Supporting Information

In-situ Formation of LDH Membranes of Different Microstructure with Molecular Sieve Gas Selectivity

Yi Liu, Nanyi Wang and Jürgen Caro**

Institute of Physical Chemistry and Electrochemistry, Leibniz University Hannover, Callinstr. 3A, D-30167 Hannover, Germany

SI-1 EDXS measurement within the substrate pores of the *ab*-oriented NiAl-CO_3 LDH membrane

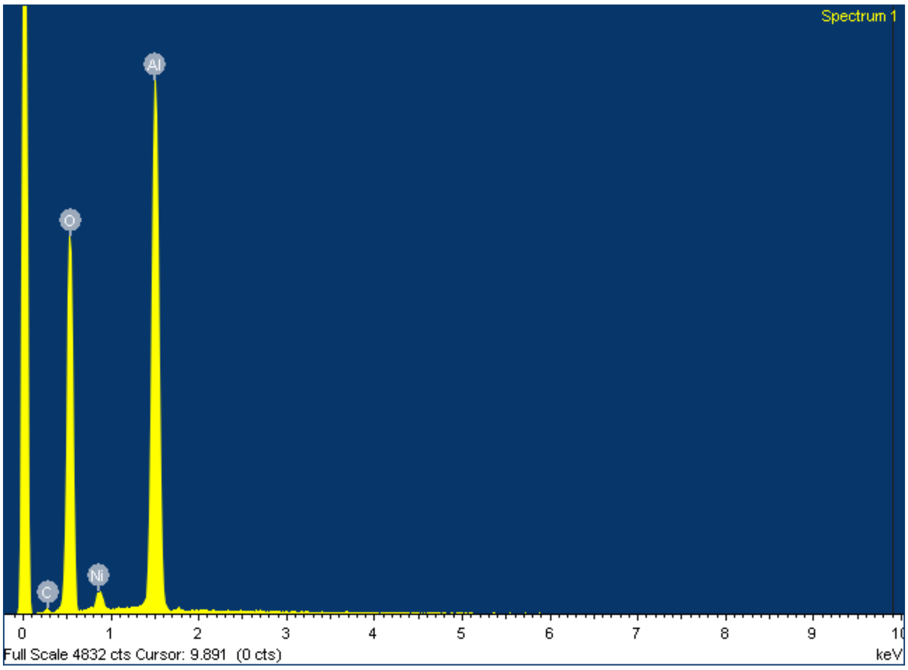

Fig. S1 EDXS of the cross-section of the *ab*-oriented NiAl-CO_3 LDH membrane.

