

Remarkably Enhanced Gas Separation by Partial Self-Conversion of a Laminated Membrane to Metal–Organic Frameworks**

Yi Liu,* Jia Hong Pan, Nanyi Wang, Frank Steinbach, Xinlei Liu, and Jürgen Caro*

Abstract: Separation methods based on 2D interlayer galleries are currently gaining widespread attention. The potential of such galleries as high-performance gas-separation membranes is however still rarely explored. Besides, it is well recognized that gas permeance and separation factor are often inversely correlated in membrane-based gas separation. Therefore, breaking this trade-off becomes highly desirable. Here, the gas-separation performance of a 2D laminated membrane was improved by its partial self-conversion to metal–organic frameworks. A ZIF-8-ZnAl-NO₃ layered double hydroxide (LDH) composite membrane was thus successfully prepared in one step by partial conversion of the ZnAl-NO₃ LDH membrane, ultimately leading to a remarkably enhanced H₂/CH₄ separation factor and H₂ permeance.

Two-dimensional (2D) laminated membranes are currently gaining widespread attention as a material for molecular sieving.^[1] In principle, membranes constructed from stacked 2D sheets can only be one atom thick to enable a minimized transport resistance and maximized flux, and to offer higher mechanical flexibility.^[2] Various 2D laminated materials, such as graphene oxide (GO),^[3–5] layered metal–organic frameworks (MOFs),^[6,7] exfoliated MoS₂,^[8] and WS₂,^[9] have been shown to be superb building blocks for the formation of high-performance molecular separation membranes. Recently, Nair et al. gave a comprehensive overview of nanoporous 2D laminated membranes as attractive materials for molecular separation and related areas.^[10]

Molecular sieving through interlayer galleries represents a new direction for 2D laminated membranes.^[11] Current studies associated with separation based on interlayer galleries mainly focus on liquid membrane permeation,^[12]

however, their potential in gas separation has thus far not been explored extensively. In order to realize accurate molecular sieving in the gas phase, precise control of a gallery height of approximately 0.01 nm is necessary, which however is very difficult to achieve with top-down methods such as suction filtration. For instance, GO membranes prepared by Yoon et al. showed humidity-dependent mixed gas selectivity in favor of CO₂ which, as admitted by authors, was derived from the interlayer gallery between neighboring GO sheets.^[13] As a result of irregular stacking caused by corrugations, wrinkles, and ripples, randomly stacked GO sheets had a broad spacing distribution, and the gas permeation behavior was mainly dominated by Knudsen diffusion (this condition could be improved by optimization of the fabrication technique). In addition to classical molecular sieves such as zeolites^[14] and MOFs,^[15] non-amorphous crystalline laminates should be ideal materials for gas separation because of their stable configuration and uniform gallery height.

Layered double hydroxides (LDHs), which have the general formula [M²⁺_{1-x}M³⁺_x(OH)₂][Aⁿ⁻_{x/n}·zH₂O] (M²⁺, M³⁺, Aⁿ⁻, and H₂O represent di- and trivalent metal ions, *n*-valent anions, and the interlayer water, respectively), are typical representatives of crystalline laminated compounds.^[16] LDHs consist of regularly arranged, positively charged brucite-like 2D layers and charge-compensating anions located in interlayer galleries.^[17] Compositional flexibility in both the positively charged layers and charge-balancing anions gives rise to functional diversity.^[18] One unique feature of LDHs is the highly uniform gallery height, which is adjustable by intercalation of different anions. LDHs can exhibit size-based selectivity when their gallery height is comparable with the kinetic diameters of gas molecules, which is analogous to other microporous materials such as zeolites, MOFs, and polymers of intrinsic microporosity (PIMs). Moreover, compared with the well-developed delamination–reassembly procedure, the formation of brucite-like 2D sheets, their self-assembly into LDH crystallites, and their attachment to the substrate can be completed in one step under hydrothermal conditions, thus offering a great opportunity to explore their potential as gas-separation membranes.^[19]

