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Jian Yu, Yichang Pan, Chongqing Wang, Zhiping
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ZIF-8 Membranes with Improved Reproducibility Fabricated from Sputter-Coated ZnO/Alumina Supports

Jian Yu,^a Yichang Pan,^{*a} Chongqing Wang,^a Zhiping Lai^b

^a State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing Tech University, Nanjing 210009, P. R. China.

^b Advanced Membrane and Porous Materials Center, Division of Chemical and Life Science and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia.

E-mail address: panyc@njtech.edu.cn

Abstract

Zeolitic imidazolate framework-8 (ZIF-8) membrane has shown great potential for propylene/propane separation based on molecular sieving mechanism. Although diverse synthesis strategies were applied to prepare ZIF-8 membranes, it is still a challenge for reproducible fabrication of high-quality membranes. In this study, high-quality ZIF-8 membranes were prepared through hydrothermal synthesis under the partial self-conversion of sputter-coated ZnO layer on porous α -alumina supports. The reproducibility was significantly improved, compared with that from sol-gel coated ZnO layer, due to the highly controllable sputtering deposition of ZnO precursor. The relationship between the quality of as-synthesized membrane and amount of deposited ZnO was also determined. The effect of pressure drop in C₃H₆/C₃H₈ separation on separating performance was also examined.

Keywords: Zeolitic imidazolate framework; ZIF-8; Membrane; Reproducibility; Propylene/propane.

1. Introduction

Separation of propylene/propane mixtures with membranes is considered as an energy efficient and environmentally friendly alternative to cryogenic distillation process (Burns and Koros, 2003). Compared with traditional polymeric and inorganic (zeolite, silica and carbon) membranes, zeolitic imidazolate framework-8 (ZIF-8) membranes with less defects exhibit impressive performance for propylene/propane separation (Brown et al., 2014; Kwon and Jeong, 2013b; Pan and Lai, 2011). The high performance was attributed to the size-exclusion mechanism, where the effective aperture size of ZIF-8 structure with SOD structure assembling from zinc ions and 2-methylimidazole ligands is just between the kinetic diameters of propylene and propane (Li et al., 2009; Zhang et al., 2012). In addition, robust hydrothermal and chemical stability of ZIF-8 structure further endows its promising application in gas separation (Low et al., 2009; Pan et al., 2011b; Park et al., 2006). Therefore, ZIF-8 membrane with negligible permeance ($\sim 10^{-10}$ mol/m² s Pa) of propane was expected to fabricate through controlling the heterogeneous nucleation of ZIF-8 crystals on supports as well as promoting the intergrowth of ZIF-8 grains (Yao and Wang, 2014).

So far, secondary growth (Kwon and Jeong, 2013a; Liu et al., 2014a; Pan et al., 2012) and contra-diffusion (counter-diffusion) methods (Brown et al., 2014; Hara et al., 2014; Kwona and Jeong, 2015) were reported to successfully prepare high-quality

ZIF-8 membranes for effective separation of propylene/propane mixtures. However, the reproducibility of these synthesis procedures was limited by some key unmanageable synthesis steps. For the secondary growth method, similar to the synthesis of traditional zeolite membrane (McLeary et al., 2006), the seeding step (i.e. anchoring of ZIF-8 seeds on support) during secondary growth of ZIF-8 membrane is the most difficult step to control, accounting for the poor reproducibility. For the contra-diffusion (counter-diffusion) methods, it is very difficult to control of diffusion rate of precursor solution (Kwona and Jeong, 2015; Yao et al., 2011), resulting in the hard control of thickness and the quality of as-synthesized membranes.

Partial self-conversion of inorganic support to metal-organic frameworks (MOFs) membrane can effectively promote the heterogeneous nucleation and enhance the binding strength between MOF grain and support, improving the reproducibility of as-synthesized membranes (Dong et al., 2012; Guo et al., 2009; Hu et al., 2011; Khaletskaya et al., 2014; Liu et al., 2014b; Marti et al., 2013; Zhang et al., 2013; Zhang et al., 2014). For example, Jin et al. (Hu et al., 2011) prepared continuous MIL-53(Al) membranes on α -alumina supports, in which the α -alumina support acted as the inorganic source reacting with the organic ligand to grow a seeding layer. Following the same protocol, zinc-based MOF (ZIF-78) membranes were also successfully fabricated through the partial self-conversion of ZnO supports (Dong et al., 2012). However, low porosity of ZnO support, besides the brittle property, limits its application as support for membrane gas separation. As a result, an ultrathin ZnO layer deposited on porous α -alumina supports was an idea candidate for preparing thin

