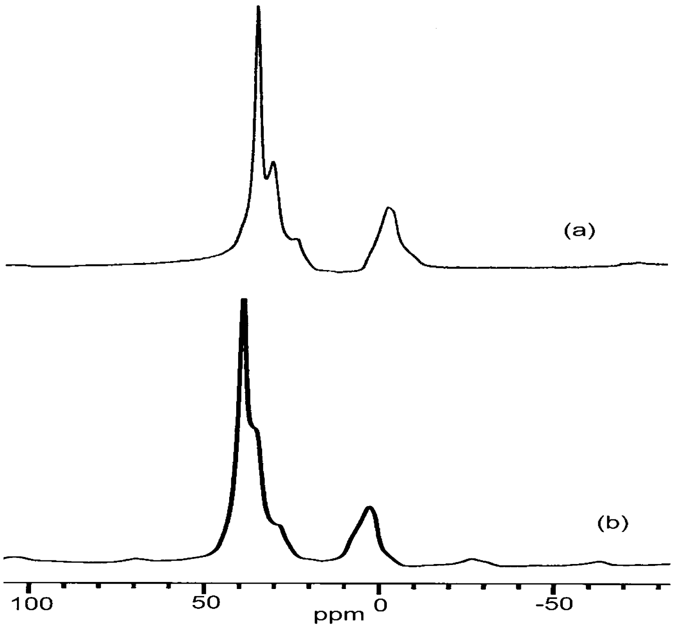

Figure 7. ^{27}Al MAS NMR spectra of Mu-4 (a) and Mu-4-L12 (b).

A linear relationship between the basal space d and the number of carbon atom n_c in the n-alkylamines can be observed, as expressed with $d = 0.14n_c + 1.64$. The mean increment of the basal spaces ($\Delta d/\Delta n_c$) is 0.14 nm, which is larger than 0.127 nm/CH_2 for an all-trans fully extended alkyl chain.[42] Therefore, the alkyl chains might be arranged as bilayers in the interlayer region with a tilt angle of $\sin^{-1}$ $(0.14/2 \times 0.127)$, i.e., 33.4°. The intercept for $n_c = 0$ (about 1.64 nm) is in agreement with the expected value for the thickness of the Mu-4 layer (1.4 nm).

To identify the coordination environments of Al and P atoms of the inorganic sheet and the C atoms of the organic amines in Mu-4-Ln, Mu-4-L12 was selected as a representative example whose ^{27}Al, ^{31}P MAS NMR and ^{13}C CP-MAS NMR are compared with those of Mu-4. Figure 7 shows the ^{27}Al MAS NMR spectra of Mu-4-L12 and Mu-4. It can be seen that the intercalation compound Mu-4-L12 shows a similar NMR spectrum to that of Mu-4, indicating that all Al atoms in Mu-4-L12 retain the same coordination states as those of Mu-4. As with Mu-4, three strongly overlapping resonances in the spectral region of 20−50 ppm can be attributed to tetrahedrally coordinated Al atoms. The fourth signal in the spectral region from −5 to 10 ppm can be attributed to the aluminum site in distorted trigonal-bipyramidal coordination.

Figure 8a shows the ^{31}P MAS NMR spectrum of Mu-4. It displays four resonance signals at −13.2, −23.5, −29.4, and −32.6 ppm with an intensity ratio close to 1:2:1:1, corresponding to the five unique phosphorus sites. The ^{31}P MAS NMR spectrum of Mu-4-L12 (Figure 8b) shows some changes compared with that of Mu-4, and four resonances at −10.8, −19.6, −23.5, and −29.7 ppm with an intensity ratio of 1:1:1:2 corresponding to five unique P atoms can

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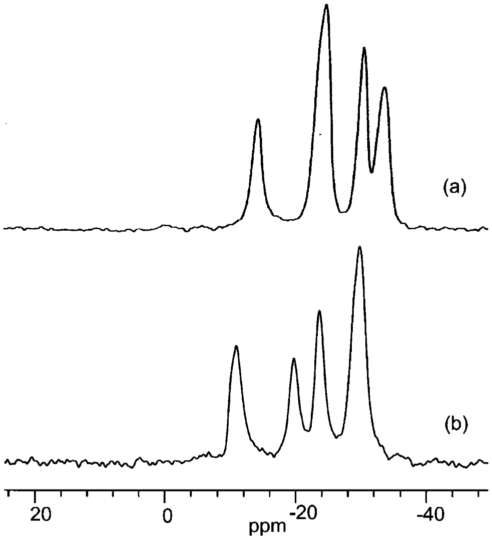

Figure 8. ^{31}P MAS NMR spectra of Mu-4 (a) and Mu-4-L12 (b).

