Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information

Layered Double Hydroxide (LDH)-based Monolith with Interconnected Hierarchical Channels: Enhanced Sorption Affinity for Anionic Species

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Supporting Methods

Supporting Figures

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Method S1: Preparation of LDH powders. Hydrotalcite-type LDH intercalated by chloride anion was synthesized by a co-precipitation reaction according to the method reported by Constantino et al.[1] A mixture of $MgCl_2 \cdot 6H_2O$ (20.0 g; 100 mmol) and $AlCl_3 \cdot 6H_2O$ (11.87 g; 50.0 mmol) was dissolved in 200 mL of ultrapure water. The aqueous solution was added to 100 mL of NaOH (>97%, Wako Pure Chemical Industries) solution at pH 10 under a N_2 flow. The pH was kept at 10 by the continuous addition of 2 M NaOH under a N_2 flow. The resultant suspension was stirred overnight under a N_2 flow at 70 °C. The solid product was isolated by centrifuging, washing with ultrapure water, and drying at 70 °C. Mg/Al ratio of the LDH powders was 2.3. The powdery LDH was used as c-gel after the heat treatment at 500 °C. Also, the LDH powders were uniaxially pressed (P-16B, Riken Seiki, Japan) into cylinders at a pressure of 40 MPa to produce a LDH pellet, followed by heating at 500 °C (c-pellet).

Supporting Figures:

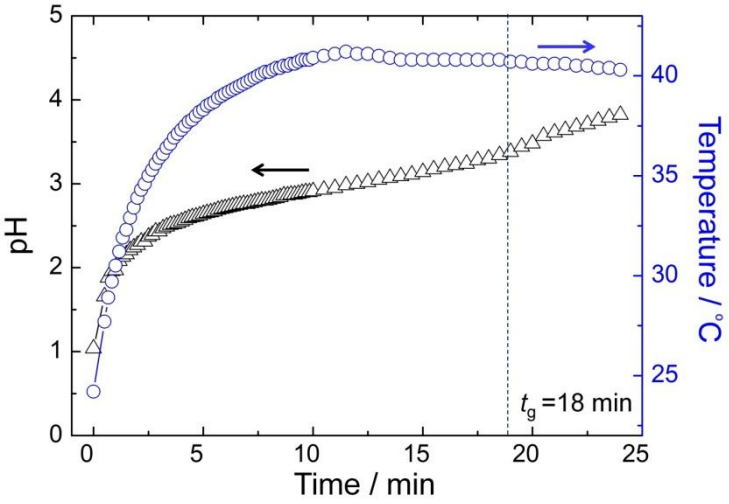

Figure S1. Increase of pH in a reaction solution with a nominal molar ratio of Mg/Al = 0.8. $AlCl_3 \cdot 6H_2O$ (6.55 mmol) and $MgCl_2 \cdot 6H_2O$ (5.23 mmol) were dissolved in a mixture of water (222 mmol) and ethanol (51.4 mmol). After the addition of PO (26.2 mmol) at 25 °C, time evolution of pH in a reaction solution was collected at 40 °C. Black triangle and blue circle correspond to pH and temperature in the reaction solution, respectively. t_g: gelation time. pH at the gelation point is 3.3.