Post-synthetic modification has been widely utilized to enhance the separation factor (SF) of molecular-sieve membranes (such as zeolites^[20] and MOFs^[21]). Nevertheless, such a modification will inevitably lead to a considerable reduction in gas permeance, owing to the elimination of nonselective defects, decrease in pore size, or increase in membrane thickness. It is therefore desirable to develop new methods for breaking the trade-off between gas permeance and selectivity. Very recently, we successfully prepared a compact ZnAl-NO₃

[*] Dr. Y. Liu, N. Y. Wang, F. Steinbach, Prof. J. Caro
Institute of Physical Chemistry and Electrochemistry
Leibniz University Hannover
Callinstr. 22, 30167 Hannover (Germany)
E-mail: yi.liu@pci.uni-hannover.de
juergen.caro@pci.uni-hannover.de

Dr. J. H. Pan
Department of Materials Science and Engineering
National University of Singapore
5 Engineering Drive 2, 117579 (Singapore)

Dr. X. L. Liu
Department of Chemical Engineering, Imperial College London
London SW7 2AZ (UK)

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LDH membrane on the porous γ - Al_2O_3 substrate by in situ hydrothermal growth.^[19] Although the gallery height of ZnAl-NO_3 LDHs (0.42 nm) was larger than the kinetic diameter of both H_2 (0.29 nm) and CH_4 (0.38 nm), the mixed H_2/CH_4 selectivity (13.7) still much exceeded the Knudsen selectivity (2.8) that was observed with some large-pore zeolite membranes.^[22] In addition, it was proposed that charge-compensating anions located in the interlayer gallery may also help to improve the gas selectivity,^[23] a hypothesis that needed further verification. In order to improve the separation performance, we developed a facile, yet efficient partial self-conversion method that significantly enhanced both H_2/CH_4 SF and H_2 permeance of the ZnAl-NO_3 LDH membrane.

Our concept is schematically illustrated in Figure 1a. First, a ZnAl-NO_3 LDH membrane is grown in situ on a porous γ - Al_2O_3 substrate. Consequently, the LDH membrane is immersed in a solution of 2-methylimidazole (2-mIm) in methanol. Under solvothermal conditions, 2-mIm serves as an organic linker of ZIF-8 and also promotes the dissolution of the ZnAl-NO_3 LDH layer and thus the gradual release of Zn^{2+} ions into the bulk solution. Finally Zn^{2+} ions coordinate with 2-mIm at the solution–substrate interface, thus leading to the formation of a well-intergrown ZIF-8 layer that is firmly attached to the remaining ZnAl-NO_3 LDH membrane. Owing to the presence of an additional H_2 -selective ZIF-8

layer, the ZIF-8- ZnAl-NO_3 LDH composite membrane is anticipated to show a significantly enhanced H_2/CH_4 SF; moreover, partial dissolution of the ZnAl-NO_3 LDH membrane leads to reduced membrane thickness and thus enhanced H_2 permeance (Figure 1b).

A representative SEM image of the ZnAl-NO_3 LDH membrane prepared by in situ hydrothermal growth is shown in Figure 2a. Well-intergrown LDH crystallites with no conspicuous cracks on the membrane surface could be clearly observed. A cross-sectional image showed that the ZnAl-NO_3 LDH membrane was uniform with a thickness of approximately 2.5 μm (Figure 2b). The XRD pattern (Figure 3b) showed two conspicuous diffraction peaks at 2θ of 9.8° and 19.8°, which could be assigned to the (003) and (006) reflection planes of the LDH phase. The $d_{(003)}$ -spacing was calculated, according to the Bragg equation, to be 9.0 Å, which corresponded to the basal spacing of LDHs and coincided with reports on LDHs intercalated with nitrate anions.^[24]