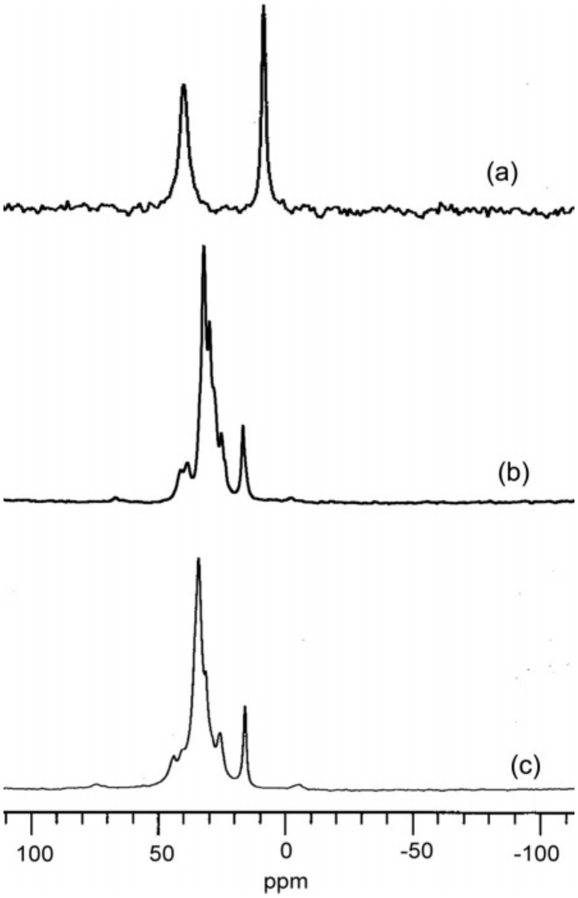

Figure 9. ^{13}C CP-MAS NMR spectra of Mu-4 (a), Mu-4-L12 (b), and pure *n*-dodecylamine (c).

be observed. According to ref 43 a ^{31}P chemical shift order P(5) > P(1) > P(3) > P(4) > P(2) is expected in Mu-4. For Mu-4 the resonances assigned to P(3) and P(1) are not resolved, leading to a single peak at −23.5 ppm, while for Mu-4-L12 the resonances assigned to P(4) and P(2) are not resolved, leading to a single peak at −29.7 ppm. The slight downfield shift from −13.2 to −10.8 ppm for P(5) and from −23.5 to −19.6 ppm for P(1) are probably due to the weaker H-bonding interactions of the intercalated *n*-alkylamine with the inorganic sheets compared with the interaction of diethylamine and/or H_2O molecules with the layers. From above results it can be concluded that the sheet structure of Mu-4 is retained after intercalation of *n*-alkylamine.

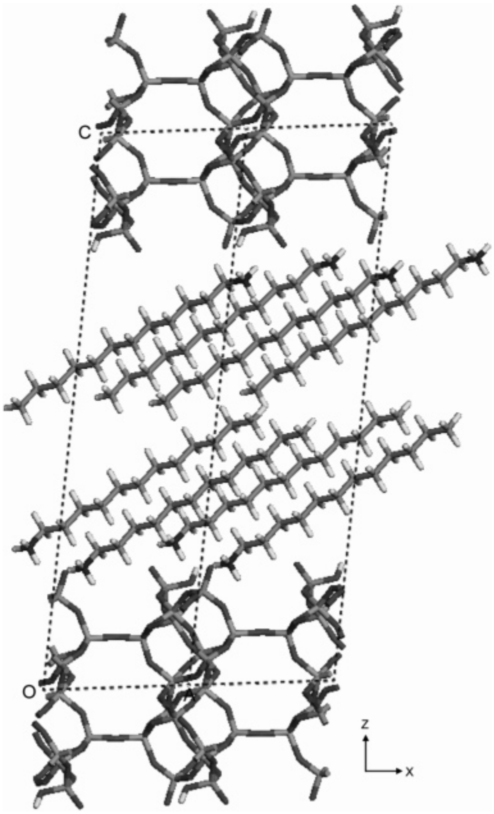

Figure 10. Ideal structural model of Mu-4-L12 along [010] showing the arrangement of the *n*-dodecylamine molecules.

