Solvothermal Ion Exchange of Aliphatic Dicarboxylates into the Gallery Space of Layered Double Hydroxides Immobilized on Si Substrates

Jong Hyeon Lee, Seog Woo Rhee, and Duk-Young Jung*

Department of Chemistry-BK21, Institute of Basic Sciences, Sungkyunkwan University, Suwon 440-746, Korea

Highly ordered Mg/Al-based layered double hydroxide (LDH) nanocrystals on Si substrates were successfully obtained by ultrasonic treatment in organic solvents. LDHs intercalated with aliphatic α,ω-dicarboxylate were prepared through anion exchange by solvothermal treatment at around 100 °C. Binary solvent mixtures of alcohol and toluene prevent dissolution of the LDH and preserve the layered crystal structure of the LDH during the anion-exchange reaction. Atomic force microscopy results present conservation of lateral positions and morphologies of the LDH crystals on Si before and after anion exchange. The interlayer spacings of LDH crystals intercalated with dicarboxylates vary directly with the chain length of the dicarboxylates, and reaction stepwise anion exchanges are possible. The results gave an original example of the direct measurement of the anisotropic nanomorphological change of the selected LDH crystals in the intercalation reaction, which opens a wide range of applications.

Introduction

Layered double hydroxides (LDHs), also known as anionic or hydrotalcite-like clays, are able to intercalate neutral guest molecules, or to exchange interlayer inorganic/organic anions. The LDHs are lamellar compounds that consist of positively charged metal hydroxide layers and anions along with water located between the layers to compensate a net positive charge. The compositions of LDHs are expressed by the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]A^{n-}_{x/n}\cdot mH_2O$, wherein M^{2+} and M^{3+} can be any divalent or trivalent metal ion capable of occupying the octahedral holes of a brucite-like layer and A^{n-} is virtually any hydrated exchangeable anion positioned in the gallery between the layers.[1,2] The LDHs have received considerable attention because of their properties as catalysts, anion exchangers, and carriers for the immobilization of biological materials.[3]

Especially, LDHs have been used to prepare nanoscale organic/inorganic hybrid materials in efforts to develop new functional materials such as biological, environmental, agricultural, and pharmaceutical materials and so on.[4] In developing these functional materials, the solubility of organic species and LDHs needs to be controlled to utilize the functional properties. Most investigations of the ion-exchange reactions of LDHs have been achieved in aqueous solutions due to utilization of water-soluble ionic compounds[5] and performed under an inert gas atmosphere because of the competitive incorporation of carbonate from carbon dioxide.[2] Since carbonate is one of the most strongly bound chemical species in the interlayer gallery of LDHs,[1] some organic acids such as carboxylic acids[6] and phenylphosphonic acids[7] do not readily undergo intercalation into the carbonate form of LDHs.

The chemical reactions and properties of the LDH materials have been extensively studied using powder samples.[8] Reaction progress for separate nanocrystals in powder samples has not been observed so far, since orientation-controlled immobilization of LDH crystals is difficult. We have developed a monolayer assembly of the LDH nanocrystals on solid surfaces with a high packing density and the preferred orientation without any chemical linkers. The assembly of nanosized inorganic particles was formed on flat solid surfaces in a well-ordered manner.[9] Thanks to structural stability, assemblies of layered inorganic materials on solid surfaces can be used as functional coatings for chemical sensors[10] and clay-modified electrodes.[11]

* To whom correspondence should be addressed. E-mail: dyjung@skku.edu. Fax: +82-31-290-7075.

(1) (a) Miyata, S. *Clays Clay Miner*. **1983**, *31*, 305. (b) Miyata, S.; Okada, A. *Clays Clay Miner*. **1977**, *25*, 14.

(2) Cavani, F.; Trifiró, F.; Vaccari, A. *Catal. Today* **1991**, *11*, 173.

(3) (a) Ogawa, M.; Kuroda, K. *Chem. Rev*. **1995**, *95*, 399. (b) Ding, W.; Gu, G.; Zhong, W.; Zang, W. C.; Du, Y. *Chem. Phys. Lett*. **1996**, *262*, 259. (c) Choy, J. H.; Kwak, S. Y.; Park, J. S.; Portier, J. *J. Am. Chem. Soc*. **1999**, *121*, 1399. (d) Choy, J. H.; Kwak, S. Y.; Jung, Y. J.; Park, J. S. *Angew. Chem., Int. Ed*. **2000**, *39*, 4042.

(4) Portier, J.; Choy, J. H.; Subramanian, M. A. *Int. J. Inorg. Mater*. **2001**, *3*, 581.

(5) (a) Meyn, M.; Beneke, K.; Lagaly, G. *Inorg. Chem*. **1990**, *29*, 5201. (b) Fogg, A. M.; Dunn, J. S.; Shyn, S. G.; Cary, D. R.; O'Hare, D. *Chem. Mater*. **1998**, *10*, 351. (c) Fogg, A. M.; Dunn, J. S.; O'Hare, D. *Chem. Mater*. **1998**, *10*, 356. (d) Fogg, A. M.; Freij, A. J.; Parkinson, G. M. *Chem. Mater*. **2002**, *14*, 232.