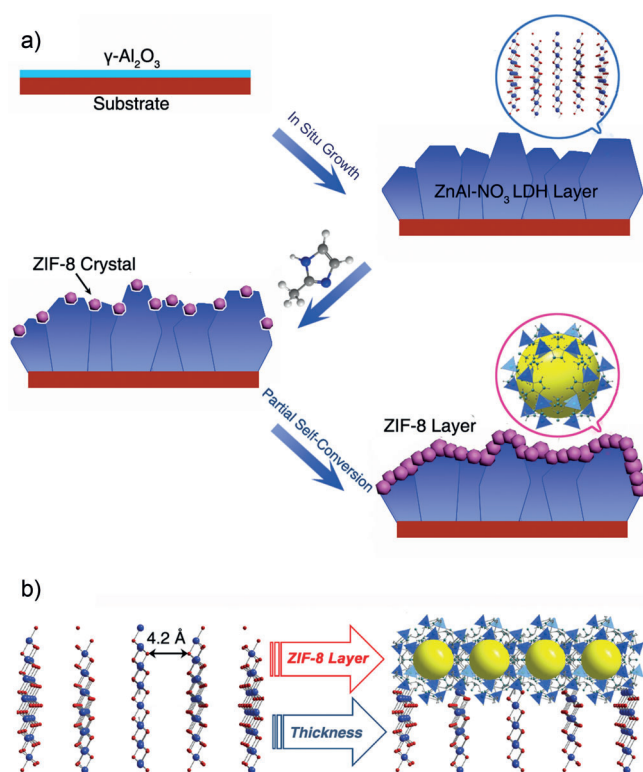


Figure 1. a) Partial self-conversion of a ZnAl-NO_3 LDH precursor layer into a ZnAl-NO_3 -ZIF-8 membrane on a γ - Al_2O_3 -modified α - Al_2O_3 substrate. b) Structural evolution of the ZnAl-NO_3 LDH membrane after the solvothermal treatment with 2-methylimidazole. Note: The vertically aligned LDH sheets are merely for elucidation of the layered framework of ZnAl-NO_3 LDHs. Actually, our prepared ZnAl-NO_3 LDH membrane showed no preferred orientation.

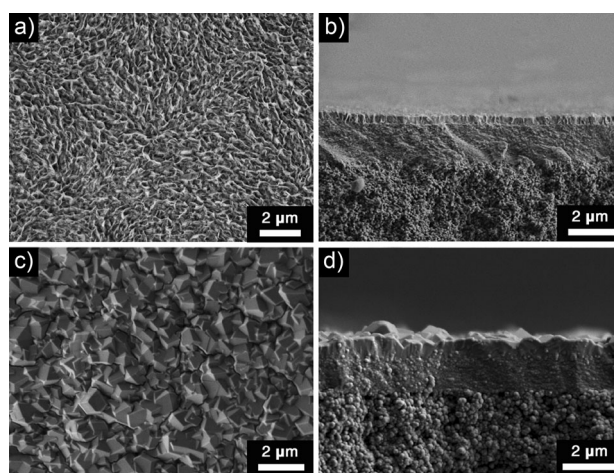


Figure 2. SEM images of the a,b) ZnAl-NO_3 LDH membrane, and c,d) ZIF-8- ZnAl-NO_3 LDH composite layer after solvothermal treatment.

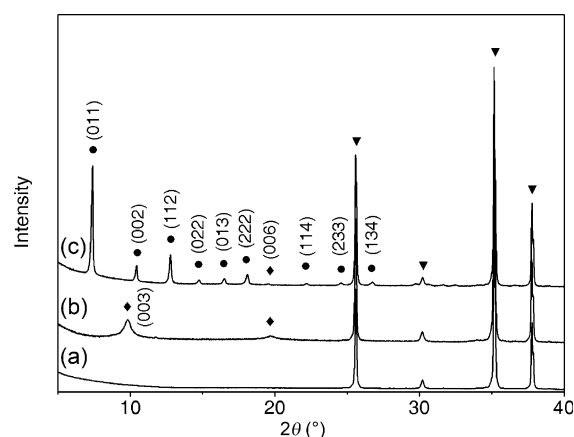


Figure 3. XRD patterns of a) the γ - Al_2O_3 -modified α - Al_2O_3 substrate, b) the ZnAl-NO_3 LDH membrane, and c) the ZIF-8- ZnAl-NO_3 LDH composite layer after solvothermal treatment. Peaks marked with black dots, rhombuses, and inverted triangles represent diffraction peaks from the ZIF-8 layer, LDH layer, and substrate, respectively.

