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Hydrothermal Synthesis of Layered Double Hydroxide−Deoxycholate Intercalation Compounds

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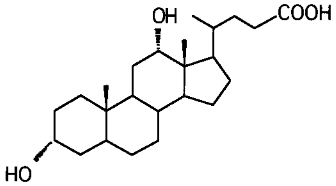
Intercalation of organic guest species into layered inorganic solids is a way of producing ordered inorganic−organic assemblies with unique microstructures controlled by host−guest and guest−guest interactions.[1,2] Among possible layered materials, layered double hydroxides (LDHs) are a class of layered materials consisting of positively charged brucite-like layers and the interlayer exchangeable anions. LDHs have extensively been investigated in a wide range of applications such as catalysts,[3] adsorbents,[4] ceramic precursors,[5] reaction media for controlled photochemical[6] and electrochemical reactions,[7] and bioactive nanocomposites.[8] Because of the unique microstructures and physicochemical properties, the syntheses of LDHs with various interlayer anions are worth investigating. In this paper, we report the synthesis of LDH−deoxycholate intercalation compounds by novel hydrothermal reactions using brucite and gibbsite as the starting materials. The molecular structure of deoxycholic acid is shown in Scheme 1.

Scheme 1. Molecular Structure of Deoxycholic Acid



Three methods, ion exchange, coprecipitation, and reconstruction, have been used for the synthesis of LDHs.[9] However, when deoxycolate was used as the guest species, all three methods were not applicable. According to the guest selectivity sequences determined by the charge and size of the anions,[10] the selectivity of the deoxycolate should be very low, so that the anion-exchange reactions using presynthesized LDHs and the coprecipitation using soluble metal salts such as chlorides and nitrates were very difficult.[11]

To overcome these synthetic limitations, magnesium and aluminum hydroxides (brucite and gibbsite) were used as the inorganic sources for the synthesis. We expected that anions, which can occupy the interlayer space of LDHs, are absent in the synthesis by using hydroxides. Because these hydroxides are almost insoluble in water, the synthesis was conducted under hydrothermal conditions. The following is a typical synthetic procedure: 0.080 g of $Mg(OH)_2$, 0.027 g of $Al(OH)_3$ ($Mg^{2+}/Al^{3+} = 4$), and 0.673 g of deoxycholic acid were mixed in deionized water at room temperature with vigorous stirring. Then, the suspension was transferred into a Teflon-lined autoclave and heated at 150 °C for 1 day. The solid precipitate was collected by filtration using a membrane filter and washed with ethanol subsequently. The pH values of the supernatant range from 8 to 10.

A sharp diffraction peak with the *d* value of 3.29 nm accompanying higher reflections was observed in the X-ray diffraction pattern[12] of the product (Figure 1), indicating the formation of a layered material. The infrared spectrum[13] of the product showed the absorption bands characteristic to the deoxycholate anions such as C−H (2935 and 2863 cm^{-1}) and COO^- (1450 and 1400 cm^{-1}). From the chemical composition of the product (Mg:13.1, Al:4.9, C:42.4 wt %, which was determined by CHN analysis and ICP), the molar ratio of Mg:Al:deoxycholate in the product was determined to be 3:1:0.8. All these observations confirmed the successful formation of the LDH−deoxycholate intercalation compound. In the present synthesis, no anions, which can occupy the interlayer space, exist except for deoxycholate and OH^-, so that deoxycholate has successfully been incorporated into the interlayer space. The hydrothermal synthesis of LDHs has been reported previously.[14] The present synthesis was conducted from

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(1) Ogawa, M. *Ann. Rep. Part C* (Royal Society of Chemistry) **1998**, *94*, 209−257.

(2) (a) *Progress in Intercalation Research*; Müller-Warmuth, W., Schöllhorn, R., Ed.; Kluwer Academic Publishers: Dordrecht, 1994. (b) Alberti, G., Bein, T., Eds.; *Comprehensive Supramolecular Chemistry. Vol. 7*; Pergamon: Oxford, 1996. (c) Ogawa, M.; Kuroda, K. *Chem. Rev.* **1995**, *95*, 399−438. (d) Ogawa, M.; Kuroda, K. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2593−2618.

