Supporting Information

Hydrogen-Bond-Driven ‘Homogeneous Intercalation’ for Rapid, Reversible, and Ultra-Precise Actuation of Layered Clay Nanosheets

Shinsuke Ishihara,* Nobuo Iyi,* Yoshihiro Tsujimoto, Satoshi Tominaka, Yoshitaka Matsushita, Venkata Krishnan, Misaho Akada, Jan Labuta, Kenzo Deguchi, Shinobu Ohki, Masataka Tansho, Tadashi Shimizu, Qingmin Ji, Yusuke Yamauchi, Jonathan P. Hill, Hideki Abe, and Katsuhiko Ariga*

Table of contents

1. Materials
2. Methods
   2.1 Synthesis of AcO-LDH
   2.2 Synthesis of AcO-LDH incorporating alcohol
   2.3 Synthesis of LDH incorporating alkylsulfonate
   2.4 Powder X-ray diffraction analysis
   2.5 Synchrotron powder X-ray diffraction (SXRD) analysis
   2.6 AFM measurement
   2.7 Solid-state $^{13}$C-CP/MAS NMR/ $T_1$ relaxation time analysis
   2.8 DSC analysis
   2.9 TG-DTA analysis
   2.10 IR spectroscopic analysis
3. Photo-image
4. Solid-state $^{13}$C-CP/MAS NMR
5. Additional data for powder XRD
6. IR spectroscopic analysis
7. TG-DTA analysis
8. DSC analysis
9. Mass change of AcO-LDH followed by incorporation of vaporous ethanol
10. $T_1$ relaxation time analysis
1. Materials

Commercially available CO$_2$-LDH, Mg$_3$Al(OH)$_6$(CO$_3$)$_4$·2H$_2$O (DHT-6, Kyowa Kagaku Kogyo Co., Ltd.), was used as starting material, and converted into Mg$_3$Al(OH)$_6$(AcO)$_2$·2H$_2$O as described below. Mg$_3$Al(OH)$_6$(ClO$_4$)$_2$·2H$_2$O was reported previously. Alcohols, acetic acid, sodium 1-pentanesulfonate, and sodium 1-decanesulfonate were purchased from Tokyo Chemical Industry Co., Ltd., and used as received. Ammonium acetate (Reagent grade, Kanto Chemical, Co., Inc.) was used as received.

2. Methods

2.1 Synthesis of AcO-LDH

AcO-LDH (Mg$_3$Al(OH)$_6$(AcO)$_2$·2H$_2$O) was prepared by anion exchange of carbonate anion (CO$_3^{2-}$) of Mg$_3$Al(OH)$_6$(CO$_3$)$_4$·2H$_2$O by modification of the reported procedures. AcO-LDHs prepared by methods (a)-(e) were identical in their properties. AcO-LDH prepared by method (a) was used in the study of incorporating alcohols.

(a) Condition 1: AcOH/AcO-Alcohol/room temperature

Mg$_3$Al(OH)$_6$(CO$_3$)$_4$·2H$_2$O (1.0 g) was dispersed in methanol (200 mL) by ultrasonic (bath-type) for 5 min, then acetic acid (0.5 mL) was dropwisely added. The suspension was stirred for 1 day under N$_2$ flow (0.1 L min$^{-1}$) at room temperature. The suspension was then centrifuged (4500 rpm, 5 min) and washed twice with methanol. Finally, the white solid was dried in vacuum overnight. Yield: 860 mg, 82.4%. No remaining CO$_3^{2-}$ was observed in the FT-IR and solid-state 13C-CP/MAS NMR profiles of the obtained AcO-LDH. (Note: Ethanol can be used throughout this ion-exchange reaction in place of methanol.)

(b) Condition 2: AcOH/AcO-Alcohol/45 °C

Mg$_3$Al(OH)$_6$(CO$_3$)$_4$·2H$_2$O (100 mg, 0.331 mmol) was suspended in methanol (40 ml) by ultrasonic, then the same molar amount of acetic acid (19.9 mg, 0.331 mmol) dissolved in methanol (10 ml) was added to the stirred suspension in a three-necked flask equipped with a water-cooled condenser under dry N$_2$ flow (0.5 L min$^{-1}$). The mixed solution was maintained stirring at 45 °C under dry N$_2$ flow. After 1-2 hours, the resulting suspension was filtrated by using a membrane filter (Omnipore, 0.2 micron) under dry N$_2$ flow. Finally, the white solid on membrane filter was dried in vacuum for 1 hour. Yield: 98 % (semi-quantitative). No remaining CO$_3^{2-}$ was observed in the FT-IR profile of the product. The same result was obtained when ethanol was used instead of methanol.

