Preparation of novel metal-carboxylate system MOF membrane for gas separation

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Abstract
A novel metal-carboxylate system metal–organic frameworks ([Zn₂(cam)₂(dabco)] (Zn-CD)) membrane was synthesized on porous ZnO support and used for gas separation. XRD and SEM were used to characterize the structure, composition, and morphology of the membrane. The results proved that the uniform Zn-CD seeding layer and continuous Zn-CD membrane were effectively achieved by reactive seeding method. Through optimizing the preparation process, the integrated Zn-CD membrane was obtained. The single and binary gas permeations of the Zn-CD membranes were systematically investigated. The separation factors of H₂/N₂ and H₂/CH₄ gas mixture reach to 19.1 and 14.5, respectively, indicating that the Zn-CD membranes are defect free and have great potential applications for hydrogen separation.

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1. Introduction

Compared with the traditional gas separation technology, including crystallization, extraction, distillation and adsorption, the membrane-based separation technology outstands from the other techniques for gas separation because of its low cost, energy saving, high capacity, continuous operation and easy scale-up [1]. In natural gas processing, conversion and syngas production, CO₂ separation and hydrogen purification, the membrane technology also plays a significant role [2–5]. Particularly, high selectivity and flux for separating hydrogen from other gas molecules via membranes are urgently required in the practical application. However, high-performance gas separation membrane materials are currently scarce [6]. Therefore, there is a critical challenge to develop a new generation of gas separation membrane materials with superior separation performance.

In recent years, as an extensive class of porous crystalline materials, metal–organic frameworks (MOFs) have attracted considerable attention because of their unique features, such as large surface areas, chemically functionalized cavities, flexible skeleton, electronic, magnetic and optical properties [7–9]. These unique features, especially varying structures, pore size, and particular adsorption ability, make MOFs the excellent and feasible candidates for gas separation [10–12]. Through many initial explorations of fabricating MOF-based separation membranes, MOFs have been confirmed to be a new generation of microporous membrane materials and own great potential for gas separation [13–20]. The first MOF membrane showing gas separation performance exceeding Knudsen diffusion behavior is fabricated by Guo et al. They used “twin copper source” growth method to prepare a continuous HKUST-1 (Cu₃(BTC)₂, BTC = benzene-1,3,5-tricarboxylate) membrane on copper net support with a H₂/N₂ separation factor of 7 [21]. Thereafter, Bux et al. prepared a zeolitic imidazole framework-8 (ZIF-8) membrane with molecular sieving properties by microwave-assisted solvothermal synthesis. The membrane achieved a fine balance between flux and selectivity [22]. Recently, Pan et al. successfully prepared hollow yttria-stabilized zirconia (YSZ) fiber-supported ZIF-8 membranes using a mild and environmentally friendly seeded growth method. The ZIF-8 membranes also displayed good gas separation performances [23].

Lately, a new series of MOFs have been widely developed by judicious choices of metal-carboxylate systems known as the secondary building units with structural modulation by N-donor derivatives [24,25]. This kind of MOFs has many advantages [26]. First, numerous coordination conformations can be achieved expeditiously by carboxylates from terminal monodentate to various bridging modes. Second, through modifying the size, shape, and the potential donor sites of carboxylates or N-donor derivatives, the structures and properties of MOFs can be tailored easily. Third, the strong coordinating ability of carboxylates and N-donor derivatives can lead to form good thermal stabilities. These outstanding and unique features enable them to own tremendous potential for fabricating gas separation membranes. Hence, we expect that the
metal-carboxylate system MOF membrane can display superior gas separation performances. To date, most of gas separation MOF membranes are focused on the MOFs based on imidazole-containing ligands, such as ZIF-8 [27,28], ZIF-7 [29], ZIF-22 [30], ZIF-90 [31], etc. By contrast, the study on the metal-carboxylate system MOFs for gas separation is still very limited.

Herein, we select a isoreticular porous MOF material [Zn2(cam)2dabco] (abbreviated as Zn-CD) [32], which is built from zinc nitrate hexahydrate, camphoric acid (carboxylate), and another rigid linear N-donor derivatives (1,4-diazabicyclo(2.2.2)octane), to fabricate the MOF membranes. This MOF material owns a scaffold-like 3D metal–organic structures with a primitive cubic topology, a large free volumes of 31%, and a high Langmuir surface area of 553 cm² g⁻¹, and simultaneously shows well rigidity for the guest-free metal–organic structure. In particular, its small pore size of 3 × 3.5 Å which is between the small molecules H₂ (2.89 Å) and other big molecules (such as, N₂ (3.64 Å) and CH₄ (3.8 Å)) makes it a fine candidate for preparing hydrogen purification membranes. Therefore, our target is to fabricate continuous and integrated Zn-CD membranes and study its hydrogen separation performance systematically.