(3) (a) Sels, B.; Vos, D. D.; Buntinx, M.; Pierard, F.; Mesmaeker, A. K.; Jacobs, P. *Nature* **1999**, *400,* 855−857. (b) Suzuki, E.; Ono, Y. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1008−1010. (c) Cavani, F.; Trifiro, E.; Vaccari, A. *Catal. Today* **1991**, *11*, 173.

(4) Pavan, P. C.; Gomes, G.; Valim, J. B. *Microporous Mesoporous Mater.* **1998**, *21*, 659−665.

(5) (a) Hibino, T.; Tsunashima, A. *Chem. Mater.* **1998**, *10*, 4055−4061. (b) delArco, M.; Malet, P.; Trujillano, R.; Rives, V. *Chem. Mater.* **1999**, *11*, 624−633. (c) Alejandre, A.; Medina, F.; Salagre, P.; Correig, X.; Sueiras, J. E. *Chem. Mater.* **1999**, *11*, 939−948.

(6) (a) Takagi, K.; Shichi, T.; Usami, H.; Sawaki, Y. *J. Am. Chem. Soc.* **1993**, *115*, 4339. (b) Costantino, U.; Coletti, N.; Nocchetti, M. *Langmuir* **1999**, *15*, 4454−4460.

(7) (a) Yao, K.; Taniguchi, M.; Nakata, M.; Takahashi, M.; Yamagishi, A. *Langmuir* **1998**, *14*, 2890−2895. (b) Yao, K.; Taniguchi, M.; Nakata, M.; Takahashi, M.; Yamagishi, A. *Langmuir* **1998**, *14*, 2410−2414.

(8) Choy, J. H.; Kwak, S. Y.; Park, S. J.; Jeong, Y. J.; Portier, J. *J. Am. Chem. Soc.* **1999**, *121*, 1399−1400.

(9) Trifiro, F.; Vaccari, A. in ref 2b, p 251.

(10) Miyata, S. *Clays Clay Miner.* **1983**, *31*, 305−311.

(11) When coprecipitation methods were employed using metal nitrates and deoxycholic acid, Mg/Al LDH−nitrates were obtained.

(12) X-ray powder diffraction patterns were recorded on a Rigaku RADIB powder diffractometer equipped with monochromatic Cu Kα radiation, operated at 20 mA, 40 kV.

(13) Infrared spectra were recorded on a Shimadzu FTIR8200PC by the KBr disk method.

(14) Nayak, M.; Kutty, T. R. N.; Jayaraman, V.; Periaswamy, G. *J. Mater. Chem.* **1997**, *7*, 2131.

10.1021/cm000455n CCC: $19.00

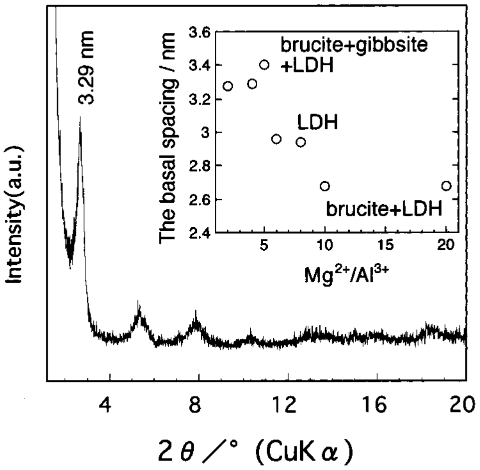

Figure 1. X-ray powder diffraction pattern of the LDH−deoxycholate intercalation compound. Inset: The relationship between the basal spacing of the products and the Mg^{2+}/Al^{3+} ratio of the starting mixtures.