(c) Condition 3: AcONH$_4$/Methanol/room temperature

Mg$_3$Al(OH)$_6$(CO$_3$)$_4$·2H$_2$O (100 mg, 0.331 mmol) was suspended in methanol (35 ml) by ultrasonic. Then, 8 equiv. molar of ammonium acetate (204.2 mg, 2.65 mmol) dissolved in methanol (15 ml) were added to the stirred suspension under dry N$_2$ flow (0.5 L min$^{-1}$). The mixed solution was maintained stirring at room temperature (approximately 25 °C) under dry N$_2$ flow. After 1 hour, the resulting suspension was filtrated by using a membrane filter (Omnipore, 0.2 micron) under dry N$_2$ flow. The white solid on membrane filter was dried in vacuum for 1 hr and AcO-LDH containing no remaining CO$_3^{2-}$ was obtained. Yield: 100 % (quantitative).

(d) Condition 4: AcONH$_4$/Methanol/45 °C

Mg$_3$Al(OH)$_6$(CO$_3$)$_4$·2H$_2$O (100 mg, 0.331 mmol) was dispersed in methanol (40 mL) by ultrasonic (bath-type), then the same molar amount of ammonium acetate (25.5 mg, 0.331 mmol) dissolved in methanol (10 ml) was added to the stirred suspension in a three-necked flask equipped with a water-cooled condenser under dry N$_2$ flow (0.5 L min$^{-1}$). The suspension was stirred under dry N$_2$ flow (0.5 L min$^{-1}$) at 45 °C. After 2 hr, the resulting suspension was filtrated by using a membrane filter (Omnipore, 0.2 micron) under dry N$_2$ flow. The white solid on membrane filter was washed with methanol, and then dried in vacuum for 1 hr. AcO-LDH containing no remaining CO$_3^{2-}$ was obtained. Yield: 98 % (semi-quantitative).

(e) Condition 5: AcONH$_4$/Ethanol/60 °C

When ethanol was used instead of methanol for "condition 4" described above, the reaction temperature should be at least 60 °C to obtain AcO-LDH containing no remaining CO$_3^{2-}$. At 60 °C, the yield was 100% (quantitative).

References


2.2 Synthesis of AcO-LDH incorporating alcohol

Procedure (a) and (b) provide same result in XRD study. (a) Approximately 10 mg of AcO-LDH was mounted on a glass slide then about 4-5 drops of blended alcohols were added. Subsequently, the mixture was ground using a spatula until the mixture was homogeneous. The resulting mixture was used for X-ray diffraction analysis. (Even if a large excess amount of alcohol (e.g. 50 equiv. in mass) was added to AcO-LDH, XRD result was identical.)
(b) Approximately 10 mg of AcO-LDH was mounted on a glass slide then a proper amount of pure alcohol A is added by microsyringe. Subsequently, the mixture was ground using a spatula until the mixture was homogeneous. Then, a proper amount of pure alcohol B is added to the mixture of AcO-LDH and alcohol A. The mixture was well mixed using a spatula until the mixture was homogeneous. The resulting mixture was used for X-ray diffraction analysis.

2.3 Synthesis of LDH incorporating alkylsulfonate

Acetate anions (AcO⁻) of Mg₂Al(OH)₆(AcO)·2H₂O were exchanged to alkylsulfonate (C₆H₄₃O⁻·SO₄²⁻) by a conventional anion exchange method. Sodium 1-pentanesulfonate (174 mg, 1 mmol) was dissolved in methanol (10 mL) and the solution was added to Mg₂Al(OH)₆(AcO)·2H₂O (20 mg). The suspension was dispersed by applying ultrasonication (bath-type) for 30 min, then it was left for 3 days at room temperature. The suspension was then collected by centrifugation (12000 rpm, 1 min) and washed twice with methanol. Finally, the white solid was dried in vacuo. LDHs incorporating sodium 1-decanesulfonate (244 mg, 1 mmol), or a mixture of sodium 1-pentanesulfonate (87 mg, 0.5 mmol) and sodium 1-decanesulfonate (122 mg, 0.5 mmol) were prepared in the same manner.