zinc-based MOF membranes using partial self-conversion strategy. For instance, Zhang et al. have successfully prepared ZIF-8 membranes through partial self-conversion of thin ZnO layer under hydrothermal synthesis (Zhang et al., 2013). However, the reproducibility of synthesized membranes is not satisfied, possibly derived from the unmanageable step for sol-gel coating of ZnO layer on α -alumina support. In addition, even though visual compactness of as-synthesized membrane, the permeance of propane through synthesized ZIF-8 membrane was higher than 10^{-9} mol/m² s Pa, accounting for the moderate selectivity for H₂/C₃H₈.

Magnetron sputtering technique was considered as a powerful methodology for highly controllable deposition of nano-scale metal oxides on various substrates (Ellmer, 2001; Khaletskaya et al., 2014). Herein, we report the successful partial self-conversion of sputtered-coated ultrathin ZnO layer to continuous ZIF-8 membranes on porous α -alumina support. The reproducibility of as-synthesized membranes was significantly improved, compared with traditional seeded-secondary growth method. The relationship between the membrane quality and amount of deposited ZnO was examined. In view of its potential application for propylene/propane separation, the effect of pressure drop on separating performance was also examined.

2. Material and methods

Partial self-conversion of ZnO layer to continuous ZIF-8 membrane on porous α -alumina support involves three main steps. The first step is the sputtering deposition

of an ultrathin ZnO layer on the surface of the α -alumina disc. In the second step the ZnO/support was converted to ZIF-8 seed/support by exposing sputter-coated ZnO/support into a 2-methylimidazole ligand aqueous solution for hydrothermal synthesis. Finally in the third step the ZIF-8 seed layer on support was further grown into a compact ZIF-8 membrane by immersing ZIF-8 seed/support into a ZIF-8 precursor solution for secondary growth. A stepwise description of the synthesis procedure was shown below.

2.1 Preparation of α -alumina support

Porous α -alumina discs (porosity = 40%, diameter = 22 mm, and thickness = 2 mm) with an average pore size of ~200 nm were used as supports. The discs were home-made by pressing α -alumina powder (CR-6, Baikowski) and sintering at 1180 °C for 3 h. One side of the sintered disc was polished with sandpaper (#1200 grit) and then dried in convection oven at 150 °C for 3 h before use.

2.2 Sputtering deposition of ZnO layer

Ultrathin ZnO layers were deposited on α -alumina supports by radio frequency (RF) magnetron sputtering at room temperature using a ZnO target (Williams Advanced Materials, purity 99.9%). Each deposition, the target was pre-sputtered for 15 min in argon gas to remove any contamination on the target. The RF power, deposition time, and gas flow of pure argon were maintained constant at 100 W, 15 min, and 10 sccm, respectively. The working pressure was also fixed as 15 mTorr. The sputtering

process was repeated several times to examine the relationship between amount of deposited ZnO and membrane quality. The corresponding samples were separately denoted as ZnO $\times$ n/support. Each deposition allows a ZnO layer with thickness of nearly 50 nm to cover the support.

2.3 Transformation of ZnO layer to ZIF-8 seed layer

The transformation of ZnO layer to ZIF-8 seed layer on porous α -alumina disc was realized through hydrothermal synthesis at 120 °C for 6 h. The ZnO $\times$ n/support was vertically placed in a 50 mL Teflon-lined stainless steel autoclave, which was filled with 40 mL of 2-methylimidazole (Sigma-Aldrich) ligand aqueous solution. The concentration of 2-methylimidazole aqueous solution was 2 M. After synthesis, the membrane was taken out and rinsed three times by DI water followed by natural cooling of autoclave to room temperature. Finally, the water on the surface of the membrane was sucked by the tissue paper and then dried at room temperature for overnight.

2.4 Formation of continuous ZIF-8 membrane by secondary growth

Dried ZIF-8 seed/support was vertically placed in a 50 ml Teflon-lined stainless steel autoclave followed by the hydrothermal synthesis at 120 °C for 6 h. The secondary growth solution was prepared by mixing 0.11 g zinc nitrate, 2.27 g 2-methylimidazole and 40 ml DI water. After synthesis, the membranes were treated

by the saturated-activation method to reduce the defects formed during activation, as shown in elsewhere (Pan et al., 2015).