SI-2 Powder XRD pattern of NiAl-CO_3 LDHs

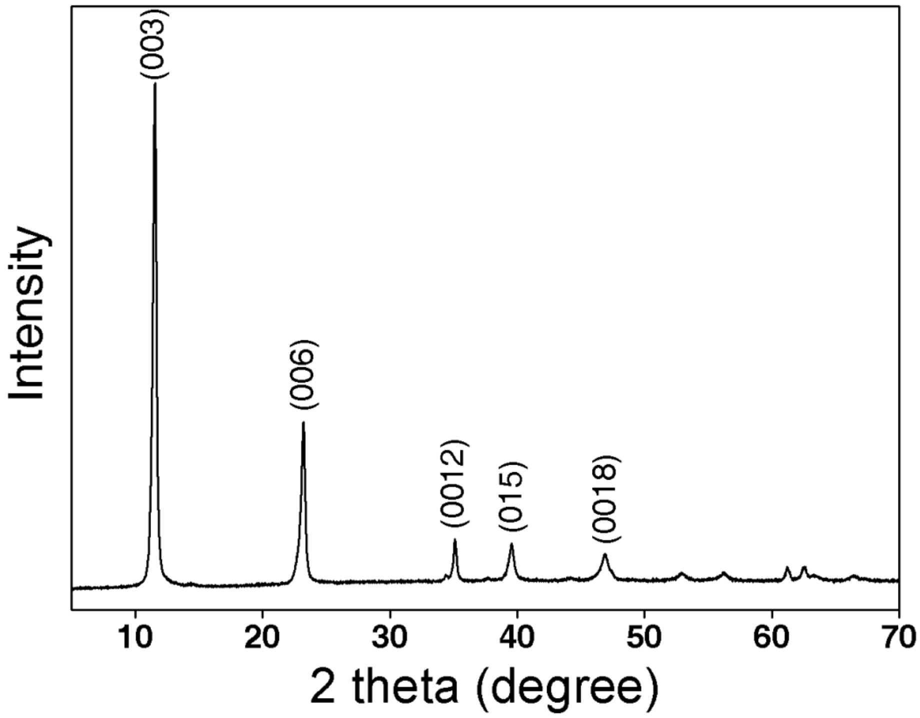

Fig. S2 Powder XRD pattern of NiAl-CO_3 LDHs which were synthesized according to the published recipe (M. Wei, X. Y. Xu, X. R. Wang, F. Li, H. Zhang, Y. L. Lu, M. Pu, D. G. Evans and X. Duan, *Eur. J. Inorg. Chem.*, 2006, 2831).

SI-3 EDXS of the top side of the randomly oriented NiAl-CO_3 LDH membrane

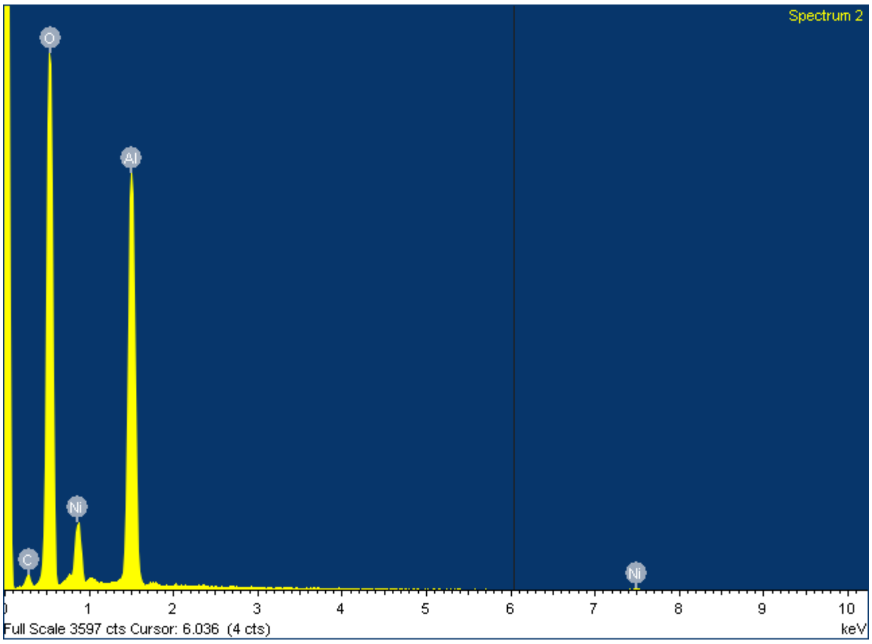

Fig. S3 Surface EDXS of the randomly oriented NiAl-CO_3 LDH membrane.

SI-4 Calculation of the concentration of CO_2 in different precursor solutions

According to *Henry's Law*: **At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid.**

Herny's Law is well-known and can be expressed as follow:

$$c_{aq} = k_H \cdot p$$

c_{aq}: concentration of gas component in solution ($molL^{-1}$);
k_H: Henry's Constant ($molL^{-1}Pa^{-1}$);
p: Partial pressure of gas above the solution (Pa).

The k_H value for CO_2 in water is available. For instance, when the temperature is between 273 K 303 K, the k_H value is 3.4×10^{-7} $molL^{-1}Pa^{-1}$ (J. A. Dean, *Lange's Handbook of Chemistry*, **McGraw-Hill, Inc.,** 1992).

CO_2 exists in Earth's atmosphere as a trace gas at a concentration of 0.039 % by volume. Data were obtained from the Earth System Research Laboratory, Global Monitoring Division (website: www.ersl.nogg.gov/gmd/ccgg/trends/#mlo). Data were collected on Oct. 2013

For the aged DI water, the concentration of dissolved CO_2 in water is calculated as follow:

(aged DI water) $c_{aq}=3.4\times10^{-7}\times1.01\times10^{5}\times3.9\times10^{-4}$ mol/L$=1.3\times10^{-5}$ mol/L.

For the CO_2-saturated water, the concentration of dissolved CO_2 in water is calculated as follow:

(CO_2-saturated water) $c_{aq}=3.4\times10^{-7}\times1.01\times10^{5}$ mol/L$=3.4\times10^{-2}$ mol/L.