2. Experimental

2.1. Preparation of Zn-CD crystals

Zn-CD crystals were synthesized by an improved hydrothermal reaction. In a typical procedure, 0.10975 g Zn²⁺ acetate dehydrate (Zn(CH₃COO)₂·2H₂O, 99%), 0.1002 g cam (D-camphoric acid, Alfa Aesar, 98%), 0.056 g dabco (1,4-diazabicyclo(2.2.2)octane, Alfa Aesar, 98%) and 30 mL ethanol was mixed and stirred vigorously several minutes. The solution was then placed in an autoclave (45 mL) and heated at 130 °C for 12 h. After cooling, the solution was centrifuged, and then Zn-CD crystals were obtained after the precipitates were washed with ethanol and dried at 90 °C overnight finally. To confirm that the synthesis of Zn-CD seeds can be achieved by zinc oxide, ZnO acetae dihydrate was changed with zinc oxide. According to the above procedure, the corresponding powder sample was obtained.

2.2. Preparation of Zn-CD membrane

In this study, the ZnO supports were lab-made as previous report [33]. The finally ZnO support has 22 mm in diameter and 2 mm in thickness. The normal pore size and the porosity of the porous support are ca. 100 nm and ca. 34%, respectively. Before the porous disks were used for growth of the Zn-CD membranes, we used the 1200-mesh SiC sandpaper to polish one side of the supports, washed in deionized water and then dried in the oven.

The Zn-CD membranes were prepared on porous ZnO support by the reactive seeding method [34]. This method involves an in situ seeding process that the porous support acts as inorganic source reacting with organic precursor to grow a seeding layer, followed by the secondary hydrothermal growth of a MOF membrane on the seeded support. A typical synthesis procedure is as follows. Seeding growth: 30 mL ethanol was added to a solid mixture of 0.02505 g cam and 0.014 g dabco with stirring (the molar composition of the synthesis solution: cam/dabco = 1:1). This clear solution was transferred into a Teflon autoclave in which a polished ZnO support was placed with the smooth surface down. The autoclave was heated at 130 °C for 12 h in the oven, and then cooled to room temperature. After this, the seeded support was washed with abundant ethanol and dried at 45 °C overnight. In the Secondary growth, 30 mL ethanol was added to a solid mixture of 0.10975 g Zn²⁺ acetate dihydrate, 0.1002 g cam and 0.056 g dabco (molar composition of the synthesis solution: Zn²⁺/cam/dabco = 1:1:1) and stirred vigorously several minutes. The seeded support was placed into the ethanol solutions with the seeded surface down. Again, the autoclave including the seeded support and synthesis solution was heated at 130 °C for 12 h. After cooling, the membrane was washed with abundant ethanol and dried at 100 °C overnight. In the experiments, Zn-CD crystals were also collected from the bottom of the autoclave after the secondary growth in order to be analyzed by gas adsorption at room temperature (25 °C).

2.3. Characterization

The crystal phases of samples were determined by X-ray diffraction (XRD) with Cu Ka radiation (Bruker, model D8 Advance). Diffraction patterns were collected at room temperature in the range of 5° ≤ 2θ ≤ 50° with a step width of 0.05° and scan rate of 0.2 s step⁻¹. The morphologies of membrane and support were examined by scanning electron microscopy (SEM) (Quanta-200, Philips FEI). The working parameters are: high voltage (HV) 20–30 kV, work distance (WD) 8-10 mm and spot 2.0–3.0. The gas adsorption measurements were recorded at room temperature (25 °C) by a Micromeritics ASAP 2020 surface area and porosity analyzer. The sample was degassed at 100 °C overnight and then to be analyzed.

The thermal gravimetric (TG, STA449F3, Netzsch) of the powder was analyzed in the temperature range of 30–800 °C with a heating rate of 10 °C min⁻¹ in nitrogen atmosphere.