2.4 Powder X-ray diffraction analysis

Powder X-ray diffraction analysis was performed at a scan rate of 2θ = 2 degree min⁻¹ using a Rigaku RINT 1200 diffractometer with Ni-filtered CuKα radiation (λ = 1.5418 Å). Measurements were conducted at 25 °C under N₂ flow (0.1 L min⁻¹). The basal spacing corresponds to the d₀₀₃ of the unit cell, which is the c-value of the sub-cell containing one interlayer space and one-third the LDH unit cell. When methanol, ethanol, and 1-propanol were incorporated into AcO-LDH, N₂ gas was saturated with alcohol vapor in order to prevent the evaporation of alcohols during XRD measurements. (In addition, LDH was confirmed to be wet after XRD measurement.)

2.5 Synchrotron powder X-ray diffraction (SXRD) analysis

SXRD measurements were carried out at room temperature using a Debye-Scherrer camera with λ = 0.65298 Å installed on NIMS beamline (BL15XU) at SPring-8. AcO-LDH (c.a. 5 mg) was loaded into a Lindemann glass capillary (Ø= 0.3 mm) then mixed with alcohols within the capillary using another Lindemann glass capillary (Ø = 0.1 mm).

2.6 Atomic Force Microscopy (AFM) measurements

AcO-LDH (20 mg) suspended in ethanol (5 ml) was treated by ultrasonication for 1 min. Then 1 drop of supernatant solution was dropped on a glass substrate. The sample was immediately made ready for AFM measurement under an atmosphere purged with dry N₂. AFM images were obtained using a commercial DFM unit (SPA-400-SPI4000, Seiko Instrument Inc., Chiba, Japan) equipped with a calibrated 20-μm xy-scan and 10-μm z-scan range PZT-scanner. AFM images were taken in dynamic force mode (DFM mode, i.e. tapping mode) at optimal force. A rectangular-shaped silicon cantilever (SI-DF-20, Seiko Instrument Inc.), with a spring constant of 13 N m⁻¹ and frequency resonance of 133 kHz, was used for imaging. All operations were performed either under dry N₂ flow or under ethanol saturated N₂ flow at room temperature. Heights of images were estimated using accessory software supplied with AFM instrument.

2.7 Solid-state ¹³C-CP/MAS NMR / T₂ relaxation time analysis

High-resolution solid-state NMR experiments were carried out at 125.7 and 500.1 MHz for ¹³C and ¹H, respectively, using a JEOL ECA500 spectrometer. This instrument is equipped with a high power amplifier for proton decoupling and a CP/MAS (cross polarization/ magic angle spinning) probe. Spectra were externally referenced to the methyl carbon signal of hexamethylbenzene (17.4 ppm relative to TMS). Samples were packed as powders in a ZrO rotor (Ø = 4 mm). The MAS frequency was set to 15 kHz and sample temperature was 300 ± 3 K. Contact time was 2 ms, with a pulse delay of 5 s. The Torchia pulse sequence was used for T₂ relaxation time measurement.

2.8 DSC analysis

Differential scanning calorimetry (DSC) measurements were conducted using a MAC DSC 3100S (MAC Science Co., Ltd.) at 5 °C min⁻¹ under N₂ flow (0.1 L min⁻¹) in the range of 30 °C to ~40 °C using Al₂O₃ powder as a standard material. The mixture of AcO-LDH (20 mg) and alcohol mixtures (8 mg) were loaded in an Al pan.

2.9 TG-DTA analysis

Simultaneous thermogravimetry/differential thermal analysis (TG-DTA) was conducted using a MAC TG-DTA 2000 (MAC Science Co., Ltd.) at 10 °C min⁻¹ under N₂ atmosphere over the range from room temperature to 1200 °C using Al₂O₃ powder as a standard. A mixture of AcO-LDH (5 mg) and octanol (5 mg) was loaded in a Pt pan.

2.10 Infrared spectroscopic analysis

FT-IR transmittance spectra were recorded using a NEXUS 670 FT-IR spectrometer at room temperature under dry N₂ atmosphere. AcO-LDH (50 mg), octanol (5 mg), and ethanol (20 mg) were mixed, then the mixture was loaded on a BaF₂ substrate. Ethanol was removed using a stream of warm air, then IR spectra were measured. Note that ethanol was used for the homogeneous dispersion of octanol into AcO-LDH.
3. Photo-image

![Photo-image](image)

**Figure S1.** Photographs of AcO-LDH (left) and AcO-LDH mixed with 1-pentanol (right).

4. Solid state $^{13}$C-CP/MAS NMR

![Solid state $^{13}$C-CP/MAS NMR spectrum](image)