(6) Carlino, S.; Hudson, M. J. *J. Mater. Chem*. **1994**, *4*, 99.

(7) Carlino, S.; Hudson, M. J.; Husain, S. W.; Knowles, J. A. *Solid State Ionics* **1996**, *84*, 117.

(8) (a) Constantino, V. R. L.; Pinnavaia, T. J. *Inorg. Chem*. **1995**, *34*, 883. (b) Gardner, E.; Huntoon, K.; Pinnavaia, T. J. *Adv. Mater*. **2001**, *13*, 1263. (c) Borja, M.; Dutta, P. K. *J. Phys. Chem*. **1992**, *96*, 5434. (d) Carlino, S. *Solid State Ionics* **1997**, *98*, 73.

Anion-exchange reactions in aqueous solutions are not able to prevent the equilibrium of the dissolution−recrystallization reaction resulting from the hydrolysis of host layers of LDHs.[12] When nonaqueous solvents were used in anion exchange of LDHs, reconstruction of the LDH crystals could be suppressed and the morphology of the LDH particles could be preserved during the anion-exchange reactions.[13] In addition, hydrophobic long-chain dicarboxylic acids are soluble enough to react with carbonate ions in the gallery of the LDH in organic solvent systems. Anion-exchange reactions using immobilized LDH crystals in a non-aqueous solvent system provide the observation of anisotropic variation of interlayer spacings of LDHs using atomic force microscopy (AFM) and X-ray diffraction (XRD) instruments without any destruction of host hydroxide layers, and the utilization of very small amounts of chemical reagents.[14]

We first immobilized LDH crystals on Si substrates and investigated the immobilized LDH nanocrystals under various solvothermal reaction conditions such as reaction medium, reaction time, and temperature. Our approach has overcome the drawback of dissolution and recrystallization of LDHs in aqueous solution, and we could observe the morphological change of the immobilized LDH crystals on the substrate before and after the anion-exchange reaction by the AFM and XRD techniques.

Experimental Section

The carbonate form of an LDH, $[Mg_4Al_2(OH)_{12}]CO_3 \cdot nH_2O$, denoted as MgAl-LDH, was prepared by the coprecipitation method.[1] To an aqueous solution containing 0.02 M $Mg(NO_3)_2$ and 0.01 M $Al(NO_3)_3$ was slowly added a mixed solution of 2.0 M NaOH and 0.2 M Na_2CO_3 with vigorous stirring. During the titration the pH of the solution was adjusted to 10.0 ± 0.1 at room temperature. The resulting precipitate was collected by centrifugation and washed with deionized water three times. Hydrothermal treatment was carried out in deionized water at 180 °C to obtain a larger crystal size and improved crystallinity of MgAl-LDH crystals, followed by drying at 120 °C in a convection oven.[15]