2.5 Characterization

Crystal phase of sample was identified using a Bruker D8 Advance X-ray diffractometer with Cu-K α radiation ($\lambda = 0.1543$ nm). The surface morphology and cross section of the membranes was examined by FEI Quanta 200 scanning electron microscope at accelerating voltage of 10 kV after platinum deposition. The diffuse reflectance UV-Vis (DR UV-Vis) absorption spectra of samples were recorded on a spectrophotometer (Shimadazu, UV 2550), with fine BaSO₄ powder as reference.

2.6 Gas permeation

The as-synthesized ZIF-8 membrane after activation was sealed into a home-made stainless steel cell using a VITON 75 O-ring. All gas permeation measurements were performed by the Wicke-Kallenbach technique. Single-component gas permeation was measured under atmospheric pressure. Both the flow rates of feeding and sweep gas (argon) were set at 100 mL/min. For the mixed-gases (propylene/propane, 50:50) separation, the flow rates of both propane and propylene were set as 50 mL/min. The feeding pressure was controlled by using a back pressure regulator, while the pressure at the permeate side was maintained at 1 atm. Argon was also used as the sweep gas, and the flow rate was set to 100 mL/min. The composition of permeate was determined by a gas chromatography (Agilent 6890A).

3. Results and discussion

3.1 Preparation of ZIF-8 membrane

Fig. 1 shows XRD patterns and SEM images of the transformation from ZnO layer/support to continuous ZIF-8 membrane. Fig. 1b and 1c display the top-view SEM pictures of α -alumina disc and ZnO/ α -alumina disc, respectively. It is difficult to distinguish these two kinds of particles by virtue of its similar particle size and shape. However, localized discharging of α -alumina disc was significantly improved after the deposition of ZnO because of its semiconducting property. Only weak ZnO peak can be seen from the XRD pattern of ZnO/support, suggesting the deposition of small amount of ZnO (Fig. 1a). After hydrothermal synthesis at 120 °C for 6 h, disappearance of ZnO peaks but appearance of weak ZIF-8 peaks suggests the transformation of ZnO layer to ZIF-8 seed layer. As shown in Fig. 1d, uniform polyhedral seed crystals with a mean particle size of ca. 1 μ m cover the support. However, macroscopic voids between grains account for the poor inter-grown. Further secondary growth promotes the well-intergrown of grains with rhombic dodecahedral shapes (Pan et al., 2011a), resulting in the formation of continuous ZIF-8 membrane with random orientation (Fig. 1a and 1e). Compared with seed layer, the XRD reflection intensity of ZIF-8 membrane increased due to the increasing amount and crystallinity of ZIF-8 grains on the surface of the support. As shown in the cross-section view SEM (Fig. 1f), the thickness of the ZIF-8 film is ca. 2.5 μ m.

Fig. 1. (a) XRD patterns and (b-e) top-view SEM pictures of α -alumina support, ZnOx3/support, ZIF-8 seed/support, ZIF-8 membrane, respectively, (f) cross-section SEM image of ZIF-8 membrane. Scale bars are 5 μm for all panels.

DR UV-Vis measurements give additional hints for the transformation of ZnO $\times$ 3 layer to ZIF-8 membrane on the support, as shown in Fig. 2. Initially, ZnO $\times$ 3/support clearly exhibits an absorption edge at around 403 nm, while α -alumina support does not show any absorption between 300~800 nm. This result indicates that the successful deposition of ZnO particles on the support (Han et al., 2012). In view of no absorption between 300~800 nm on pure ZIF-8 materials (Esken et al., 2011), the absorption edge blue shift to 392 nm on ZIF-8 seed/support can be considered as the increase of the band gap in correlation to the intimate interfacial interaction between ZnO and ZIF-8 materials. In addition, the reduction of absorption intensity between 300~400 nm can be attributed to the partial conversion of ZnO and the coverage of ZIF-8 crystals on ZnO layer. As a consequence, the absorption intensity further decreased after the formation of a more dense ZIF-8 layer after secondary growth.

Fig. 2. DR UV-Vis spectra of α -alumina support, ZnO $\times$ 3/support, ZIF-8 seed/support, ZIF-8 membrane. The onset of light adsorption in sample was determined by extrapolating the steep part of the rinsing absorption curve (Esken et al., 2011).