After solvothermal treatment of the ZnAl-NO₃ LDH membrane, a well-intergrown ZIF-8 top layer with an average grain size of around 1.3 μm and thickness of about 1.1 μm was formed. Simultaneously, the thickness of the bottom ZnAl-NO₃ layer was reduced to around 1.3 μm . No marginal gap was present between ZnAl-NO₃ LDH and the ZIF-8 layers, which indicated that the ZIF-8 top layer was indeed firmly attached to the ZnAl-NO₃ LDH bottom layer. The XRD pattern of the composite membrane (Figure 3c) showed that new emerging diffraction peaks matched well with the standard diffraction pattern of the ZIF-8 phase (see the Supporting Information, Figure S1). We would like to stress that the peak overlapping between ZIF-8 and ZnAl-NO₃ LDHs brought difficulties in the unambiguous identification of all diffraction peaks derived from the LDH phase. In view of this observation, energy-dispersive X-ray spectroscopy (EDXS) analysis (Figure 4a) was carried out on a cross-

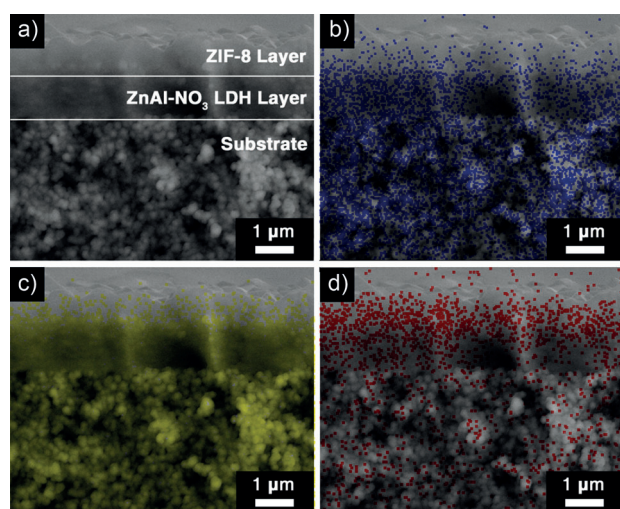


Figure 4. SEM image (a) and EDXS mappings (b,c,d) of the cross-section of the prepared ZIF-8-ZnAl-NO₃ LDH composite membrane. Color code: blue = O (b); yellow = Al (c); red = Zn (d).

section of the composite membrane to determine the elemental distribution. Figure 4b–d showed distributions of elemental O, Al, and Zn. Elemental Zn, which originated from Zn²⁺ ions of the ZIF-8 phase, were uniformly distributed in the top layer; while elemental O, Zn, and Al, which arose from ZnAl brucite-like sheets of the ZnAl-NO₃ LDH phase, were evenly spread over the bottom layer. In particular, the absence of both elemental O and Al in the top layer clearly indicated that the upper section of the ZnAl-NO₃ LDH precursor membrane had been readily corroded and afterwards converted to the ZIF-8 layer upon solvothermal treatment. In brief, the results of EDXS were in good accordance with both SEM and XRD studies, thus confirming that a ZIF-8-ZnAl-NO₃ LDH composite membrane had been successfully grown *in situ* on the substrate through our strategically designed partial self-conversion route.

Methanol was the best solvent for the incubation of high-quality ZIF-8-ZnAl-NO₃ LDH composite membranes, as it balanced the dissolution rate of the ZnAl-NO₃ LDH mem-

brane and the growth rate of the ZIF-8 top layer. A control experiment showed that when H₂O was used as the solvent, ZnAl-NO₃ LDHs were fully converted to a ZIF-8 layer and then detached from the substrate, owing the low chemical affinity between the ZIF-8 layer and the substrate. In comparison, it turned out to be extremely difficult to form a continuous ZIF-8 layer by solvothermal treatment of the ZnAl-NO₃ LDH membrane in DMF as solvent, owing to the low chemical reactivity of 2-mIm in this medium (Figure S2).^[25]

