

Supporting Information

Molecular sieving through interlayer galleries

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SI-1 Structure illustration of LDHs

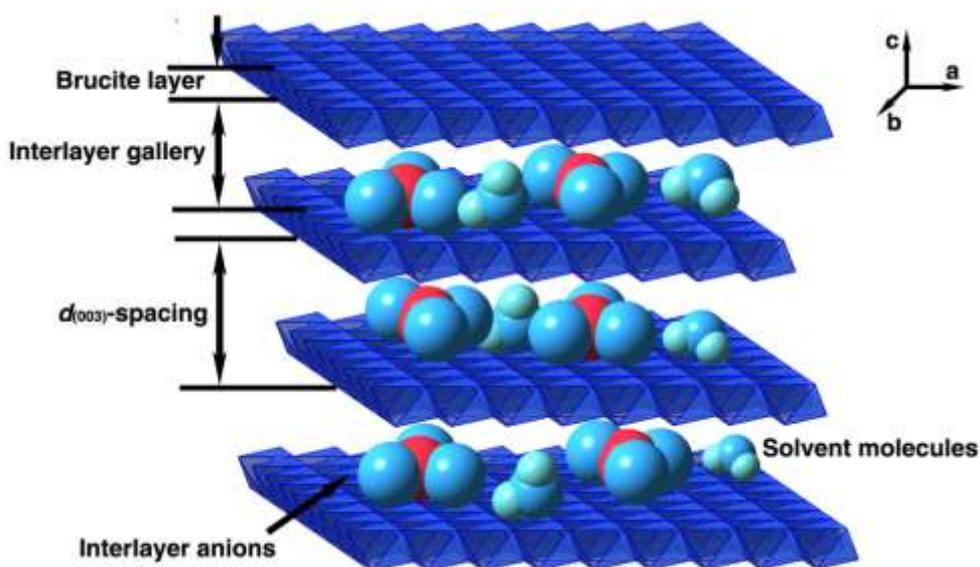


Fig. S1 Schematic illustration of the structure of layered double hydroxide crystals. Brucite-like layers composed of interconnected M^{2+} and M^{3+} metal hydroxide in octahedral geometry stack along the crystallographic c -axis, while water molecules and charge compensating anions are located in the interlayer gallery.

SI-2 Synthesis of asymmetric NiAl-NO₃ LDH membrane

Preparation of the substrate: Porous alumina asymmetric porous substrates were supplied by Fraunhofer-Institut. Diameter and thickness of the substrate were 18mm and 1 mm, respectively. Before in-situ growth, a γ -Al₂O₃ intermediate layer was deposited onto the top of the porous alumina substrate.

In-situ growth of NiAl LDH membrane: The precursor solution was prepared by adding 5.8 g Ni(NO₃)₂·6H₂O (98.0 wt. %, Merck) and 4.8 g NH₄NO₃ (Aldrich, 98.0 wt.%) into 100 ml CO₂-saturated water (Vitalitasia Classic, containing saturated CO₂). Consequently 10 ml 1 wt.% NH₃·H₂O (Aldrich, 28 wt.%) was added dropwise into the aqueous solution and stirred in an ice bath for 10 min.

γ -Al₂O₃-modified alumina asymmetric substrate was vertically placed into a 50 ml Teflon-lined stainless vessel. Then 35 ml of aqueous solution was poured into the vessel and sealed. The vessel was put into convective oven with the temperature pre-heated to 85 °C. After an elapsed time of 40 h, it was taken out and cooled to room temperature in air. Finally the membrane was taken out and washed with copious of DDI water. Before gas separation measurement, the membrane was dried in a convective oven at 60 °C for 12 h.

SI-3 LDH layer grown on bare α - Al_2O_3 substrate

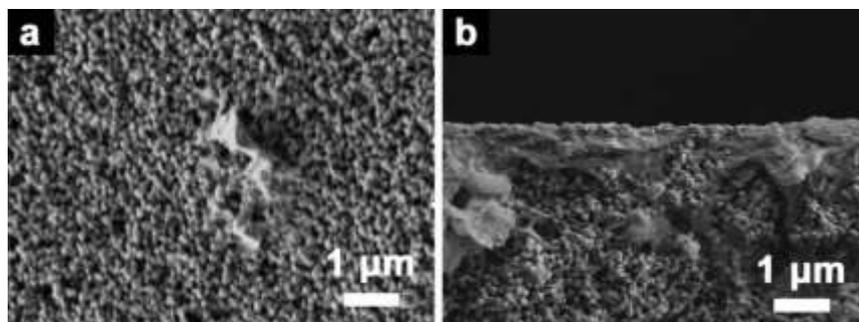


Fig. S2 SEM image of LDH layer directly in-situ grown on bare porous asymmetric α - Al_2O_3 substrate. Hydrothermal growth was kept at 85 °C for 40 h. (a) The top image, and (b) the cross-sectional image.