3.2 Membrane gas permeation

Single-component gas permeations were first performed to evaluate the quality of as-synthesized ZIF-8 membrane by Wicke-Kallenbach (W-K) technique. As shown in Fig. 3, the gas permeances through the ZIF-8 membrane decrease with the increase in the kinetic diameters of permeating molecules. A sharp cut-off was also expected to observe between ethane and propane, which was reported from our previous ZIF-8 membrane prepared from traditional seeded-growth method (Pan and Lai, 2011). The permeance of hydrogen is 5.2×10^{-7} mol/m² s Pa, comparable with high-permeable ZIF-8 membranes prepared by other methods (Liu et al., 2014a). The ideal selectivity of H₂/propane, ethane/propane and propylene/propane are 4300, 466 and 50 respectively, accounting for the good quality of the as-synthesized ZIF-8 membrane prepared.

3.3 Reproducibility

In order to examine the membrane reproducibility, separation performances of five ZIF-8 membranes for equal-molar propylene/propane binary mixtures were tested at room temperature (~ 22 °C). The ZIF-8 membranes were prepared from same batch for sputtering deposition of ZnO $\times$ 3, but from different batches for both the formation

of seed layer and subsequent secondary growth (120 °C for 6h). As shown in Table 1, the permeances of propane through these five membranes are all below 2×10^{-10} mol/m² s Pa and the separation factors for propylene/propane mixtures are all higher than 47. The standard deviation of selectivity is calculated as 2, which is much lower than the value (~16) of ZIF-8 membranes prepared from traditional seeded-secondary growth method (Pan et al., 2015). In addition, compared with membrane from the sol-gel coated ZnO precursor, the reproducibility is significantly improved, possibly derived from the highly-controllable sputtering technique for the deposition of ZnO layer.

Fig. 3. Single-component gas permeation results measured on the as-synthesized ZIF-8 membrane by W-K technique at room temperature.

3.4 Effect of ZnO layer

In view of the crucial role of ZnO layer in partial self-conversion to continuous ZIF-8 membrane, the amount of deposited ZnO was also examined. As shown in Fig.

4a-c, the surfaces of as-synthesized ZIF-8 membranes prepared from various amounts of deposited ZnO do not show obvious difference. The ZIF-8 grains with rhombic dodecahedral shapes all exhibit well-intergrown, independent of the amount of deposited ZnO. The thickness of the formed ZIF-8 membrane slightly increases with the deposited layers of ZnO material, ranging from 1.7~2.7 μm , due to the increase of metal source during formation of ZIF-8. Fig. 4d shows the single-component gas permeation results of these ZIF-8 membranes. The permeation results for permanent gases and C2 hydrocarbons are similar, independent of the amount of deposited ZnO. However, the permeances of C3 hydrocarbons (propylene and propane) obviously decrease with the increase of amount of ZnO. The $\text{H}_2/\text{C}_3\text{H}_8$ selectivity on ZIF-8 membranes derived from $\text{ZnO}\times 1/\text{support}$, $\text{ZnO}\times 2/\text{support}$ and $\text{ZnO}\times 4/\text{support}$ is 69, 164 and 4855, respectively. Therefore, the quality of as-synthesized ZIF-8 membrane was very sensitive to the permeance of propane, by virtue of similar values of H_2 permeances ($\sim 5\times 10^{-7}$ mol/m^2 s Pa) through these three membranes. Furthermore, the corresponding selectivity for $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ selectivity on these three membranes is 3, 5 and 61, respectively, suggesting ZIF-8 membranes with moderate selectivity (<1000) for $\text{H}_2/\text{C}_3\text{H}_8$ are not suitable for separation of $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ systems. In addition, it was also found that the permeance of H_2 decrease from 5305×10^{-10} mol/m^2 s Pa to 4612×10^{-10} mol/m^2 s Pa, when the treating number of ZnO support increase from four to five. Furthermore, the permeance of H_2 was 4286×10^{-10} mol/m^2 s Pa as the $\text{ZnO}\times 6/\text{support}$ was used. However, the decrease of permeance of H_2 is sharper than that of C_3H_8 , resulting in the decrease of selectivity for $\text{H}_2/\text{C}_3\text{H}_8$. As a result, the

optimum number of ZnO/support treatment is four (i.e. the thickness of ZnO is ~200 nm).

Fig. 4. SEM images of as-synthesized ZIF-8 membranes from various amounts of deposited ZnO support: (a) ZnOx1/support, (b) ZnOx2/support, (c) ZnOx4/support, and (d) single-component gas permeation results measured on these three ZIF-8 membranes. The insets in (a-c) are the cross-section SEM pictures of the corresponding membranes.