Immobilization of MgAl-LDH nanocrystals was performed on clean silicon(100) wafers as a substrate. The MgAl-LDH crystals (10 mg) were suspended in dry organic solvents (20 mL) such as 1-butanol or 2-propanol in a covered laboratory glass flask, and then the flask was immersed in an ultrasonic bath (95 W, 28 kHz) under ambient pressure at room temperature. The Si substrates cleaned with oxygen plasma (Harrick, 30 W) were dipped in the colloidal suspension of MgAl-LDH and were coated with the LDH by ultrasonic treatment for 2 min. The LDH-coated Si was removed from the reaction suspension followed by sonication for an additional 1 min in
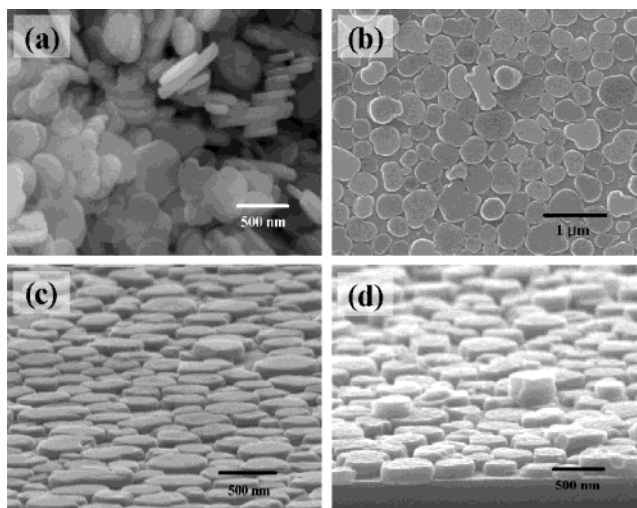
(9) (a) Fendler, J. H. *Nanoparticles and Nanostructured Film: Preparation, Characterization and Application*; John Wiley & Son Ltd.: New York, 1998. (b) Shenton, W.; Davis, S. A.; Mann, S. *Adv. Mater.* **1999**, *11*, 449. (c) Choi, S. Y.; Lee, Y. J.; Park, Y. S.; Ha, K.; Yoon, K. B. *J. Am. Chem. Soc.* **2000**, *122*, 5201.
(10) (a) Thompson, M. E. *Chem. Mater.* **1994**, *6*, 1168. (b) Mallouk, T. E.; Gavin, J. A. *Acc. Chem. Res.* **1998**, *31*, 209.
(11) (a) Itaya, K.; Chang, H. C.; Uchida, I. *Inorg. Chem.* **1987**, *26*, 624. (b) Mousty, C.; Therias, S.; Forano, C.; Besse, J. P. *J. Electroanal. Chem.* **1994**, *374*, 63. (c) Ballarin, B.; Gazzano, M.; Seeber, R.; Tonelli, D.; Vaccari, A. *J. Electroanal. Chem.* **1998**, *445*, 27.
(12) Boclair, J. W.; Braterman, P. S. *Chem. Mater.* **1999**, *11*, 298.
(13) Hibino, T.; Tsunashima, A. *Chem. Mater.* **1997**, *9*, 2082.
(14) Lee, J. H.; Rhee, S. W.; Jung, D. Y. *Chem. Commun.* **2003**, 2740.
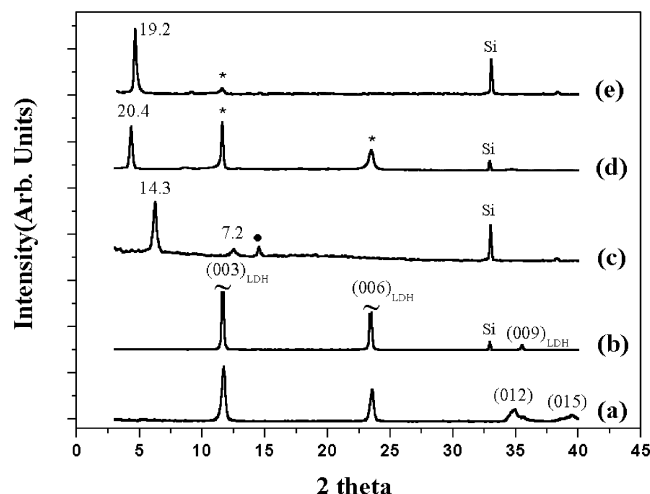(15) Hickey, L.; Kloprogge, J. L.; Frost, R. L. *J. Mater. Sci.* **2003**, *35*, 4347.

Figure 1. Typical SEM images of the pristine MgAl-LDH powder sample (a), a monolayer assembly of MgAl-LDH crystals on Si prepared in 1-butanol (b, c), and DC-MgAl-LDH crystals (d).

1-butanol or 2-propanol to remove the excess LDH crystals from the substrates, and the samples were dried at 70 °C in air.

The MgAl-LDH crystals on Si were transferred into a Teflon-coated autoclave vessel containing a solution of 2 mM aliphatic dicarboxylic acid in a binary mixture of alcohol and toluene, and heated at 80−120 °C for 12−48 h. The alcohol/toluene ratio (v/v) was varied in each experiment. The residual acids on the substrates were washed out with 2-propanol, and the samples were dried at 70 °C in air.

XRD patterns were measured with a Rigaku X-ray diffractometer, D/MAX-2000 Ultima, in $\theta \angle 2\theta$ scanning mode. The measurements were performed under the conditions of 40 kV, 30 mA, and Cu Kα radiation ($\lambda = 1.5405$ Å). All XRD spectra were calibrated using the Si(200) peak from the substrates ($2\theta = 32.9°$, $d = 2.74$ Å). AFM measurements were performed in air with a Nanoscope II scanning probe microscope (Digital Instruments). A cantilever [Si$_3$N$_4$] integral tip with a spring constant of 0.06 nm^{-1} was used. The "E" scan head was used for a 10 μm maximum scan. The images were obtained in the contact mode with the filter off. The atomic force micrscope was calibrated on a gold grid of 1 μm × 1 μm dimensions and with a 200 nm deep pit. The FT-IR spectra of the DC-MgAl-LDH on Si were obtained with a vacuum optics available spectrometer (IFS 66 v/s, Bruker). The wavenumber resolution is 4 cm^{-1}, and the signal was detected by a photovoltaic liquid-cooled MCT detector.