2.4. Gas permeation

The permeations of small gas molecules (H₂, CH₄, N₂, and CO₂) were measured through Zn-CD membrane on the permeation set-up as reported in our previous work [35]. Before measuring gas permeation, the as-synthesized Zn-CD membrane was activated at 100 °C for more than 24 h to remove the occluded ethanol molecules in the Zn-CD channels. Then, the disk was sealed in a permeation module with rubber blankets. Each permeation test should be done after the system remained stable (at least 5 h). For the single gas measurements, the feed side was regulated at different pressures and the permeate side was open to atmosphere. Each side was fed at a volumetric flow rate of 30 mL min⁻¹. For the binary mixed gas, atmosphere pressure was applied to both sides of the permeation cell. The feed side was fed at a total volumetric flow rate of 60 mL min⁻¹ with each gas of 30 mL min⁻¹. The permeate side was swept with helium and at a flow rate of 30 mL min⁻¹.

The membrane permeance (F_i) is defined as:

\[ F_i = \frac{N_i}{A \Delta P_i} \]  

where \( N_i \) is the permeation rate of component \( i \) (mol s⁻¹), \( \Delta P_i \) is the transmembrane pressure difference of \( i \) (pa), and \( A \) is the membrane area (m²).

The ideal selectivity is calculated by the ratio of single gas permeances.

The separation factor was calculated as:

\[ \alpha_{yi} = \frac{y_i / y_j}{x_i / x_j} \]  

where \( x \) and \( y \) are the molar fractions of the one component in the feed and permeate, respectively.
3. Results and discussion

3.1. Preparation of Zn-CD membranes

The morphology of the seeded ZnO support is shown in Fig. 1a. A strong adhesive and uniform seeding layer forms well on the support. The dimension of seed particles is ca. 3 µm. To confirm the feasibility of the reactive seeding method for the preparation of the Zn-CD membrane on a porous ZnO support, the crystal structure of the seeding layer was analyzed. As shown in Fig. 2, compared with the single crystal diffraction data [32], the relatively weak characteristic peaks of the Zn-CD crystal are observed clearly on the seeding layer, indicating that a Zn-CD seeding layer is formed via the reaction of cam and dabco with the ZnO. Based on the uniform seeding layer, continuous and intergrown MOF membranes are easily synthesized. In order to optimize the Zn-CD membrane, we investigated the fabrication of membranes on the uniform seeding layer at varied second growth times. Combining with the top-view SEM images in Fig. 1 and the cross-section SEM images in Fig. 3, it is found that the size of crystal particles and the thickness of Zn-CD membrane increase with increasing the growth time. This result is further confirmed by the corresponding XRD patterns (Fig. 2) which show the pure Zn-CD and ZnO phase. After 12 h, the Zn-CD membrane becomes continuous and highly intergrown, and defects are not observed (Fig. 1d). The grain size is about 3–8 µm and has no preferential orientation. The cross-section of Zn-CD membrane (Fig. 3c) indicates that the membrane layer is well bonded with the support, and the thickness of the Zn-CD membrane reaches to ca. 6 µm, which is much thinner than most of the reported MOF membranes (Table 1). It is worth mentioning, as discussed in our previous report [35], the removal of DMF is an intrinsic factor that results in the cracks of MOF membranes because of the nonlinear expansion behavior. Herein, compared with the reported synthetic method, ethanol and zinc acetate dehydrate were used instead of DMF and zinc nitrate hexahydrate to prepare the Zn-CD membranes in this work. It is very easy to eliminate defects of Zn-CD membranes and prepare compact Zn-CD membranes when ethanol and zinc acetate dehydrate were used.

The seeding layer fabricated from the first step was very necessary to form the continuous Zn-CD membrane. For comparison, the Zn-CD membrane was prepared via an in situ growth method. The polished ZnO was directly placed in a Teflon autoclave with the same synthesis solution at 130 °C for 12 h. As shown in Fig. 4a, the top-view SEM image of the membrane prepared by in situ growth method is poriferous, and is similar to a net. The cross-section SEM image shows the membrane is composed of fibrous crystals that in the disordered arrangement (Fig. 4b). This result proves that the seeding step is very crucial.

To confirm that Zn-CD seeds can be achieved by employing ZnO, we conducted an experiment using ZnO powders to replace the support to synthesize the Zn-CD powder. The corresponding XRD patterns (Fig. 5b) show that the crystal structure of the powder sample using the ZnO as source is consistent with the simulation date. We also tested the moisture stability of the Zn-CD material. Unfortunately, it is unstable in moisture (Fig. 5d). Therefore, the moisture is to be avoided in the application.
Fig. 3. Cross-section SEM images of the Zn-CD membrane fabricated at different times: (a) 3 h, (b) 6 h, and (c) 12 h.