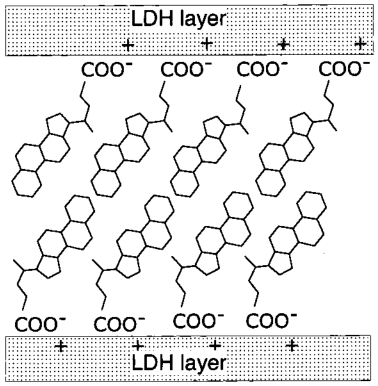

Figure 2. Schematic drawing for the microstructure of the LDH−deoxycholate intercalation compound.

brucite and gibbsite, which are insoluble in water at room temperature, to avoid the precipitation of metal salts during the mixing. Consequently, the LDH−deoxycholate intercalation compound has successfully been synthesized.

Because the thickness of the brucite-like LDH sheet is 0.48 nm, the gallery height of the LDH−deoxycholate intercalation compound was estimated to be 2.81 nm. Taking the molecular size and geometry into consideration, the intercalated deoxycholate formed a bilayer in the interlayer space where the anionic substituents (carboxylate) are thought to orient to the surface of the cationic brucite-like sheet by electrostatic interactions as schematically shown in Figure 2.

The morphology of the product is worth noting as an important characteristic feature of the present system. The morphology of inorganic-surfactant mesostructured materials have attracted attention from both fundamental and practical viewpoints.[15] The morphology of LDHs may affect their physicochemical properties and concerns about their practical applications. It is known that hydrotalcite possesses hexagonal platy morphology if carefully crystallized. (Figure 3b) However, the scanning electron micrograph[16] of the LDH−deoxycholate intercalation compounds (Figure 3a) showed a curved platy morphology. During the hydrothermal treatment, brucite and gibbsite dissolved and the LDH−deoxycholate intercalation compounds are thought to crystallize subsequently. In the present system, the cooperative organization of deoxycholate and cationic hydroxides are thought to cause the unique morphology.

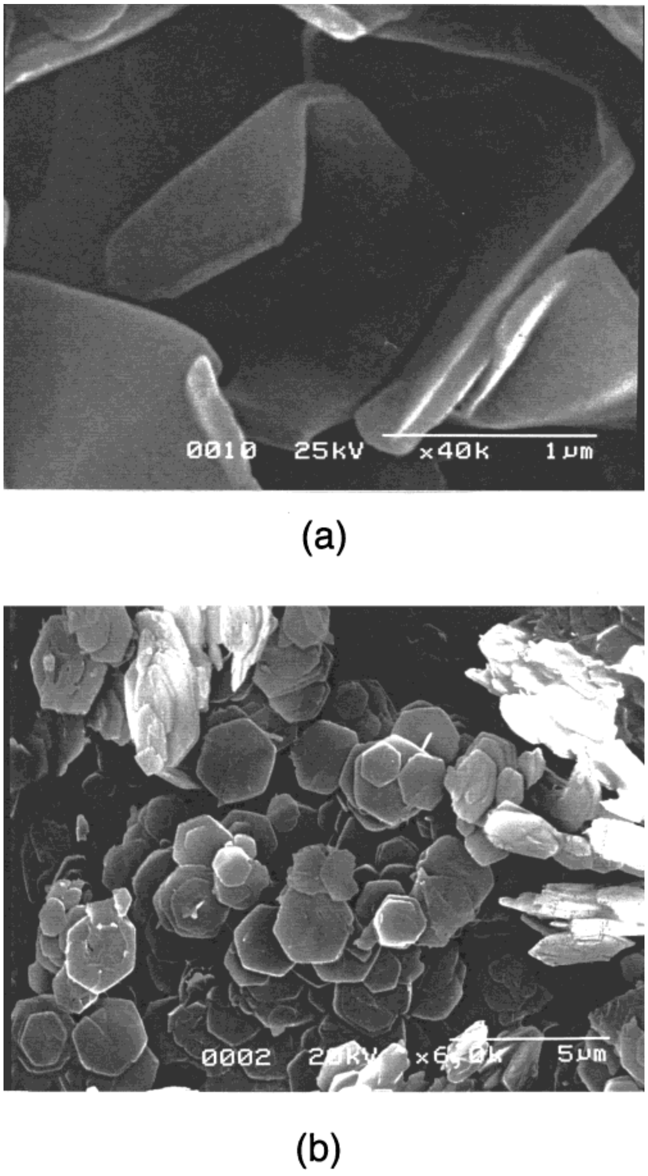

Figure 3. Scanning electron micrographs of (a) the LDH−DCA^- intercalation compound and (b) the LDH−CO_3^{2-}.