Results and Discussion

LDH Deposition on a Si Substrate. The diameter of the prepared MgAl-LDH crystals in powder samples ranging from 100 to 500 nm and a thickness of about 100 nm were determined by scanning electron microscopy (SEM) as shown in Figure 1a. The XRD spectra of the prepared MgAl-LDH powder samples confirmed the LDH structure[1] with random orientation, as shown in Figure 2a, which gives the (012) and (015) peaks. The monolayer assembly of MgAl-LDH crystals on Si substrates was successfully prepared in 1-butanol using sonication treatment as shown in Figure 1b,c. The XRD spectra shown in Figure 2b present the Si substrate of attached MgAl-LDH crystals, indicating the highly ordered orientation confirmed by the strongly enhanced (00*l*) peaks up to *l* = 9, as well as the absence of both the (012) and (015) peaks. To prepare the monolayer

Figure 2. XRD spectra and basal spacings (Å) of the MgAl-LDH powder sample (a) and MgAl-LDH on Si prepared in 1-butanol (b). (c)−(e) are for MgAl-LDH exchanged with 1,10-decanedicarboxylate in toluene (c), 2-propanol (d), and 1-propanol (e). The scales of the XRD spectra of (c)−(e) are multiplied by 10 to be compared with those of (a) and (b). The asterisk corresponds to the pristine LDH peaks and the circle to AlO(OH). Anion-exchange reactions were performed at 120 °C for 24 h.
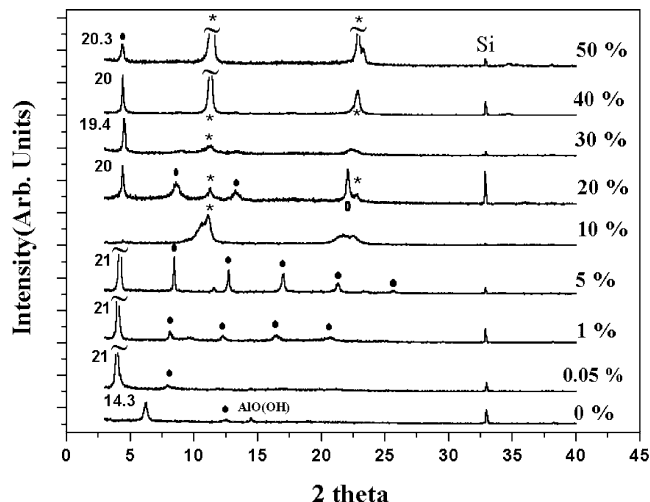
Figure 3. XRD spectra and basal spacings (Å) of MgAl-LDH obtained by anion exchange with 1,10-decanedicarboxylate in various 1-propanol/toluene mixtures (%, v/v): 0% indicates the reaction medium contains only toluene, and 0.05% indicates a 1-propanol/toluene mixture in a 0.05/99.5 ratio. The asterisk corresponds to the pristine LDH peaks, the full circle to (00*l*) harmonics, and the hollow circle to an unknown phase. Anion-exchange reactions were performed at 120 °C for 24 h.

assembly of LDH nanocrystals on Si substrates, we used a very small amount (10 mg) of powdery LDH in 20 mL of solvent. Adhesion of LDH or clay nanocrystals on solid substrates by solvent evaporation of the colloidal dispersion according to a previous report[16] gives randomly oriented crystals on the substrate, and it is very difficult to obtain the highly ordered aniosotropic array as reported in the present work. The bonding between the LDH and Si wafer is ascribed to physisorption resulting from the hydroxyl group of the LDH. Not only is the present method more facile than the Langmuir−Blodgett film deposition method for the preparation of LDH thin films,[17] but it is also possible to control the area coverage of the MgAl-LDH crystals on Si.

Solvent Dependence of the Anion Exchange of Dicarboxylates. We chose one of the long-chain dicarboxylic acids, 1,10-decanedicarboxylic acid, as a guest molecule in the interlayer gallery of LDHs (samples denoted as DC-MgAl-LDH). In Figure 2c−e, the XRD spectra for the DC-MgAl-LDH products were obtained by solvothermal reaction at 120 °C for 24 h in different solvents such as toluene, 2-propanol, and 1-propanol. Basal spacings of 19.2 and 20.4 Å were observed for the DC-MgAl-LDH prepared in alcohol systems, close to 21 Å, where 1,10-decanedicarboxylate ions were vertically arranged within the layers of the LDHs. The pristine LDH peaks almost disappeared for the 1-propanol system. On the contrary, incomplete anion exchange was observed in the 2-propanol system, and the pristine LDH peaks remained as shown in Figure 2d. The difference in exchange reaction progress could be partially ascribed to the solvent polarity at polar solid surfaces as a function of the solvent structure.[18] Solvo-

thermal treatment in toluene gave a sample with smaller basal spacings of 14.2 and 7.2 Å, and a peak assigned to AlO(OH) probably resulting from a partial decomposition of the pristine LDHs.

