Supporting Information

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

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1. Materials

Commercially available **CO₃-LDH**, Mg₃Al(OH)₈(CO₃)_{0.5}·2H₂O (DHT-6, Kyowa Kagaku Kogyo Co., Ltd.), was used as starting material, and converted into Mg₃Al(OH)₈(AcO)·2H₂O as described below. Mg₃Al(OH)₈(ClO₄)·2H₂O was reported previously.^{S1} 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 $(Mg_3Al(OH)_8(AcO) \cdot 2H_2O)$ was prepared by anion exchange of carbonate anion $(CO_3^{2^-})$ of $Mg_3Al(OH)_8(CO_3)_{0.5} \cdot 2H_2O$ by modification of the reported procedures. ^{S2,S3,S4} **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/Alcohol/room temperature

 $Mg_3Al(OH)_8(CO_3)_{0.5}$ •2H₂O (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 N₂ 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 vaccum 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/Alcohol/45 °C

 $Mg_3Al(OH)_8(CO_3)_{0.5}$ ·2H₂O (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 threenecked flask equipped with a water-cooled condenser under dry N₂ flow (0.5 L min⁻¹). The mixed solution was maintained stirring at 45 °C under dry N₂ flow. After 1-2 hours, the resulting suspension was filtrated by using a membrane filter (Omnipore, 0.2 micron) under dry N₂ flow. Finally, the white solid on membrane filter was dried in vaccum 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: AcONH₄/Methanol /room temperature

 $Mg_3Al(OH)_8(CO_3)_{0.5}$ · $2H_2O$ (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 N₂ flow (0.5 L min⁻¹). The mixed solution was maintained stirring at room temperature (approximately 25 °C) under dry N₂ flow. After 1 hour, the resulting suspension was filtrated by using a membrane filter (Omnipore, 0.2 micron) under dry N₂ flow. The white solid on membrane filter was dried in vaccum for 1 hr and AcO-LDH containing no remaining CO_3^{2-} was obtained. Yield: 100 % (quantitative).

(d) Condition 4: AcONH₄/Methanol /45 °C

 $Mg_3Al(OH)_8(CO_3)_{0.5} \cdot 2H_2O$ (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 N₂ flow (0.5 L min⁻¹). The suspension was stirred under dry N₂ 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 N₂ flow. The white solid on membrane filter was washed with methanol, and then dried in vaccum for 1 hr. AcO-LDH containing no remaining $CO_3^{2^-}$ was obtained. Yield: 98 % (semi-quantitative).

(e) Condition 5: AcONH₄/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

- S1. N. Iyi, H. Yamada, Chem. Lett. 2010, 39, 591.
- S2. A. Hayashi, H. Nakayama, Chem. Lett. 2011, 40, 276.
- S3. N. Iyi, H. Yamada, T. Sasaki, 2011, Jpn. Pat. Pend. 2011-188138.
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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 eqiv. 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 microsyrinege. 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 Mg₃Al(OH)₈(AcO)·2H₂O were exchanged to alkylsulfonate ($C_nH_{2n+1}SO_3^-$) 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 Mg₃Al(OH)₈(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 $2\theta = 2$ degree min⁻¹ using a Rigaku RINT 1200 diffractometer with Ni-filtered CuK_a radiation ($\lambda = 1.5418$ Å). Measurements were conducted at 25 °C under N₂ flow (0.1 L min⁻¹). The basal spacing corresponds to the d_{003} 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 $\lambda = 0.65298$ Å installed on NIMS beamline (BL15XU) at SPring-8. AcO-LDH (c.a. 5 mg) was loaded into a Lindemann glass capillary ($\emptyset = 0.3$ mm) then mixed with alcohols within the capillary using another Lindemann glass capillary ($\emptyset = 0.1$ 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- μ m xy-scan and 10- μ m 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 / T_1 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 ($\emptyset = 4$ 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 T_1 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 N_2 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 homogenesous dispersion of octanol into **AcO-LDH**.

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3. Photo-image



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

4. Solid state ¹³C-CP/MAS NMR



Figure S2. Solid state ¹³C-CP/MAS NMR spectrum of **AcO-LDH**. No remaining ¹³C-signal for CO₃²⁻ was observed.

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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.

5. Additional data for powder XRD



Figure S5. Powder XRD patterns of the mixture of **AcO-LDH** and alcohol at 25 °C under N₂ atmosphere. Black: $A_8 + A_{12}$ (3:2), Red: $A_8 + A_{12}$ (4:1).



Figure S6 Powder XRD patterns of CO_3 -LDH with and without A_5 , indicating that CO_3 -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 **ClO₄-LDH** with and without C₅H₁₁OH, indicating that **ClO₄-LDH** does not incorporate alcohol.



Figure S8 Powder XRD patterns of LDH incorporating alkylsulfonate, indicating that $C_5H_{11}SO_3^-$ and $C_{10}H_{21}SO_3^-$ are not homogeneously incorporated into the inter-layer gap of LDH.

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Figure S9. (A) Powder XRD patterns for **AcO-LDH** incorporating A_5 - A_6 mixture measured at 25°C under N₂ atmosphere. (B) Relationship between composition of A_5 in 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 A_5 - A_6 .



Figure S10. Powder XRD patterns for AcO-LDH incorporating A_8 at different relative humidity (RH) conditions, indicating that water molecules replace with 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 $A_1 + A_2$.

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





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





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 (A_2V). **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 A_2 vapor flow (0.1 L min⁻¹). Mass changes of **AcO-LDH** were determined after saturation with N₂ or A_2V . **AcO-LDH** showed 28.4% increase of its mass, which almost corresponds to the adduct of two ethanol molecules with Mg₃Al(OH)₈(AcO)·2H₂O.

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10. T_1 relaxation time analysis





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