The ^{13}C CP-MAS NMR spectrum of Mu-4 consists of two resonances at 42.06 and 10.57 ppm (Figure 9a). Such chemical shifts are attributed to $-CH_2-$ and $-CH_3$ groups of diethylamine, respectively. Mu-4-L12 exhibits a ^{13}C CP-MAS NMR spectrum (Figure 9b) similar to that of pure *n*-dodecylamine (Figure 9c). These suggest the fact that the *n*-dodecylamines remain intact after being intercalated between the inorganic layer and that the original diethylamine molecules occluded in the interlayer region of Mu-4 have been replaced by the *n*-dodecylamine molecules in Mu-4-L12.

Molecular Simulations. Molecular simulations are used for a better understanding of the arrangement of *n*-alkylamines in the interlayer regions of Mu-4-L*n*. The simulation procedure consists of two main steps. The first step involves building a theoretical model; the second step is to optimize the location of *n*-alkylamine molecules in the interlayer spaces by molecular mechanical energy optimization.

Taking Mu-4-L12 as an example, an ideal model is built up as follows. The inorganic sheet of Mu-4 is built up according to its crystal structure data. Its interlayer distance is adjusted to 3.3 nm according to the experimental XRD data of Mu-4-L12, and the crystal symmetry is decreased to *P*1. On the basis of the charge balance of $[Al_8P_{10}O_{40}H_2]^{4-}$ as well as the deduced empirical formula, four protonated

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(43) Marichal, C.; Vidal, L.; Delmotte, L.; Patarin, J. *Microporous Mesoporous Mater.* **2000**, *34*, 149.

n-dodecylamine molecules are loaded in one unit cell. These amine molecules are in a *trans*-conformation, arranging in a bilayer form. Energy optimization is carried out based on the Burchart 1.01-Dreiding 2.21 force field[44−46] in which the unit cell is fixed and the amine molecules are treated as rigid molecules. Figure 10 shows the final optimized structure for Mu-4-L12 along the [010] direction. The *n*-dodecylamine molecules take a bilayer arrangement in the interlayer space with a tilt angle of 35°, which is very close to the tilt angle of 33.4° induced by the linear relationship of $d = 0.14n_c + 1.64$.

Conclusion

Our present results provide a novel approach to obtaining mesostructured lamellar aluminophosphate compounds using ultrasonic technique. The *n*-alkylamines ($C_nH_{2n+1}NH_2$, $n = 4, 8, 12, 16$) can be successfully intercalated into the layered aluminophosphate Mu-4 in methanol to form intercalation compounds. The inorganic sheet structure can be kept intact after the intercalation reaction. The interlayer distance of Mu-4-L*n* increases with an increase of the number of carbon atoms in the *n*-alkyl chain, and *n*-alkylamines exhibit a bilayer arrangement in the interlayer space with a tilt angle of 33.4°. Furthermore, the mesostructured lamellar aluminophosphates show reversible intercalation and deintercalation behavior. The interesting feature of this approach to the synthesis of mesostructured aluminophosphate phases is that it is possible to obtain a mesolamellar phase having the same Al−O−P connectivity as the starting phase. It is believed that a similar strategy could be applicable to the synthesis of novel mesostructured phases from other layered metal phosphates. Considering the devise structure ranges of porous layered metal phosphates it will be an interesting subject for the study of the intercalation chemistry of various layered metal phosphates. The mesostructured metal phosphates pillared with functional molecules will be interesting materials in various applications, such as heterogeneous catalysis and specific adsorbents.

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Supporting Information Available: Figures of TG and DTA curves of Mu-4-L*n*, SEM images of Mu-4 and Mu-4-L12, Plot of basal space *d* versus number of carbon atoms in the alkyl chain n_c for the Mu-4-L*n* compounds, and ^{27}Al, ^{31}P MAS NMR spectra of Mu-4-L*n* ($n = 4, 8, 16$). This material is available free of charge via the Internet at http://pubs.acs.org.

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