

Molecular sieving through interlayer galleries†

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Cite this: *J. Mater. Chem. A*, 2014, 2, 1235Received 21st September 2013
Accepted 24th November 2013

DOI: 10.1039/c3ta13792a

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This study demonstrates that the interlayer galleries of layered compounds can exhibit size selectivity. A compact NiAl-CO₃ layered double hydroxide membrane was prepared showing a selectivity of ~80 for the H₂-CH₄ mixture. The use of the γ -Al₂O₃ modified α -Al₂O₃ substrate and CO₂-saturated water solvent was essential for high-quality membrane fabrication.

Microporous membranes with pore apertures below the nano-level can exhibit size selectivity by serving as a molecular sieve, showing significant potential for energy-efficient and environmentally benign separation of gas mixtures. Zeolites,^{1–3} polymers of intrinsic microporosity (PIMs),⁴ amorphous microporous silica⁵ and the recently developed metal-organic frameworks (MOFs)^{6–8} are typical materials used for this purpose. The potential of layered compounds for size-based separation, however, is rarely explored so far. Layered compounds may exhibit molecular sieving property, in case their gallery height is comparable with the kinetic diameter of gas molecules (Fig. 1).

Layered double hydroxides (LDHs), which have the general formula $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2][A^{n-}]_{x/n} \cdot z\text{H}_2\text{O}$ (M^{2+} , M^{3+} , A^{n-} and H₂O represent di- and tri-valent metal ions, n -valent anions and the interlayer water, respectively), are a typical representative of layered compounds. LDHs consist of positively charged brucite-like layers and interlayer galleries containing charge compensating anions (shown in ESI-1†).⁹ Metal cations are located in the centers of edge sharing octahedra, whose vertexes contain hydroxide ions that connect to form infinite 2D brucite-like layers.¹⁰ Compositional flexibility in both the positively charged layers and charge-balancing anions gives rise to a functional diversity.¹¹ Currently, LDHs have been evaluated as catalysts,¹²

ion exchangers,¹³ drug delivery hosts,¹⁴ bio-active materials,¹⁵ fire retardant additives¹⁶ and polymer stabilizers.¹⁷ By an appropriate choice of metal ions and charge compensating anions, the gallery height can be tuned from nano-meter to sub-nanometer scale. So it is of great importance to explore their potential in gas separation.¹⁸

Currently the fabrication of functional LDH films has become one of the most rapidly growing areas in intercalation chemistry.¹⁹ LDH films can serve as highly efficient heterogeneous catalysts,²⁰ anti-corrosion coatings²¹ and selective sensors.²² In contrast, only limited effort was devoted to investigate their gas separation properties. With the vacuum-suction method, T. T. Tsotsis first prepared MgAl-CO₃ hydrotalcite membranes, showing an ideal selectivity of pairs of inert gases higher than their Knudsen values.¹⁸ However, as described by

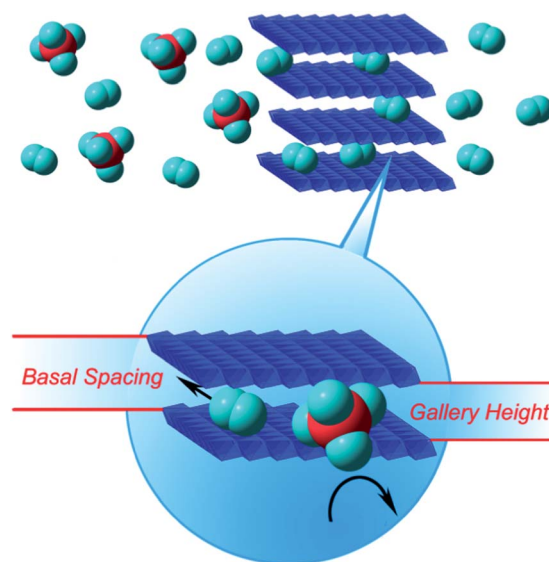


Fig. 1 Schematic illustration of the framework structure of layered double hydroxides (LDHs), and elucidation of the concept of selective molecular sieving through interlayer galleries of LDHs.