Mixed Solvent System. Figure 3 shows the XRD spectra of DC-MgAl-LDH using solvothermal reactions in a toluene/1-propanol mixture with various ratios between 0% and 50% (v/v). The data suggest layer expansion in all cases of 1-propanol addition, showing (003) reflections close to 19.2−21 Å as well as large intensities of (00*l*) harmonics. Assuming the thickness of the brucite layer including hydrogen bonding is approximately 6.8 Å,[2] the gallery height is close to 13.2 Å. Given that the size of the 1,10-decanedicarboxylate anion is approximately 13.3 Å,[19] such a value is generally associated with the formation of a vertical orientation within the interlayer space. In this arrangement the carboxyl groups are linked by hydrogen bonding to the hydroxide sheets and the aliphatic groups vertically oriented within the center of the gallery.

When a small amount of 1-propanol (0.05−5%, v/v) was used in the solvothermal reaction, the carbonate anions were successfully exchanged with 1,10-decanedicarboxylate, which vertically arranged into the layers. Especially, although extremely small quantities of 1-propanol (0.05%, v/v) were used in this system, the 1,10-decanedicarboxylic anions were intercalated into the interlayer space with a vertical arrangement, indicating that alcohol is very effective for the dissolution of dicarboxylic acid. Surprisingly, the extremely high crystallinity of DC-MgAl-LDH prepared in a 1-propanol/toluene mixture (5%, v/v) was reflected in six (00*l*) peaks up to *l* = 18. The SEM image of DC-MgAl-LDH on Si in Figure 1d showed sharp edges, indicating that the anion-exchange reaction using a small amount of 1-propanol may have little influence on the crystallinity of the LDH layers. Preswelling with alcohol[8d] and/or

(16) (a) Ghosh, P. K.; Bard, J. *J. Am. Chem. Soc.* **1983**, *105*, 5691. (b) Itaya, K.; Chang, H. C.; Uchida, I. *Inorg. Chem.* **1987**, *26*, 624.
(17) He, J. X.; Yamashita, S.; Jones, W.; Yamagishi, A. *Langmuir* **2002**, *18*, 1580.
(18) Zhang, X.; Cunningham, M. M.; Walker, R. A. *J. Phys. Chem. B* **2003**, *107*, 3183.

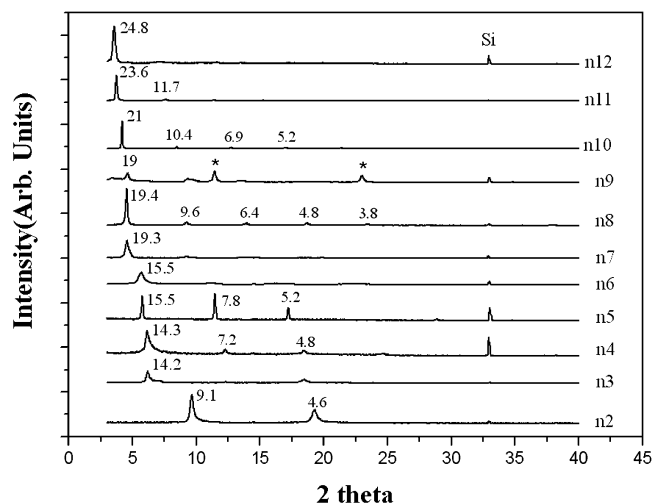(19) Kim, Y. J.; Lee, E. W.; Jung, D. Y. *Chem. Mater.* **2001**, *13*, 2684.

Figure 4. XRD spectra and basal spacings (Å) for the various dicarboxylate-LDH products obtained by anion exchange in a 1-propanol/toluene mixture (0.5%, v/v). n2 (succinate) to n12 (1,12-dodecanedicarboxylate) correspond to the number of carbons in the aliphatic chain in α,ω-dicarboxylates, $(CH_2)_n$-$(COO^-)_2$. The asterisk corresponds to the pristine LDH peaks.

solvation of acid in alcohol[20] are attributed to the driving forces of the exchange reaction because it is well-known that carbonate LDH compounds generally only with difficulty exchange with other anions. The solubility of dicarboxylic acid in alcohol may be the most important factor for the complete anion-exchange reaction. A large amount of 1-propanol (10−50%, v/v) gives partial exchange, and the pristine MgAl-LDH peaks remain, though most of the cases involve peaks for basal spacings around 20 Å.

Temperature and Time Dependence. The DC-MgAl-LDH samples prepared at 120 °C showed that anions were exchanged into the interlayer space, and the pristine LDH peaks completely disappeared. On the contrary, the DC-MgAl-LDH samples prepared at 80 and 100 °C presented pristine LDH peaks (Supporting Information, Figure S1). The exchange reaction could be enhanced by elongation of the reaction time, and the pristine LDH peak intensities were reduced as the solvothermal reaction period increased for the sample prepared at 100 °C (Supporting Information, Figure S2). The exchange reaction at 120 °C for 24 h using a small amount of 1-propanol was sufficient to intercalate dicarboxylates with vertical orientation in the LDH. For the solvothermal reaction at 80 °C, a metastable phase with a basal spacing of 15.7 Å was also observed (Supporting Information, Figure S1), which disappeared when the sample was treated for an additional 48 h.