SI-4 Demonstration of the gas separation equipment

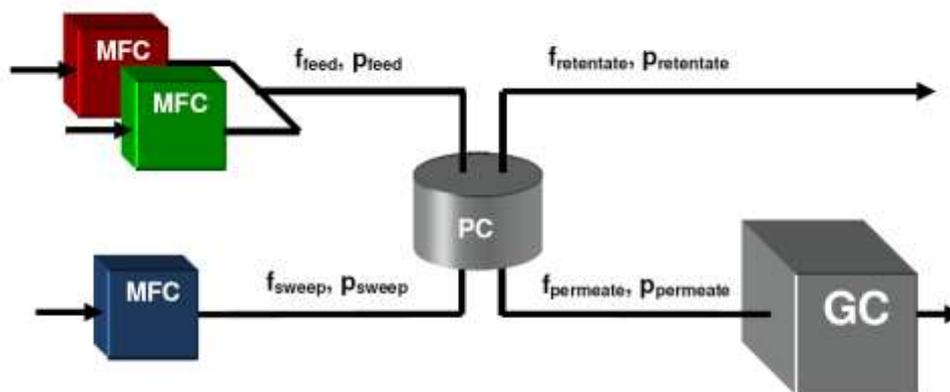


Fig. S3 Measurement equipment for both single and mixed gas permeation. MFC: mass flow controller; PC: permeation cell with mounted membrane; GC: gas chromatograph; f : volumetric flow rate; p : pressure.

SI-5 Details on gas separation experiment

For the mixed gas permeation measurements, the prepared LDH membrane was fixed in a module sealed with high-temperature-resistant silicone O-rings. A1:1 mixture of gas is applied to the feed side of the membrane, and the permeate gas is removed from the permeate side by sweep gas. The feed flow rate was kept constant with a total volumetric flow rate of 100 ml min⁻¹ (each gas of 50 ml min⁻¹). Pressures at both feed side and permeate side were kept at 1 bar. In the H₂/CH₄ measurement, N₂ was employed as the sweep gas.

A calibrated gas chromatograph (HP6890) is used to measure the concentration of gas mixtures on the permeate side. The separation factor $\alpha_{i,j}$ of a binary gas mixture is defined as the quotient of the molar ratios of the components (i, j) in the permeate side, divided by the quotient of the molar ratio of the components (i, j) in the feed side:

$$\alpha_{i/j} = \frac{x_{i,\text{perm}}/x_{j,\text{perm}}}{x_{i,\text{feed}}/x_{j,\text{feed}}}$$

SI-6 Relationship between operation temperature and gas separation performance of NiAl-CO₃ LDH membrane

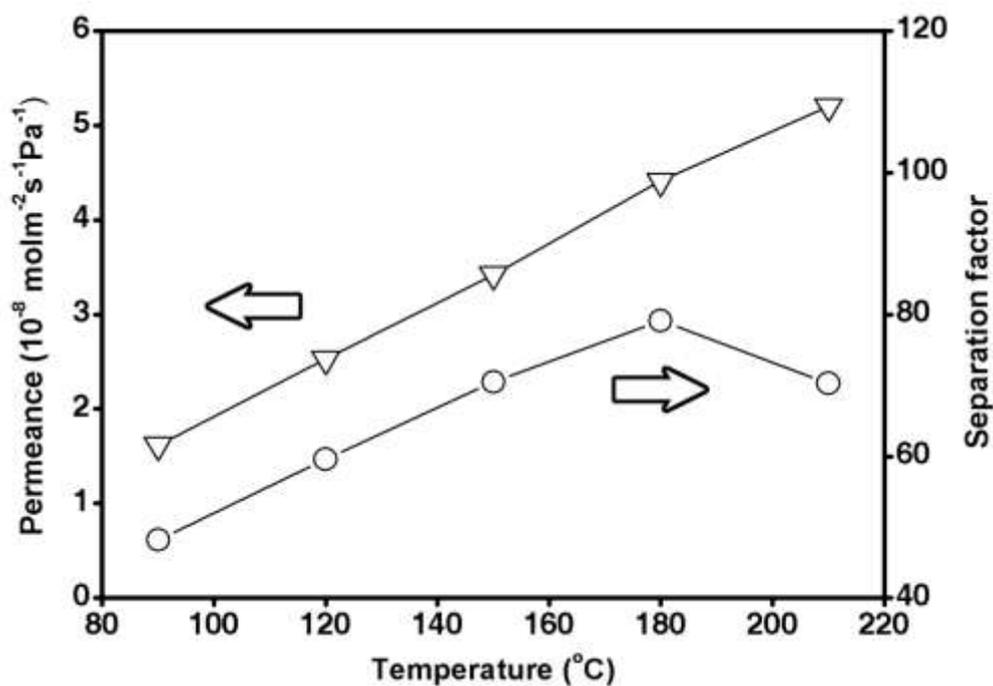


Fig. S4 H₂ Permeance and the separation factor of equimolecular H₂/CH₄ mixture on NiAl-CO₃ LDH membrane as a function of temperature. $\Delta P = 1$ bar.