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† Electronic supplementary information (ESI) available: Experimental details, SEM images of the LDH layer on the α -Al₂O₃ substrate, gas permeation details and the XRD pattern of ZnAl LDH. See DOI: 10.1039/c3ta13792a

authors, there were substantial mesoporous voids and pinholes in these membranes, which had negatively affected their gas separation performances.^{18c} Therefore, one may expect a significantly improved gas separation performance, in case LDH crystallites were well-intergrown. Different from the aforementioned top-down method, with the *in situ* growth method, here we successfully prepared well-intergrown NiAl-CO₃ LDH membranes on porous alumina substrates. The selectivity of activated LDH membranes reached ~80 for H₂-CH₄, making them attractive in H₂ purification.

The precursor solution was prepared by dissolving Ni(NO₃)₂·6H₂O, NH₄NO₃, and NH₃·H₂O mixtures in CO₂-saturated water (ESI-2†). Initially, it was assumed that the bare α -Al₂O₃ substrate could serve as the Al³⁺ source as well as a support. However, LDH crystallites grew only sparsely on the substrate (ESI-3†). In order to enhance its chemical reactivity, an intermediate γ -Al₂O₃ layer was dip-coated on the surface of an alumina substrate (shown in Fig. 2a).²³ After *in situ* growth, the substrate had been fully covered with LDH crystallites with no conspicuous pinholes or grain boundary defects (Fig. 2b). Higher magnification of the image (Fig. 2c) demonstrated that these LDH crystallites were well-intergrown. A cross-sectional image revealed that the LDH layer was 5 μ m thick (Fig. 2d).

Fig. 3 showed the XRD pattern of the supported NiAl LDH membrane. For comparison, randomly oriented NiAl LDH powders were also prepared,²⁴ and the XRD pattern was shown in Fig. 3a. The prepared membrane showed two clearly distinguishable diffraction peaks at 2θ values of 11.2° and 22.3° (Fig. 3b), which were coincident with the reflections of (0 0 3) and (0 0 6) crystal planes of the NiAl LDH powders and thus confirmed that the formed layer indeed belonged to the LDH phase.

The $d_{(003)}$ -spacing, which was calculated according to the Bragg equation, equalled to the basal spacing of LDHs.²⁵ In this study, the (0 0 3) diffraction peak of the LDH layer appeared at 2θ values of 11.2°, which corresponded to a basal spacing of

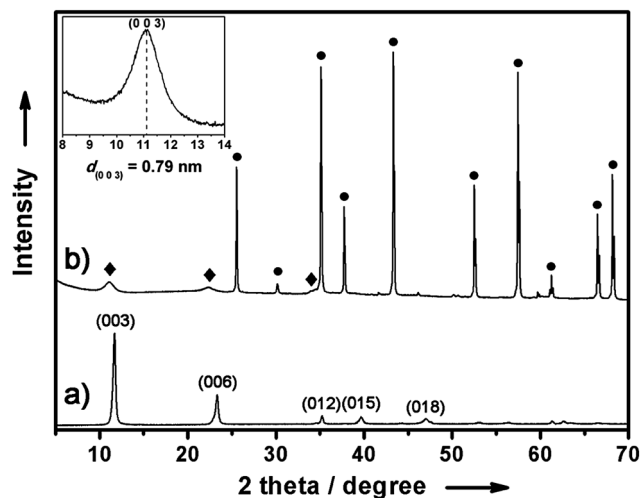


Fig. 3 XRD patterns of (a) the NiAl-CO₃ LDH powders, and (b) the prepared LDH membrane. Peaks marked with black dots and black rhombuses represent the diffraction peaks from the substrate and LDH phase, respectively. The inset displays the magnified image of the (0 0 3) diffraction peak of the LDH membrane.

0.79 nm. This value coincided well with the values in the literature for LDH materials intercalated with CO₃²⁻.²⁶ It was deduced that the CO₃²⁻, which was intercalated into the interlayer space of the LDH phase, arose from the dissolved CO₂ in the precursor solution. It is well-known from the literature that dissolved CO₂ in the synthesis solution could act as a source of carbonate anions and participate in the formation of CO₃²⁻ intercalated LDHs. X. Duan *et al.* also observed this phenomenon in the preparation of NiAl LDH on the PAO/Al substrate²⁶ and proposed a heterogeneous nucleation mechanism which could be extended here to explain why carbonate rather than nitrate anions were incorporated into the interlayer space.