These data are used in the main text to evaluate the influence of concentration of dissolved CO_2 on the microstructure and gas separation performance of prepared LDH membranes.

SI-5 Magnified cross-sectional images of the NiAl-CO_3 LDH layer with CO_2-saturated water as solvent

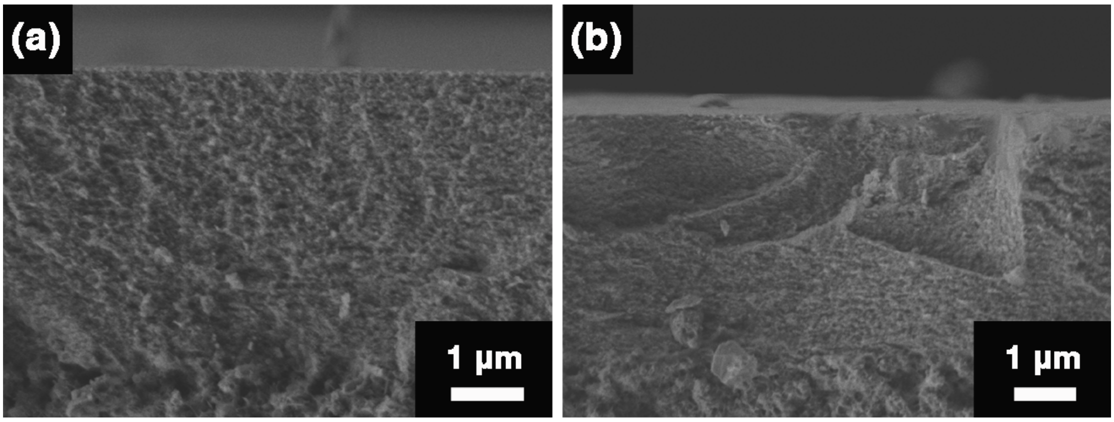

Fig. S4 (a) and (b) SEM image of cross-sectional images of LDH layer in-situ grown on γ-Al_2O_3 modified asymmetric α-Al_2O_3 substrate with CO_2-saturated water as solvent. Hydrothermal growth was kept at 85 ^{o}C for 40 h.

Fig. S4 showed the magnified images of the cross-sectional images of NiAl-CO_3 LDH membranes prepared with CO_2-saturated water as solvent. Unlike the LDH membrane prepared with aged DI water as the solvent, no plate-like morphology characteristic of LDH crystallites was observed, implying that a well-intergrown LDH membrane was formed before LDH crystallites had a chance to evolve with specific crystal faces.

SI-6 Demonstration of the gas separation equipment

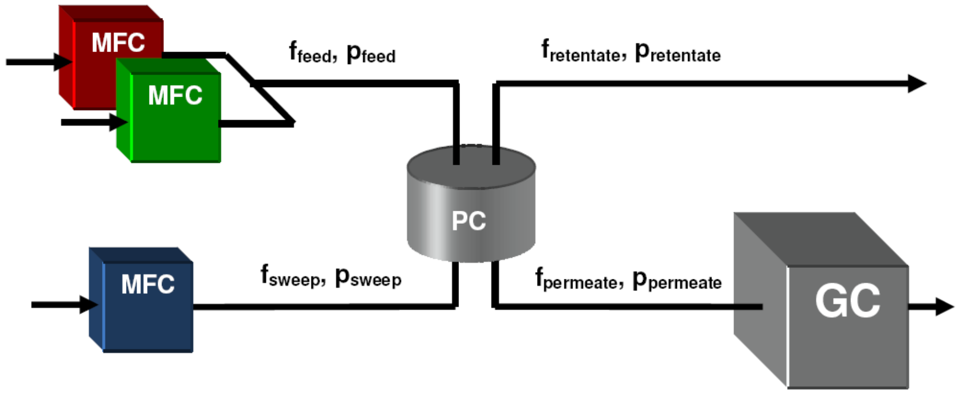

Fig. S5 Measurement equipment for both single and mixed gas permeation. MFC: mass flow controller; PC: permeation cell with mounted membrane; GC: gas chromatograph; f: volumetric flow rate; p: pressure.