SI-7 Mixed gas separation performance of NiAl-CO₃ LDH membrane

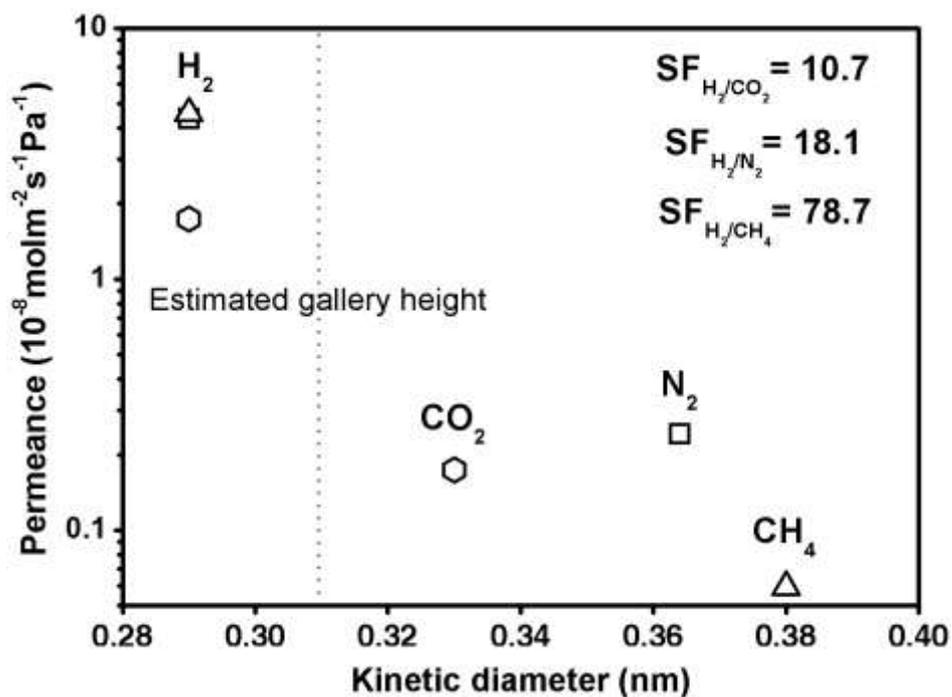


Fig. S5 Permeances of the components of 1:1 mixtures of H₂/CO₂ (hexagons), H₂/N₂ (squares) and H₂/CH₄ (triangles) of the NiAl-CO₃ LDH membrane at $\Delta P = 1$ bar, $T = 180$ °C as a function of molecular kinetic diameters.

SI-8 XRD pattern of prepared ZnAl LDH

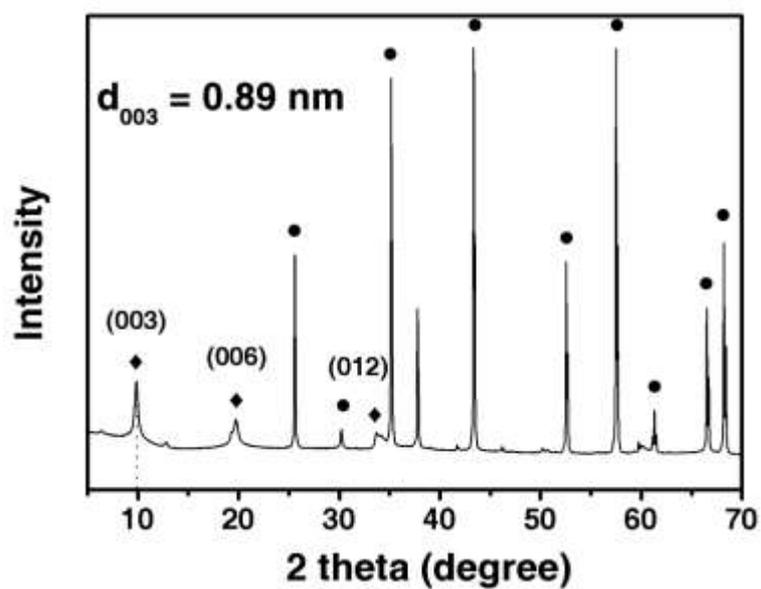


Fig. S6 XRD pattern of prepared ZnAl LDH membrane. Peaks marked with black dots and black rhombuses represent the diffraction peaks from substrate and LDH phase, respectively.