In order to evaluate the gas permeance of the membrane, the volumetric flow rates of both single and mixed gases through the ZIF-8-ZnAl-NO₃ LDH composite membrane were measured. Additionally, the data for H₂/CH₄ separation on ZnAl-NO₃ LDH, NiAl-CO₃ LDH,^[19] and ZIF-8 membranes (prepared by Eddaoudi et al.)^[26] were listed in Figure S4 as references. At room temperature, the membrane was almost impermeable to any gases, because solvent molecules fully occupied the interlayer galleries of the ZnAl-NO₃ LDH bottom layer, as we demonstrated in our previous studies.^[19] Hence, permeances of H₂, CO₂, N₂, and CH₄ as single and mixed gases through the ZIF-8-ZnAl-NO₃ LDH composite membrane were measured starting from 90 °C (Figure S3). At this temperature, there was a cut-off between H₂ and other gas molecules (Figure 5). The SF of

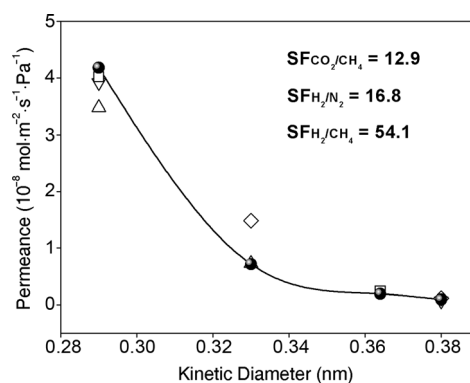


Figure 5. Permeances of single gases (●) and components of mixed H₂/CO₂ (Δ), H₂/N₂ (□), H₂/CH₄ (▽), and CO₂/CH₄ (◇) gases on the prepared ZIF-8-ZnAl-NO₃ LDH composite membrane at $\Delta P = 1$ bar and $T = 90$ °C as a function of molecular kinetic diameters.

mixed H₂/CH₄, H₂/N₂, and CO₂/CH₄ gases reached 54.1, 16.8, and 12.9, respectively, with an H₂ permeance of about $4.1 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. These values exceeded the corresponding Knudsen values (2.8, 2.6 and 0.6) by far, thus giving a clear indication of the superiority of the molecular-sieving mechanism. Compared with the permeance of H₂ as a single component, the H₂ permeance in the gas mixture was slightly reduced, which could be attributed to the slight hindrance of the permeation of the highly mobile H₂ by larger molecules (CO₂, N₂, and CH₄), and was in good agreement with our previous observations.^[15a,c] On the contrary, the permeance of CO₂ in the CO₂/CH₄ mixture was higher than that of CO₂ as a single component, because LDHs generally have a specific affinity for CO₂.^[27] As a result, the transport rate of CO₂ in the

composite membrane was enhanced, which ultimately led to the increased CO₂ permeance in the separation of the CO₂/CH₄ mixture. It is worth noting that Z. P. Lai and R. A. Fisher recently also reported the higher permeance and selectivity of CO₂ in mixture compared with its single-component permeation on ZIF-69^[28] and [Cu₂(BME-bdc)₂(dabco)]_n^[29] membranes.

Compared with the pure ZnAl-NO₃ LDH membrane, the H₂/CH₄ SF and H₂ permeance increased by about 5 and 2 times, respectively, on the ZIF-8-ZnAl-NO₃ LDH composite membranes at 90°C. This result was reasonable, as partial dissolution of the ZnAl-NO₃ LDH membrane indeed led to a reduced diffusion barrier. Furthermore, the H₂/CH₄ SF and H₂ permeance on the ZIF-8-ZnAl-NO₃ LDH composite membrane even surpassed those on the NiAl-CO₃ LDH (gallery height: 0.32 nm) and ZIF-8 membranes (Figure S4) under the given conditions.^[26] It should be noted that the ZIF-8 membrane used as a reference was prepared by the liquid-phase epitaxy (LPE) method, because both membrane fabrication processes were similar (Zn²⁺ ions were gradually released to the bulk solution), and both ZIF-8 membranes had similar grain size and membrane thickness. Apart from the separation of H₂/CH₄, we found that CO₂/CH₄ SF on the ZIF-8-ZnAl-NO₃ LDH composite membrane also reached 12.9. This value was considerably higher than most reported for MOF and LDH membranes.^[30]