SI-7 Detailed information on the composition and flux of feed, retentate and permeate during the gas permeability tests

For *ab*-oriented NiAl-CO_3 LDH membrane

H_2/CO_2 mixture:
Feed side: H_2: 50.00 ml/min; CO_2: 50.00 ml/min; H_2/CO_2=1.00.
Permeate side: H_2: 0.89 ml/min; CO_2: 0.15 ml/min; H_2/CO_2=5.80.
Retentate side: H2: 49.11 ml/min; CO2: 49.85 ml/min. H2/CO2=0.99.

H_2/N_2 mixture:
Feed side: H_2: 50.00 ml/min; N_2: 50.00 ml/min; H_2/N_2=1.00.
Permeate side: H_2: 0.96 ml/min; N_2: 0.12 ml/min; H_2/N_2=8.20.
Retentate side: H_2: 49.04 ml/min; N_2: 49.88 ml/min. H_2/N_2=0.98.

H_2/CH_4 mixture:
Feed side: H_2: 50.00 ml/min; CH_4: 50.00 ml/min; H_2/CH_4=1.00.
Permeate side: H_2: 1.02 ml/min; CH_4: 0.12 ml/min; H_2/CH_4=8.80.
Retentate side: H_2: 48.98 ml/min; CH_4: 49.88 ml/min. H_2/CH_4=0.98.

For randomly oriented NiAl-CO_3 LDH membrane

H_2/CO_2 mixture:
Feed side: H_2: 50.00 ml/min; CO_2: 50.00 ml/min; H_2/CO_2=1.00.
Permeate side: H_2: 0.30 ml/min; CO_2: 0.03 ml/min; H_2/CO_2=10.70.
Retentate side: H2: 49.70 ml/min; CO2: 49.97 ml/min. H2/CO2=0.99.

H_2/N_2 mixture:
Feed side: H_2: 50.00 ml/min; N_2: 50.00 ml/min; H_2/N_2=1.00.
Permeate side: H_2: 0.78 ml/min; N_2: 0.04 ml/min; H_2/N_2=18.10.
Retentate side: H_2: 49.22 ml/min; N_2: 49.96 ml/min. H_2/N_2=0.99.

H_2/CH_4 mixture:
Feed side: H_2: 50.00 ml/min; CH_4: 50.00 ml/min; H_2/CH_4=1.00.
Permeate side: H_2: 0.82 ml/min; CH_4: 0.01 ml/min; H_2/CH_4=78.70.
Retentate side: H_2: 49.18 ml/min; CH_4: 49.99 ml/min. H_2/CH_4=0.98.

For randomly oriented ZnAl-NO_3 LDH membrane

H_2/CO_2 mixture:
Feed side: H_2: 50.00 ml/min; CO_2: 50.00 ml/min; H_2/CO_2=1.00.
Permeate side: H_2: 0.64 ml/min; CO_2: 0.11 ml/min; H_2/CO_2=5.80.
Retentate side: H2: 49.36 ml/min; CO2: 49.89 ml/min. H_2/CO_2=0.99.

H_2/N_2 mixture:
Feed side: H_2: 50.00 ml/min; N_2: 50.00 ml/min; H_2/N_2=1.00.
Permeate side: H_2: 0.71 ml/min; N_2: 0.08 ml/min; H_2/N_2=9.00.
Retentate side: H_2: 49.29 ml/min; N_2: 49.92 ml/min. H_2/N_2=0.99.

H_2/CH_4 mixture:
Feed side: H_2: 50.00 ml/min; CH_4: 50.00 ml/min; H_2/CH_4=1.00.
Permeate side: H_2: 0.66 ml/min; CH_4: 0.05 ml/min; H_2/CH_4=8.80.
Retentate side: H_2: 49.34 ml/min; CH_4: 49.95 ml/min. H_2/CH_4=0.99.