Controllable chemical composition (M^{2+}/M^{3+} ratio, which directly correlates to the anion-exchange capacity) is one of the important characteristics of LDHs. In the present study, LDH−deoxycholate intercalation compounds were prepared at different Mg^{2+}/Al^{3+} ratios (from 2 to 20). The basal spacings of the products are summarized in the Figure 1 inset in relation to the Mg^{2+}/Al^{3+} ratio of the starting mixtures. The basal spacing decreased to ≈2.7 nm with the decrease in the relative Al^{3+} amounts. The variation of the basal spacing from 3.4 to 2.7 nm suggests the change in the orientation of the intercalated deoxycholate anions probably caused by the change in the anion-exchange capacity. Because the density of the anion sites decreased at a lower anion-exchange capacity, the inclina-

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(15) Mann, S.; Ozin, G. *Nature* **1996**, *382*, 313.

(16) Scanning electron micrographs were obtained on a Hitachi S-2840N scanning electron microscope.

tion of the deoxycholate anions (Figure 2) becomes lower, resulting in the smaller basal spacings. The controlled orientation of the intercalated species is a current subject of intercalation chemistry,[1c,d,6] and the orientation and the ordering of the anions in the interlayer space of LDHs have been reported recently.[17−22] The variation in the basal spacings suggests that the controlled orientation of the guest species in LDHs was achieved in the present system. However, in addition to the change in the basal spacings, brucite was detected in the XRD patterns of the products when the Mg^{2+}/Al^{3+} ratios were larger than 5 and both gibbsite and brucite were detected for the products prepared at the Mg^{2+}/Al^{3+} ratios of 1 and 2. The difficulty in the removal of the byproducts made it difficult to determine the chemical compositions of the products.

In summary, the LDH−deoxycholate intercalation compounds, which are not available by the conventional syntheses, have been successfully synthesized by the present hydrothermal reactions using brucite and gibbsite as the starting materials. Deoxycholic acid is known as the host compound that forms molecular channels and their inclusion complexes have already been documented.[23] Alkylammonium salts of deoxycholate have also been investigated to construct a three-dimensional framework.[24] The LDH−deoxycholate intercalation compound can be a new class of material and their inclusion chemistry is worth investigating.

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(17) Tagaya, H.; Sato, S.; Kuwahara, T.; Kadokawa, J.; Karasu, M.; Chiba, K. *J. Mater. Chem.* **1994**, *4*, 1907−1912.

(18) Fogg, A. M.; Rohl, A. L.; Parkinson, G. M.; O'Hare, D. *Chem. Mater.* **1999**, *11*, 1194−1200.

(19) Cooper, S.; Dutta, P. K. *J. Phys. Chem.* **1990**, *94*, 114−118.

(20) Park, I. Y.; Kuroda, K.; Kato, C. *Chem. Lett.* **1989**, 2057−2058.

(21) Dutta, P. K.; Daniel, S. R. *Langmuir* **1994**, *10*, 1851−1856.

(22) Kanoh, T.; Shichi, T.; Takagi, K. *Chem. Lett.* **1999**, 117−118.

(23) Miyata, M.; Sada, K. In *Comprehensive Supramolecular Chemistry. Vol. 6*; MacNicol, D., Toda, F., Bishop, R., Eds.; Pergamon: Oxford, 1996; p 147.

(24) Sada, K.; Shiomi, N.; Miyata, M. *J. Am. Chem. Soc.* **1998**, *120*, 10543.