Size Effect of Dicarboxylates on the Basal Spacings. The XRD spectra and basal spacings for the LDH samples exchanged with the various α,ω-dicarboxylic acids are shown in Figure 4, indicating variable layer expansions depending upon the chain lengths of each dicarboxylate for the general formula $(CH_2)_n(COO^-)_2$. We believe that the carbonates are exchanged with dicarboxylate in the galleries. The deprotonated carboxylic groups of DC-MgAl-LDH on Si prepared in 1-propanol/toluene were confirmed by FT-IR measure-
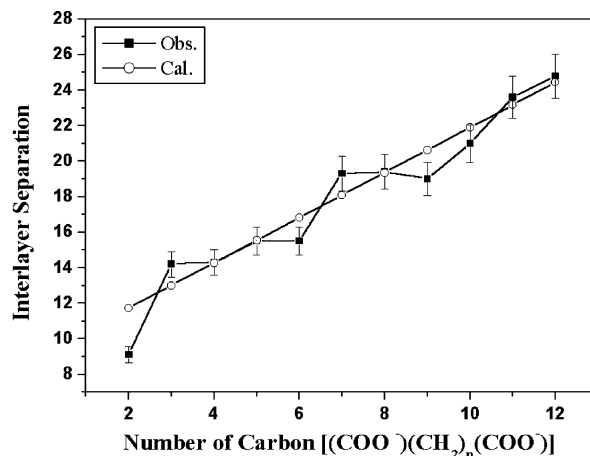

Figure 5. Interlayer separation of the various dicarboxylate-LDH products against the number of carbon atoms, *n*, in the chain of $(CH_2)_n(COO^-)_2$. The full squares correspond to observed values and the hollow circles to theoretical ones. Error bars are also given for the experimental *d* values.

ments, which gave characteristic peaks at 2919, 2850, 1470, 991 cm^{-1} corresponding to the C−H vibration, and at 1600 cm^{-1} corresponding to the C−O stretching mode. On the contrary, the peaks of CO_3^{2-} at around 1360 cm^{-1} were rarely observed in the spectra. For the selected α,ω-dicarboxylates from n3 (intercalated with glutarate) to n12 (1,12-dodecanedicarboxylate), the XRD spectra indicate that the dicarboxylates were vertically arranged or slightly tilted within the host layers. The n2 (succinate)-LDH sample gave a basal spacing of about 9.1 Å, which implies a horizontal arrangement in the interlayer space, similar to that of the terephthalate LDH samples, as discussed by Kooli et al.[21] For n9 (1,9-nonanedicarboxylate)-LDH, the pristine LDH peaks also remained. The n5 (pimelate)-LDH sample was prepared under reaction conditions different from those of the other diacids (vide infra).

Figure 5 presents a plot of interlayer separation (Å) against the carbon number (*n*) in $(CH_2)_n(COO^-)_2$. The basal spacing values (*d*) linearly increase with the chain length, *n*. Assuming the mean increase $\Delta d = 1.27$ Å/CH$_2$ from succinate to 1,12-dodecanedicarboxylate,[5a,22] the basal spacings of the (003) reflection for n4, n8, n10, n11, and n12 are close to the theoretical *d* values. The n2-, n6-, and n9-LDH compounds have basal spacings lower than the corresponding theoretical values, but the n3 and n7 compounds have basal spacings higher than the corresponding theoretical values. The basal spacings of the (003) reflection approximately correspond to the theoretical *d* values (except for n2). Because all the products above were obtained under the same solvothermal reaction conditions (except for n5), the principal factor for the interlayer separation is not clear. The XRD spectra of several samples, n4, n5, n8, and n10, show several (00*l*) harmonics, indicating their good crystallinity in the dicarboxylate-LDH samples.

We note that pimelic acid (n5) was exchanged by stepwise reaction in the mixture system (Supporting

(20) Fogg, A. M.; Green, V. M.; Harvey, H. G.; O'Hare, D. *Adv. Mater.* **1999**, *11*, 1466.

(21) Kooli, F.; Chisem, I. C.; Vucelic, M.; Jones, W. *Chem. Mater.* **1996**, *8*, 1969.