Table 1
Comparison of the H₂/N₂ and H₂/CH₄ binary separation factors of the Zn-CD membrane with other MOF membranes from literatures.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Pore size (nm)</th>
<th>Thickness (µm)</th>
<th>Separation factor</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₂-MIL-53(Al)</td>
<td>0.75</td>
<td>~15</td>
<td>23.9</td>
<td>20.7</td>
</tr>
<tr>
<td>Cu(hfipbb)</td>
<td>0.32</td>
<td>~20</td>
<td>23°²</td>
<td>~</td>
</tr>
<tr>
<td>(H₂hfipbb)₀.₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HKUST-1</td>
<td>0.9</td>
<td>~20</td>
<td>7.5°</td>
<td>5.7°</td>
</tr>
<tr>
<td></td>
<td>~60</td>
<td></td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>0.34</td>
<td>~30</td>
<td>11.6°</td>
<td>11.3</td>
</tr>
<tr>
<td></td>
<td>~2</td>
<td>11°</td>
<td>13</td>
<td>[23]</td>
</tr>
<tr>
<td></td>
<td>~20</td>
<td>11.6°</td>
<td>13°</td>
<td>[27]</td>
</tr>
<tr>
<td></td>
<td>~16</td>
<td>4.3°</td>
<td>~</td>
<td>[28]</td>
</tr>
<tr>
<td>ZIF-7</td>
<td>0.3</td>
<td>~2</td>
<td>18</td>
<td>14</td>
</tr>
<tr>
<td>ZIF-22</td>
<td>0.3</td>
<td>~40</td>
<td>6.4</td>
<td>5.2</td>
</tr>
<tr>
<td>ZIF-90</td>
<td>~</td>
<td>~20</td>
<td>15.8</td>
<td>18.9</td>
</tr>
<tr>
<td>Zn-CD</td>
<td>0.3 × 0.35</td>
<td>~5</td>
<td>19.1</td>
<td>14.3</td>
</tr>
</tbody>
</table>

H₂hfipbb:4,4°-(hexafluoroisopropylidene)-bix(benzoic acid).

° Ideal separation factor.

Fig. 4. (a) Top-view and (b) cross-section SEM images of the Zn-CD membrane fabricated via in situ growth.

Fig. 6 is the thermogravimetric curve of Zn-CD powders in nitrogen atmosphere. The thermogravimetric curve of Zn-CD powders after activation show no weight-loss step up to 200 °C, indicating that the ethanol molecules in the Zn-CD channels can be completely removed using heat treatment. Furthermore, an obvious weight loss is found between 350 and 550 °C, which could
be attributed to the collapse of Zn-CD crystals. The TG analysis shows that the structure of Zn-CD is stable.

3.2. Gas permeation performance of Zn-CD membranes

The permeation performances of the compact Zn-CD membrane were measured using gas permeation setup. The H₂ selectivity with respect to N₂, CH₄, and CO₂ was investigated in detail. All tests were conducted at 25 °C. As shown in Fig. 7, the permeances of the single small gas molecules are independent of the trans-membrane pressure drops, indicating the absence of macroscopic defects [36]. The corresponding permeances of N₂, CH₄, and CO₂ reach to 1.61 × 10⁻⁸, 1.47 × 10⁻⁸, and 0.77 × 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹, respectively. It is notable that the H₂ permeance slightly increases from 3.37 × 10⁻⁸ to 3.7 × 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹ with increasing the trans-membrane pressure (0.1–0.3 MPa). This may be because that the influence of the reverse He permeation on the H₂ permeation is weakened at higher H₂ feed pressures. It is clear that the permeances have an obvious dividing line between H₂ and the other gases, owing to the molecular sieve of the Zn-CD membrane. Furthermore, due to the existence of the non-size selective mass transport through the imperfect sealing or through the grain boundaries of the polycrystalline Zn-CD membrane, CO₂, N₂, and CH₄ show non-zero permeances in the experiment [29].

Based on the single gas permeation measurement, the ideal selectivity of H₂ over N₂, CH₄, and CO₂ was calculated by the ratio of single gas permeances, showing ~21.7, ~24, and ~46, respectively (Fig. 8). All of them are higher than the corresponding Knudsen separation factors (3.74, 2.83 and 4.69, respectively). Therefore, it is expected that the Zn-CD membranes will display excellent hydrogen selectivity in mixed-gas permeation.