**Figure S2.** Solid state $^{13}$C-CP/MAS NMR spectrum of AcO-LDH. No remaining $^{13}$C-signal for CO$_3^{2-}$ was observed.
5. Additional data for powder XRD

Figure S3. (A) Powder XRD patterns of the mixtures of AcO-LDH with different alcohols at 25 °C under N₂ atmosphere. Red, green, blue indicate \(d_{003}\), \(d_{006}\), and \(d_{009}\), respectively. \(n\) indicates the number of carbon atoms in the primary alcohols, \(C_nH_{2n+1}OH\). (B) Relationship between the number of carbon atoms \(n\) in the primary alcohol and distance \(d\) between LDH-nanosheets. \(d = (d_{003} + 2d_{006} + 3d_{009})/3\). (C) Schematic representation of alcohol molecules within the interlayer of LDH. Note that water and acetate anions are omitted for clarity.

Figure S4. Powder XRD patterns of AcO-LDH demonstrating reversible intercalation of ethanol.
Figure S5. Powder XRD patterns of the mixture of AcO-LDH and alcohol at 25 °C under N₂ atmosphere. Black: A₈ + A₁₂ (3:2), Red: A₈ + A₁₂ (4:1).

Figure S6. Powder XRD patterns of CO₃-LDH with and without A₈, indicating that CO₃-LDH does not incorporate alcohol. A typical example of the segregation of differently-sized guest molecules when guests are incorporated into LDH by ion-exchange reaction.
Figure S7 Powder XRD patterns of ClO$_4$-LDH with and without C$_5$H$_{11}$OH, indicating that ClO$_4$-LDH does not incorporate alcohol.

Figure S8 Powder XRD patterns of LDH incorporating alkylsulfonate, indicating that C$_{3}$H$_{11}$SO$_3$ and C$_{10}$H$_{21}$SO$_3$ are not homogeneously incorporated into the inter-layer gap of LDH.
Figure S9. (A) Powder XRD patterns for AcO-LDH incorporating $\text{A}_5$-$\text{A}_6$ mixture measured at 25°C under N$_2$ atmosphere. (B) Relationship between composition of $\text{A}_5$ in $\text{A}_6$ and averaged distance between nanosheets $d$. $d = (d_{003} + 2d_{006} + 3d_{009})/3$. (C) Detailed results for powder XRD analysis of AcO-LDH incorporating $\text{A}_5$-$\text{A}_6$.

Figure S10. Powder XRD patterns for AcO-LDH incorporating $\text{A}_8$ at different relative humidity (RH) conditions, indicating that water molecules replace with $\text{A}_8$ at a RH of 83.8%.
Figure S11. (A) XRD patterns of AcO-LDH under exposure to vaporous alcohols, $A_nV$. (B) XRD patterns of AcO-LDH under exposure to vapors such as $A_1$, $A_2$, and $A_1 + A_2$. 

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013
6. IR spectroscopic analysis

![IR spectra of AcO-LDH and CO3-LDH](image)

**Figure S12.** IR spectra of AcO-LDH and CO3-LDH on BaF₂ substrate at 25°C under N₂ atmosphere.

7. TG-DTA analysis

![TG-DTA diagrams](image)

**Figure S13.** TG-DTA diagram for (A) AcO-LDH (5.2 mg) + octanol (6.2 mg) and (B) AcO-LDH (10.0 mg).
8. DSC analysis

Figure S14. DSC traces of mixtures of AcO-LDH and octanol with different mixing ratios. Exo- and endo-thermic peaks are not symmetric because of slow scan rate during cooling processes. It appears that octanol incorporated within AcO-LDH cannot be distinguished from not incorporated octanol from DSC data.
9. Mass change of AcO-LDH followed by incorporation of vaporous ethanol

Figure S15. Mass changes of AcO-LDH on exposure to ethanol vapor (A2V). AcO-LDH was placed in a glass bottle with rubber cap, and the environment inside glass bottle was replaced by dry N2 flow (0.1 L min⁻¹) or A2 vapor flow (0.1 L min⁻¹). Mass changes of AcO-LDH were determined after saturation with N2 or A2V. AcO-LDH showed 28.4% increase of its mass, which almost corresponds to the adduct of two ethanol molecules with Mg₃Al(OH)₆(AcO)·2H₂O.
10. $T_1$ relaxation time analysis