(22) Costantino, U. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1895. (b) Newman, S. P.; Jonse, W. *New J. Chem.* **1998**, *22*, 105. (c) Miyata, S.; Kumura, T. *Chem. Lett.* **1973**, 843.
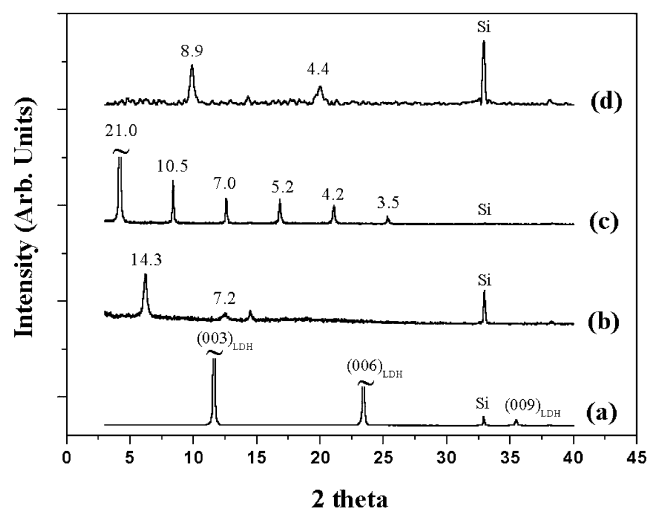
Figure 6. XRD spectra and basal spacings (Å) of the monolayer assembly of MgAl-LDH crystals on Si (a), DC-MgAl-LDH prepared in toluene (b), DC-MgAl-LDH prepared in a 1-propanol/toluene mixture (0.5%, v/v) (c), and GL-MgAl-LDH prepared using DC-MgAl-LDH in a 1-propanol/toluene mixture (0.5%, v/v) (d). The scales of the XRD spectra of (b) and (d) are multiplied by 10 to be compared with those of (a) and (c).

Information, Figure S3). First, 1,10-decanedicarboxylic acid was solvothermally exchanged into the MgAl-LDH in the 1-propanol/toluene mixture (5%, v/v) at 120 °C for 24 h, which had a basal spacing of 21 Å and a good crystallinity. The DC-MgAl-LDH samples and pimelic acid were applied under similar conditions for 24 h, which gave no XRD peak except the Si peak, but in 48 h in air, the XRD peak corresponding to a basal spacing of 15.5 Å appeared for the same sample. The aging effect for the above reaction was reproducible, showing that the aging effect is also an important factor for crystallization in the exchange reaction. Recently, Iyi et al.[23] also reported that the basal spacing of organic/LDH (starting ratio 0.75) complexes varied according to aging at different temperatures, a monophase with a vertical arrangement at a low aging temperature (25 °C), and a second staging structure at a high aging temperature (100 °C). The fact that the length of the pimelic acid anion is approximately 8.7 Å[19] is associated with the formation of a vertically arranged structure within the interlayer space.

AFM Observations for the Selected LDH Crystals. Figures 7 and 8 present the AFM images for the as-adsorbed MgAl-LDH crystals on Si and the same samples after solvothermal anion-exchange reactions. Surprisingly, most of the LDH crystals kept their lateral positions on Si after the anion exchange, and the size of the LDH crystals remained constant. For the AFM study, deposition of MgAl-LDH crystals was carried out in 2-propanol, resulting in a medium coverage of 70% for the selected surface. The heights of DC-MgAl-LDH crystals prepared in a 1-propanol/toluene mixture dramatically expanded to 2.7 times that of MgAl-LDH, as shown in the line profiles over a selected crystal (Figure 7b), corresponding to the ratio of basal spacing values, 2.7, based on the above XRD data as shown in Figure 6c. The SEM image of DC-MgAl-LDH on Si in Figure 1d showed sharp edges, indicating that the anion-
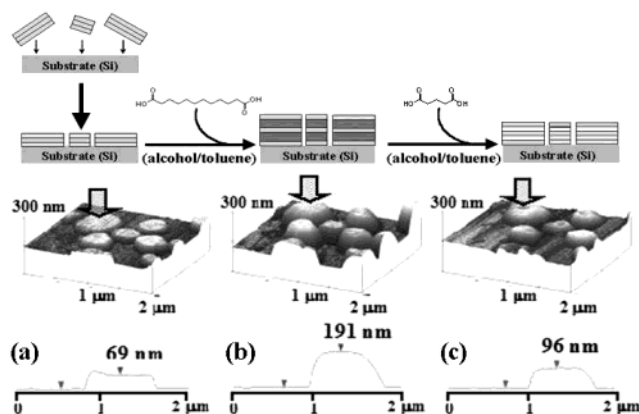

Figure 7. AFM images of selected MgAl-LDH crystals adsorbed onto silicon for MgAl-LDH (a), DC-MgAl-LDH (b), and GL-MgAl-LDH (c) prepared in a 1-propanol/toluene mixture (0.5%, v/v). Line profiles over the selected LDH crystals are also shown. The arrows indicate the selected LDH crystals.
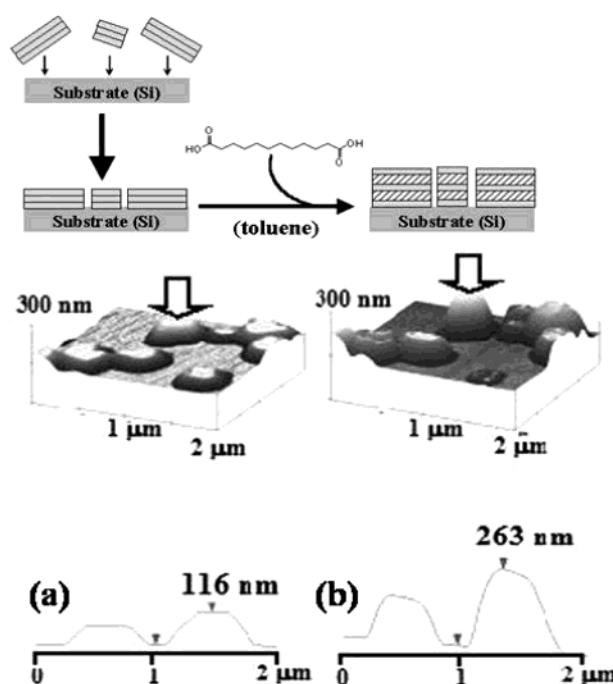