Subsequently, the binary mixtures (H₂/N₂, H₂/CH₄, and H₂/CO₂) separation performances of the continuous Zn-CD membrane were studied. Each experiment was tested after the system remained stable at least 5 h. The binary separation factors of the Zn-CD membrane for the H₂ over N₂, CH₄, and CO₂ are defined as the molar ratios in permeate and retentate, which are 19.1, 14.5, and 2.6, respectively (Fig. 9), and are almost unchanged. The binary separation factors and the permeances are smaller than those of the single component permeation. This phenomenon is similar to the mixtures diffusion in zeolites [37]. In addition,
compared with the other MOF membranes (Table 1), the H$_2$/N$_2$ and H$_2$/CH$_4$ binary separation factors of the Zn-CD membrane prepared in this study are better than most of literatures. Figs. 10 and 11 show the gas permeation performances of H$_2$ and N$_2$ for the Zn-CD membrane at different temperatures. As temperature increases, ideal selectivities and separation factors increase slightly, however, the permeance values of H$_2$ and N$_2$ for the single and binary gas decrease. The similar phenomenon was found in other literatures [19,20].

Nevertheless, the H$_2$/CO$_2$ binary separation factor of the compact Zn-CD membrane is only 2.6 and less than the corresponding Knudsen separation factors (4.69). In order to deeply understand this phenomenon, the H$_2$/CO$_2$ binary gas permeances and separation factors of the compact Zn-CD membrane in the separation of 1:1 H$_2$/CO$_2$ mixture were measured as a function of permeation time at room temperature, and the results are shown in Fig. 12. The permeances of H$_2$ and CO$_2$ simultaneously dropped with a fast speed in 5 h, and then tended to be slow. After 20 h, the permeation achieved balance and the low separation factors of H$_2$/CO$_2$ were measured. According to the above experimental results, a reasonable explanation for this unusual phenomenon may be that Zn-CD material owns a strong adsorption of CO$_2$ molecules, which results in blocking the channels (or pores) and affecting the transport of following molecules. The strong adsorption amount of CO$_2$ can be ascribed to its large quadrupole moment and polarizability.

To further prove this phenomenon, the Zn-CD powders were collected from the bottom of the autoclave after the second growth to analysis by gas adsorption at room temperature. As shown in Fig. 13, the gas adsorption capacity of Zn-CD powders increases in the order of H$_2$, N$_2$, CH$_4$, and CO$_2$. Obviously, the CO$_2$ adsorption capacity of Zn-CD powders is the strongest and quickly enhances with increasing the pressure. For instance, at 100 kPa, the gas adsorption capacity of H$_2$, N$_2$, CH$_4$, and CO$_2$ are about 1.05, 5.05, 26.67, and 48.5 cm$^3$ g$^{-1}$, respectively. Compared with the adsorption capacity of H$_2$, N$_2$, and CH$_4$, the CO$_2$ adsorption capacity is 46.2, 9.6, and 1.82 times larger than others. These results demonstrate our previous viewpoint that the Zn-CD crystals exhibit strong adsorption of CO$_2$ than other gas, which affects the transport of following molecules and results in a decrease of the gas permeances and the permeation selectivity.

Fortunately, it was found that the gas separation performance of the Zn-CD membrane which is poisoned by CO$_2$ can be recovered by heating method easily. In the experiment, the poisoned Zn-CD membrane was heated at 100 $^\circ$C for 12 h and then measured its gas separation performance. As shown in Table 2, the results show that the performance of the recovered Zn-CD membrane is very
and H2
and CO2
separation performance of
10 metal–organic frameworks based on 9,9–
capture characteristics of
with high permeability and
binary gas mixture separations, Sep. Purif.
membrane.
hydrogen separation. The separation factors of H2
the membranes were defect free and had good performance for
The single gas permeations of the Zn-CD membranes indicated that
in fields such as chemistry and separation science, especially
in the practical application for hydrogen separation.

4. Conclusion

A metal-carboxylate system Zn-CD membrane was successfully synthesized on ZnO support. By controlling the fabrication conditions, the uniform Zn-CD seeding layer and continuous Zn-CD membrane were effectively adopt by reactive seeding method. The single gas permeations of the Zn-CD membranes indicated that the membrane were defect free and had good performance for hydrogen separation. The separation factors of H2/N2 and H2/CH4 gas mixture reached to 19.1 and 14.5, respectively, which were more much higher than the Knudsen separation factors. The metal-carboxylate system MOF membrane can be expected to be applied in fields such as chemistry and separation science, especially hydrogen separation.

Acknowledgments

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References