By subtracting the thickness of a brucite-like layer (*i.e.* 0.48 nm), which was well-recognized in the field of LDHs,^{24,27} the gallery height for the prepared NiAl-CO₃ LDH membrane was estimated to be 0.31 nm, which was smaller than the kinetic diameter of most gas molecules such as CO₂ (0.33 nm), N₂ (0.36 nm) and CH₄ (0.38 nm) except H₂ (0.29 nm). So it was anticipated that for a H₂-containing gas mixture, H₂ would preferentially pass through the membrane and be separated *via* a molecular sieve mechanism.

The prepared NiAl LDH membrane was initially impermeable to any gases since the interlayer region was still occupied with H₂O molecules. To open interlayer galleries, an on-stream thermal activation was carried out by using a Wicke-Kallenbach permeation cell.^{6b} After activation, permeances of H₂, CO₂, N₂ and CH₄ as single gases through the LDH membrane were measured at 180 °C and 1 bar (more details are shown in ESI-4†). As shown in Fig. 4, there was a sharp cut-off between H₂ and CO₂, and the ideal selectivity of H₂-CO₂, H₂-N₂ and H₂-CH₄ reached 25.5, 27.6 and 76.8, respectively, which had by far exceeded their Knudsen values (4.7, 3.7 and 2.8) and thus was a clear indication of the domination of a molecular sieving mechanism. In comparison, MgAl-CO₃ LDH membranes

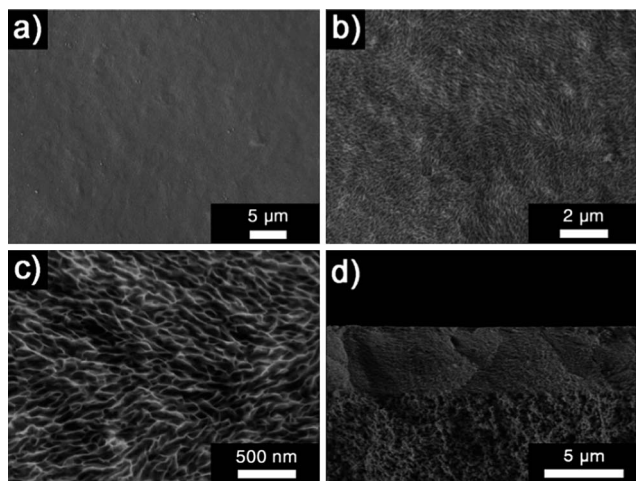


Fig. 2 SEM images of the (a) γ -Al₂O₃ modified alumina substrate; (b) and (c) top images of the prepared LDH membrane and (d) the cross-sectional image of the LDH membrane.

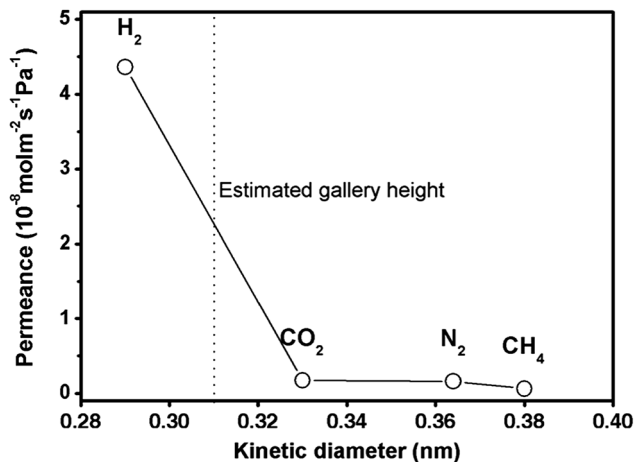


Fig. 4 Permeances of the single gases (H_2 , CO_2 , N_2 and CH_4) of the NiAl-CO_3 LDH membrane at $\Delta P = 1$ bar, $T = 180$ °C as a function of molecular kinetic diameters with the Wicke–Kallenbach technique.

synthesized by T. T. Tsotsis showed moderate ideal selectivity towards He-CO_2 (5.40), He-N_2 (3.65) and He-Ar (3.73) gas pairs with a He permeance of $0.75 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at a similar temperature (473 K).^{18c}