Figure 8. AFM images of selected MgAl-LDH crystals adsorbed onto silicon for MgAl-LDH (a) and DC-MgAl-LDH prepared in toluene (b). Line profiles over the selected MgAl-LDH crystals are also shown. The arrows indicate the selected LDH crystals.

exchange reactions in organic solvents have little influence on the crystallinity of the LDH layers. The edge slopes of LDH crystals in the AFM image result from the lateral tip artifacts, which have been reported in the studies for clay compounds.[24]

The consecutive anion exchange for the DC-MgAl-LDH using glutaric acid (denoted as GL-MgAl-LDH) was carried out under the same reaction conditions as the formation of DC-MgAl-LDH, resulting in an intermediate height, 96 nm, for the selected LDH crystal (Figure 7c) as well as a change of the basal spacing to 8.9 Å (Figure 6d). Thus, the anionic species can be controlled by sequential solvothermal reactions. Accord-

(23) Iyi, N.; Kurashima, K.; Fujita, T. *Chem. Mater.* **2002**, *14*, 583.

(24) Plaschke, M.; Schäfer, T.; Bundschuh, T.; Ngo Manh, T.; Knopp, R.; Geckeis, H.; Kim, J. I. *Anal. Chem.* **2001**, *73*, 4338.

ingly, in these anion-exchange processes, an important observation is that the height changes indicated in the AFM results are directly correlated with the Δd value based on the XRD data before and after anion exchange, as mentioned above. We also note that the repeated solvothermal treatments produce a rough surface of the LDH in AFM and poor crystallinity in XRD spectra.

On the other hand, for the toluene system, the heights of DC-MgAl-LDH crystals expanded to 2.3 times larger than that of the pristine LDH, as shown in the profiles over a selected crystal (Figure 8), disagreeing with the ratio of the d value, 1.8, based on the XRD data as shown in Figure 6b. Figure 8b shows an expansion along the c direction of the selected crystal without a size change along the a and b directions. The observed basal spacing values of 14.3 and 7.2 Å (this may be the second-order reflection of the former one) do not correspond to the $(00l)$ reflections as in the 1-propanol/toluene solvent system. When we regard the AFM data as direct information on the interlayer anions, the XRD data imply a different unit cell. The calculated basal spacing based on the AFM data is 17.5 Å and belongs to the many possibilities of interlayer anions: (1) a tilted linear carbon chain with $\theta = 73°$, (2) a bilayer consisting of two folded diacids with a gauche conformation in the middle of the carbon chain, (3) two-thirds of a second staging intercalate with a tilted orientation of the DC-MgAl-LDH (<21.0 Å) and carbonate-LDH (7.6 Å). Analysis of the AFM images and the XRD data of the products confirmed the presence of complex phases with different (hkl) indexing. It is possible that AFM results indicate the three-dimensional structure and the real expansion of LDH nanocrystals in the anion-exchange reactions in toluene, though the detailed structure is not solved clearly.

Conclusion

The 1-propanol/toluene mixture system prevents dissolution of LDHs and preserves the layered structure of an immobilized LDH on Si during anion-exchange reaction. The basal spacings for the MgAl-LDH samples using the various aliphatic α,ω-dicarboxylic acid anions indicated that the diacids were vertically arranged within the LDH layers, except for succinic acid, and the pimelic acid was incorporated into the LDH by stepwise reactions, involving DC-MgAl-LDH as an intermediate material. The anion-exchange reactions using immobilized LDH crystals in the 1-propanol/toluene solvent system allow the observation of the anisotropic lattice expansion of the host layer along the c axis by AFM, corresponding to an increment of basal spacings based on the XRD data with vertically arranged anions. For the toluene system, the ratio of the layer expansion based on the XRD data did not correspond to the increase of height from the AFM data, which implies that only XRD investigation of the anion-exchange reaction may drive an incorrect interpretation of the real volume expansion of LDHs.

Supporting Information Available: XRD spectra for dicarboxylate-MgAl-LDH samples prepared in various temperatures and reaction periods and for the pimelate-MgAl-LDH sample (Figures S1−S3) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM049357I