3.5 Effect of operating pressure on C₃H₆/C₃H₈ separation

The different pressure drops was applied on the ZIF-8 membrane prepared from ZnO $\times$ 4/support, in order to explore its potential application for propylene/propane separation. As shown in Table 2, it was found that the selectivity decreases with the increase of pressure drops. The separation factor of the as-synthesized membrane for propylene/propane mixtures is 61 when both feeding and permeating sides were 1 atmosphere, i.e. the pressure drop is zero. However, the separation selectivity drops significantly (~40%) when the pressure drop increases to only 0.7 bar. As the pressure drop further increases, the decrease of selectivity becomes slower. Finally, the selectivity was decreased to 14 as the pressure drop was increased to 3 bars. However, when the total pressure drop is reversed to 0 bar, the separation factor can return back to 29. Therefore, the sharp reduction of selectivity is due to the gate opening of window of ZIF-8 structure (Ania et al., 2012; Fairen-Jimenez et al., 2011), rather than the damage of the membrane under high-pressure feeding. Propane molecules with close diameter (~0.43 nm) may enlarge the window of ZIF-8 framework under high pressure drop. In addition, the permeance of propylene decreases but the permeance of propylene increases with the increase of pressure drop (Table 2). On the contrary, as shown in Fig. 5, both the single-gas permeances of propylene and propane increase with the pressure drop, possibly resulting from the slight increase of window size of ZIF-8 framework. Under this circumstance, propylene and propane in the mixed gas may competitively diffuse through enlarged windows of ZIF-8 membrane. In other words, the separation mechanism may switch from the original molecular sieving (i.e. gas-translational diffusion) to the surface diffusion mechanism. Overall, ZIF-8

membranes exhibit better separating performances for propylene/propane separation under lower pressure drop.

Fig. 5. Single-gas permeance and ideal selectivity for C_3H_6 and C_3H_8 on ZIF-8 membrane synthesized from $\text{ZnO} \times 4/\text{support}$ under various pressure drops at room temperature.

4. Conclusion

In summary, we have demonstrated that partial self-conversion of sputter-coated ZnO layer to continuous ZIF-8 membranes through hydrothermal synthesis is an effective method to improve the membrane reproducibility. The repeatable synthesis is benefit from the highly-controllable sputtering technique for deposition of ZnO precursor. The separation factors for equal-molar propylene/propane mixtures on five ZIF-8 membranes, derived from one batch of ZnO deposition but different batches of hydrothermal synthesis, are all higher than 47. The standard deviation of separation factors is only 2. The amount of deposited ZnO is tightly related to the quality of as-synthesized ZIF-8 membrane. The optimum number of

ZnO/support treatment for high performance ZIF-8 membrane is four (i.e. the thickness of ZnO is ~200 nm). The separation factor of propylene/propane mixtures decreases with increase of pressure drop. The separation factor drops from 61 to 14 as the pressure drop increases from 0 to 3 bar, suggesting lower pressure drop favors better separating performance.

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Table 1. Permeances and separation factors of propylene/propane mixtures on ZIF-8 membranes synthesized from different batches.

Samples	Permeance (10^{-10} mol/m ² s Pa)		Separation factor
	Propylene	Propane	
M1	64.3	1.25	51
M2	55.2	1.10	50
M3	70.1	1.32	53
M4	58.8	1.15	51
M5	77.3	1.63	47

Table 2. Effect of pressure drops on the separation performance of equal-molar propylene/propane mixtures on synthesized ZIF-8 membrane prepared ZnO×4/support.

No.	Pressure (bar)		Pressure drop (bar)	Permeance (10 ⁻¹⁰ mol/m ² s Pa)		Separation factor
	Feeding side	Permeate side		propylene	propane	
1	1	1	0	62	1.02	61
2	1.7	1	0.7	58	1.62	36
3	2.0	1	1.0	54	1.99	27
4	2.8	1	1.8	50	2.42	21
5	3.4	1	2.4	47	2.83	17
6	4.0	1	3.0	43	3.13	14

Highlights

1. Partial self-conversion of sputtering ZnO layer to continuous ZIF-8 membrane.
2. The reproducibility is improved, compared to that from sol-gel coated ZnO layer.
3. There exists an optimal amount of ZnO precursor for high quality ZIF-8 membranes.
4. Lower pressure drop favors better performance for propylene/propane separation.