A further increase in the operating temperature resulted in the reduction of H₂/CH₄ SF to a certain extent; however, both the SF and H₂ permeance remained considerably higher than those on the pure ZnAl-NO₃ LDH membrane (Figure S5). Finally, the thermal stability of the ZIF-8-ZnAl-NO₃ LDH composite membrane was tested for the separation of an equimolecular mixture of H₂ and CH₄. Both the H₂ permeance and H₂/CH₄ SF were unchanged for at least 30 h (Figure S6). Considering the high chemical flexibility of both LDHs and MOFs, we firmly believe that MOF-LDH composite membranes prepared in this way hold great potential for further performance improvements.

Very recently we demonstrated that the surface modification of substrates with ZnAl-CO₃ LDH buffer layers enabled a great enhancement of the heterogeneous nucleation of ZIF-8 crystals and resulted in the formation of 20 µm-thick ZIF-8 membranes.^[31] Nevertheless, the ZnAl-CO₃ LDH buffer layer neither served as the Zn²⁺ source of the ZIF-8 phase nor did it lead to an enhanced gas selectivity. In contrast, in the present study the prepared ZIF-8 top layer had a thickness of merely 1.1 µm. Moreover, the ZnAl-NO₃ LDH membrane served as the Zn²⁺ source of the ZIF-8 layer and greatly contributed to the enhancement of gas selectivity.

In summary, we successfully prepared high-quality ZIF-8-ZnAl-NO₃ LDH composite membranes by a partial self-conversion of laminated membranes to MOFs. First ZnAl-NO₃ LDH membranes, which also served as the Zn²⁺ source for ZIF-8, were grown in situ on the γ-Al₂O₃ substrate. Subsequent solvothermal treatment of LDH membranes in methanol containing 2-mIm led to a partial dissolution of the ZnAl-NO₃ LDH layers and the final formation of ZIF-8-ZnAl-NO₃ LDH composite membranes, which showed remarkably enhanced mixed H₂/CH₄ gas selectivity and H₂

permeance. This post-synthetic partial conversion of a laminated membrane to a MOF layer paves a new avenue for designing and fabricating high-performance gas-separation membranes.

Experimental Section

Preparation of the ZnAl-NO₃ LDH membrane: The asymmetric porous α-Al₂O₃ substrate was supplied by Fraunhofer IKTS. Its diameter and thickness were 18 mm and 1 mm, respectively. Before in situ growth, a γ-Al₂O₃ intermediate layer was dip-coated on the substrate.^[32]

The precursor solution was prepared by dissolving Zn(NO₃)₂·6H₂O (98.0 wt.%, Sigma-Aldrich, 5.8 g), NH₄NO₃ (98.0 wt.%, Aldrich, 4.8 g), and glycine (sodium salt, 98.0 wt.%, Acros, 0.8 g) into double deionized water (100 mL). Then NH₃·H₂O (1 wt.%, Aldrich, 10 mL) was added dropwise over 10 min to the aqueous solution under stirring in an ice bath. Consequently the γ-Al₂O₃-modified alumina substrates were placed vertically into a 50 mL Teflon-lined stainless-steel vessel. Next, precursor solution (35 mL) was poured into the vessel, which was then sealed. The vessel was put into a convection oven preheated at 65°C. After 40 h, the membrane was removed, washed with copious amounts of deionized water and dried in a convection oven at 60°C for 12 h.

Preparation of ZIF-8-ZnAl-NO₃ LDH composite membrane: The precursor solution was prepared by dissolving 2-mIm (≈99%, Sigma-Aldrich, 0.25 g) in methanol (99.9%, Roth, 50 mL). Consequently, the substrate covered with a ZnAl-NO₃ LDH membrane was vertically placed in a 50 mL Teflon-lined stainless-steel vessel and precursor solution (35 mL) was poured into the vessel and sealed. The vessel was then put into a convection oven preheated to 80°C. After 36 h, the vessel was taken out and allowed to cool to room temperature in air. Finally, the membrane was removed and washed with copious amounts of deionized water. The thus prepared ZIF-8-ZnAl-NO₃ LDH composite membrane was then dried in air.

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