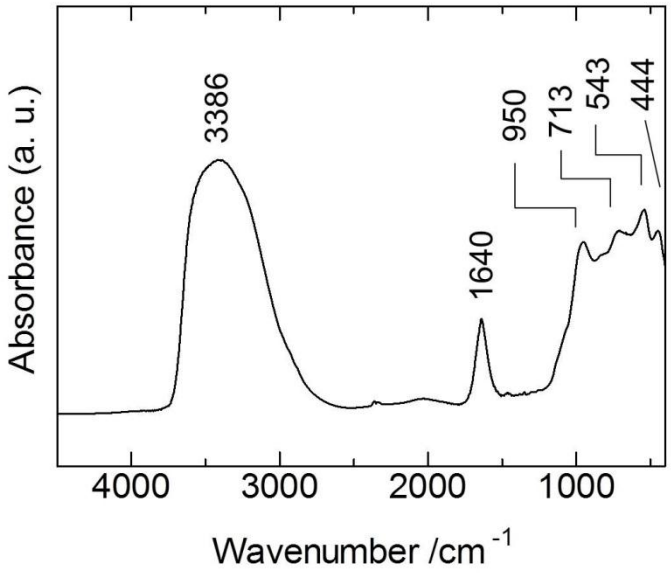

Figure S2. FT-IR spectrum of monolithic xerogel. The absorption bands around 400−900 cm^{-1} are interpreted as the lattice vibration modes of M–O and M−OH (M: Al or Mg),[2, 3] The bands at 1640 cm^{-1} and 3386 cm^{-1} are derived from vending vibration of water molecules,[4, 5] and a superposition of O−H stretching bands, respectively.[3] The notable is that there is no peak corresponding to CO_3^{2-}; absorption peaks derived from CO_3^{2-} in a hydroxide gallery appear in a range of 1400−1500 cm^{-1}.[6]

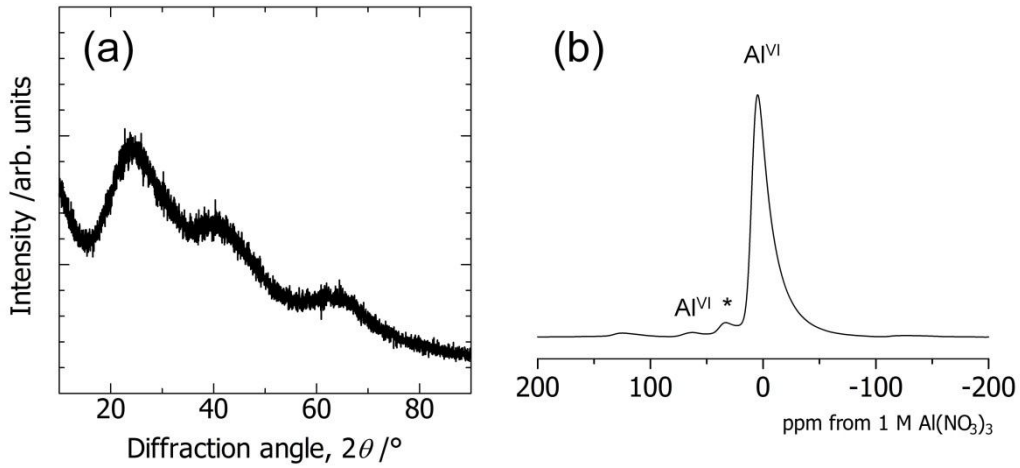

Figure S3. (a) XRD pattern and (b) ^{27}Al MAS NMR spectrum of xerogel prepared without $MgCl_2 \cdot 6H_2O$. (a) Broad unidentified peaks indicate low crystallinity (amorphous-like crystalline nature). (b) It is known that fully crystallized aluminum hydroxides are comprised of octahedral-coordinated Al (Al^{Vl}) and tetrahedral-coordinated Al (Al^{IV}). The additional peak at 32 ppm marked asterisk is generally attributed to pentahedral-coordinated Al (Al^{V}),[7] which are observed in aluminates with poor crystallinity.[8] Thermal gravimetric (TG) analysis reveals the obtained material is $Al(OH)_3$.