SI-8 The relationship between operation temperature and gas permeation behavior of the H_2/CH_4 mixture

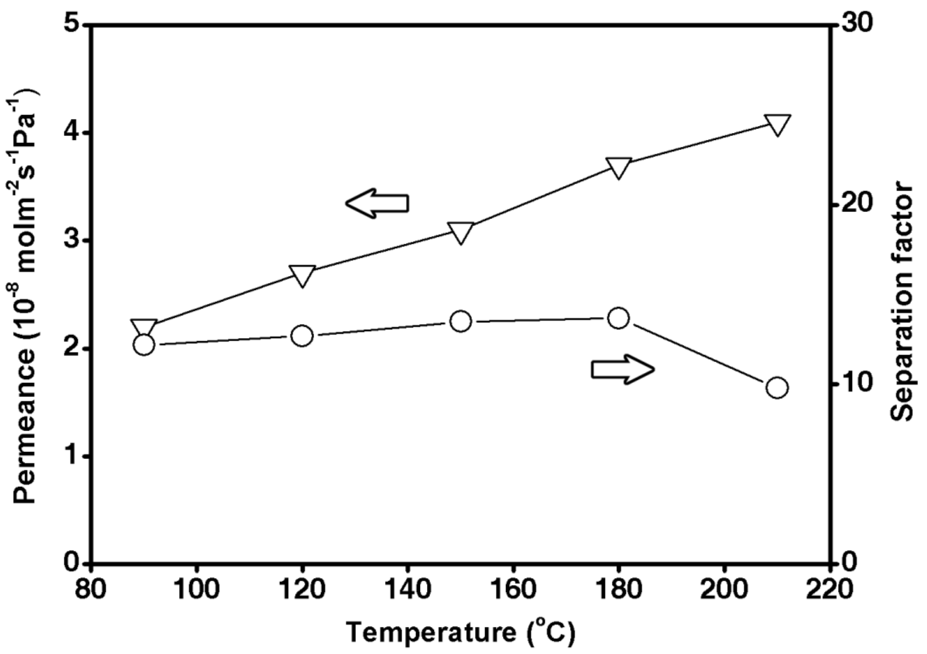

Fig. S6 H_2 Permeance and the separation factor of equimolecular H_2/CH_4 mixture on ZnAl-NO_3 LDH membrane as a function of temperature. ΔP = 1 bar.

SI-9 Thermal stability of prepared ZnAl-NO_3 LDH membrane

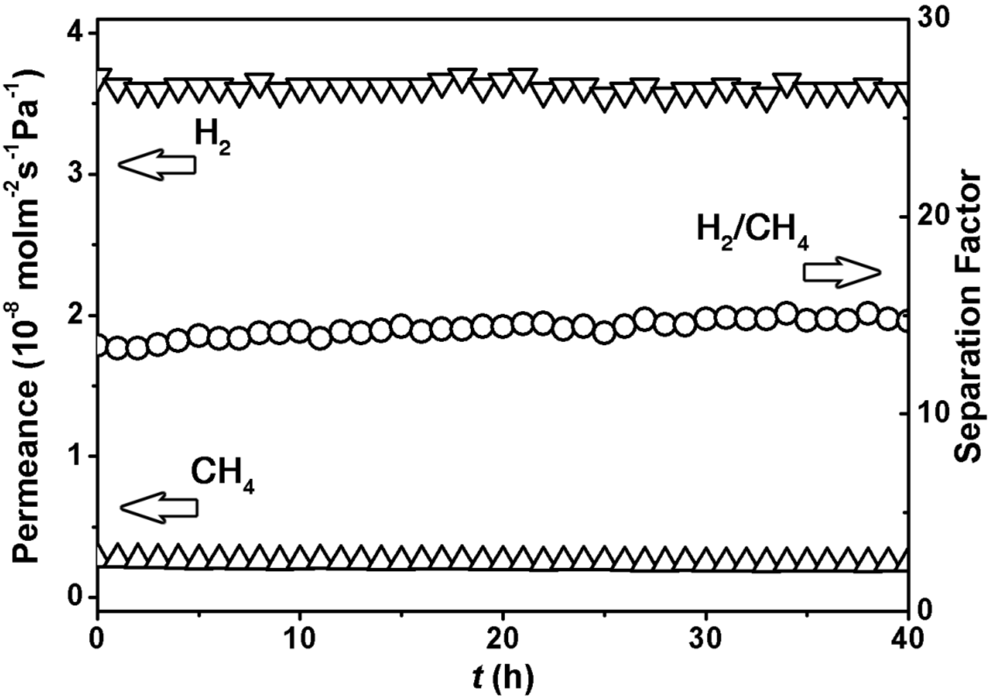

Fig. S7 Thermal stability test on prepared ZiAl-NO_3 LDH membrane. Equimolecular H_2/CH_4 mixture was used as feed gas. Test conditions: $\Delta P = 1$ bar. T = 180 ^oC.