We further investigated the relationship between operation temperature and $\text{H}_2\text{-CH}_4$ mixed gas permeation performance of the LDH membrane (operation details are shown in ESI-5†). In the temperature range from 90 °C to 210 °C, the separation factor (SF) of the $\text{H}_2\text{-CH}_4$ mixture increased with increasing operation temperature firstly, reached the maximum value (78.7) at 180 °C, and then decreased. In contrast, the H_2 permeance increased almost linearly with temperature and reached the maximum value ($5.2 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) at 210 °C (shown in ESI-6†). The prepared LDH membrane could withstand the operation temperature of up to 210 °C for at least 2 days. Besides $\text{H}_2\text{-CH}_4$, gas separation performance of equimolecular $\text{H}_2\text{-CO}_2$ and $\text{H}_2\text{-N}_2$ mixtures was also measured at 180 °C and 1 bar (details are shown in the ESI-7†). It should be noted that the SF of the $\text{H}_2\text{-CO}_2$ mixture was 10.7, which was

lower than their ideal selectivity. The phenomenon could be explained by considering the strong adsorption of CO_2 molecules to positively charged NiAl brucite layers, which had negatively affected the free diffusion of hydrogen molecules across the LDH membrane.

Finally, thermal stability of the LDH membrane was studied by separation of an equimolecular $\text{H}_2\text{-CH}_4$ mixture at 180 °C and 1 bar for two days. The results showed that both H_2 permeance and $\text{H}_2\text{-CH}_4$ selectivity were unchanged. The SF of the $\text{H}_2\text{-CH}_4$ mixture was around 78 with a hydrogen permeance of $4.5 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. The excellent mixed gas selectivity made the NiAl-CO_3 LDH membrane very promising for application in H_2 purification (Fig. 5).

The basal spacing of the LDH layer was adjustable. For instance, the ZnAl LDH layer could be grown on a $\gamma\text{-Al}_2\text{O}_3$ modified porous alumina substrate, provided that $\text{Zn}(\text{NO}_3)_2$ instead of $\text{Ni}(\text{NO}_3)_2$ was used. The gallery height of the prepared ZnAl LDH layer, however, was 0.41 nm (shown in the ESI-8†). The intercalation of different anions could lead to LDHs with diverse gallery heights and functionalities. Currently, a variety of anions were incorporated into LDHs, ranging from simple inorganic anions (such as Cl^- , NO_3^- and CO_3^{2-})²⁸ through organic anions (such as benzoate, succinate and amino acids)²⁹ to complex biomolecules (such as DNA).³⁰ Owing to the rich intercalation chemistry, LDHs will find widespread applications in gas separation in case they are fabricated as membranes.

In summary, with the *in situ* growth method, we successfully prepared the NiAl-CO_3 LDH membrane on a porous alumina substrate. Deposition of a $\gamma\text{-Al}_2\text{O}_3$ intermediate layer on the surface of the substrate and the use of CO_2 -saturated water as the solvent were two critical factors to prepare a high performance LDH membrane. The activated LDH membrane showed considerable selectivity for $\text{H}_2\text{-CH}_4$ mixtures. Moreover, the adjustability of the gallery height makes the LDH membrane very attractive in gas separation.

Acknowledgements

Yi Liu is grateful for the financial support from Alexander von Humboldt Foundation. We gratefully acknowledge financial support by EU CARENA (FP7-NMP-2010-LARGE-4, no. 263007).

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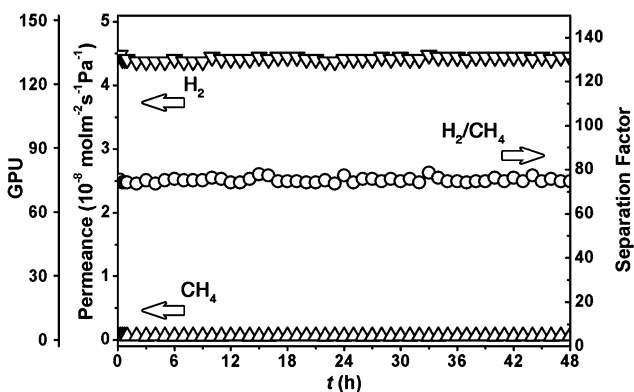


Fig. 5 Thermal stability test on the prepared NiAl LDH membrane. Equimolecular $\text{H}_2\text{-CH}_4$ mixture was used as feed gas. Test conditions: $\Delta P = 1$ bar, $T = 180$ °C. 1 GPU = $1 \times 10^{-6} \text{ cm}^3$ (STP) $\text{cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$.

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