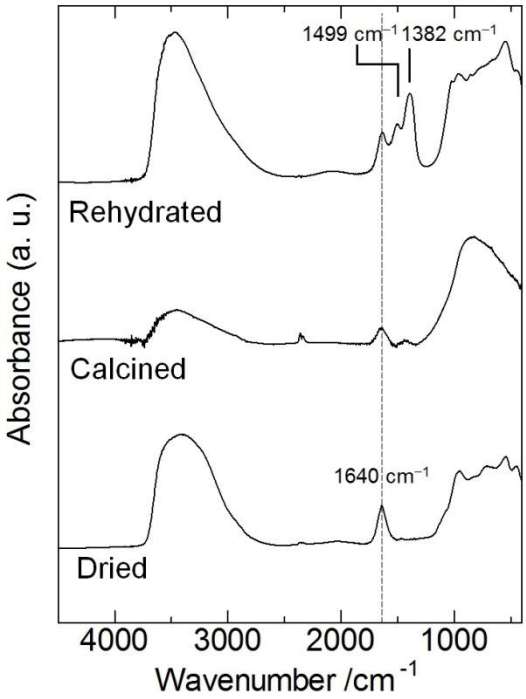

Figure S4. FT-IR spectra of xerogel at respective steps in rehydration process. The dotted line is guide for see. The peaks of 1499 and 1382 cm^{-1} observed after rehydration are ascribed to CO_3^{2-} ions introduced in interlayers.[6]

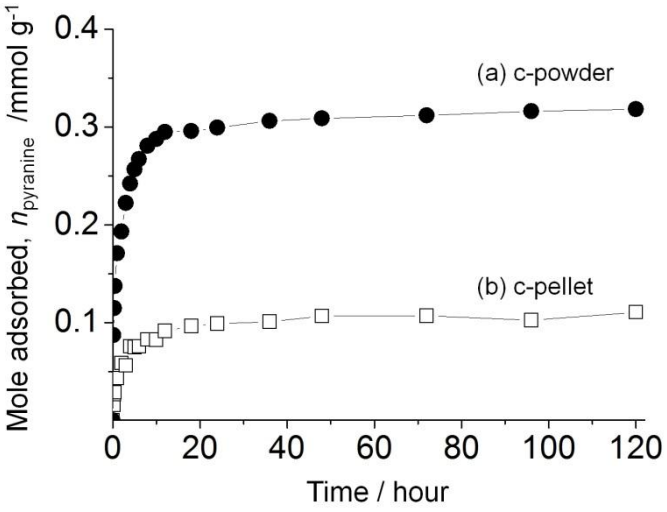

Figure S5. Pyranine adsorption properties of c-pellet and c-powder. Sample mass: 0.23 g; outer surface are of c-pellet: 185 mm^2. The result clearly shows the diffusion limitation; c-pellet shows lower pyranine accumulation due to smaller amount of accessible reaction sites.

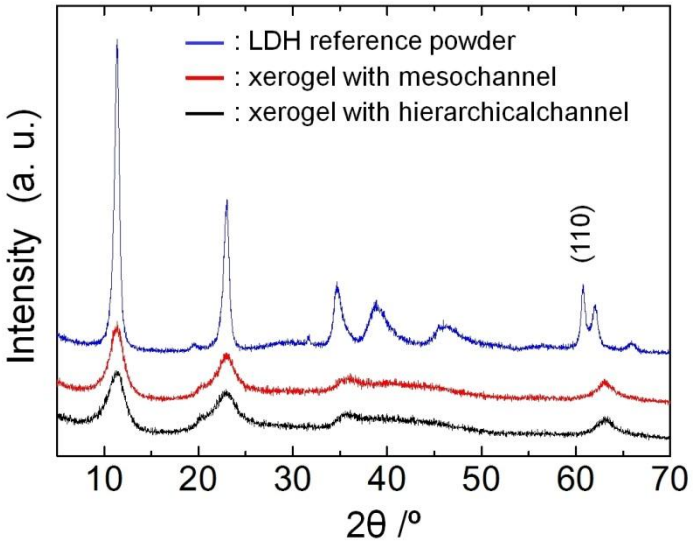

Figure S6. XRD patterns of the reference LDH powder and xerogels. The sharp (110) diffraction observed in LDH reference pellet indicates large in-plane dimension of crystallites. The crystalline size estimated by Scherrer's equation is 24 nm. Broad diffraction lines at ~63° for xerogels can be assigned to supernatant of (110) and (113) diffractions, indicating small in-plane dimension of their crystallite sizes

References

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