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Communication

Enhanced hybrid membrane of ZIF-8 and zeolite T for CO_2/CH_4 separation †

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An unprecedented hybrid membrane was synthesized for CO_2/CH_4 separation. Intermediate ZIF-8 was prepared *via* novel vacuum thermal seeding, followed by fabrication of zeolite T on the ZIF-8 layer. The high CO_2/CH_4 selectivity of the hybrid membrane was likely due to the double multiplying effect of CH_4 sieving through the hybrid membrane.

Metal organic frameworks (MOFs) are an emerging class of nanoporous materials made up of metal centers and coordinated by organic linkers to create porous structures. MOFs have well established themselves in materials science over the past 10 years [1, 2]. A subclass of MOFs, *i.e.* zeolite imidazole frameworks (ZIFs), consists of tetrahedral units where bivalent transition metals are coordinated to imidazolate ligands. ZIF-8 has a sodalite (SOD) zeolite-type structure with outstanding chemical and thermal stability where their imidazolate linkers form large cages of 1.16 nm connected through narrow windows of 0.34 nm[3]. It has been reported that ZIF-8 is chemically stable in the presence of aromatic hydrocarbons (*e.g.* benzene)[4], making ZIF-8 potentially suitable for the separation of CO_2 from natural gas. Several researchers have also reported gas separation using MOF membranes such as MOF-5[5, 6], ZIF-7[7], HKUST-1 [$Cu_3(BTC)_2$][8-10], and ZIF-8[11, 12].

On the other hand, zeolite T with an intergrowth of erionite and offretite is appealing for CO_2/CH_4 gas separation. Erionite possesses 8-ring channels parallel to c-axis with pore size of 0.36 x 0.51 nm; while offretite has 12-ring channels parallel to c-axis together with 8 ring sub-channels normal to c-axis, and their pore sizes are 0.67 x 0.68 nm and 0.36 x 0.49 nm, respectively. Stacking of erionite sheets in offretite, resulting in microchannels of 0.36 x 0.51 nm[13-15], is fascinating for CO_2/CH_4 separation.

Theoretically, CO_2 (0.33 nm) molecules could easily permeate through zeolite T pore channels but larger molecules such as CH_4 (0.38 nm) are restricted. This preferential molecular sieving of CO_2 over CH_4 makes zeolite T membrane a great potential for CO_2 removal from natural gas. In the present work, we synthesized zeolite T on top of ZIF-8 to form a hybrid membrane to characterize its CO_2/CH_4 separation performance in comparison to standing free ZIF-8 and zeolite T membrane. Here, we report a facile vacuum thermal seeding method followed by rapid secondary seeded growth for ZIF-8 membrane. For the first time, we are demonstrating a hybrid membrane with both MOF and zeolite for attractive CO_2/CH_4 gas-separation performance.

Though secondary seeded growth has the advantage of decoupling nucleation from growth steps for easier control of membrane microstructure, it is of crucial importance to anchor the seed crystals to the supports. In order to achieve a strong binding between ZIF-8 seeds and α-alumina support, vacuum thermal seeding was adopted for the formation of a continuous ZIF-8 membrane, as illustrated in Figure 1. Vacuum thermal seeding ensured ZIF-8 seeds with precursor strongly anchored to the porous α-alumina support. The precursor solutions containing ZIF-8 seeds and un-reacted ligands were hypothesized to serve as binders for binding between ZIF-8 seeds and the α-alumina support. In order to justify our hypothesis, we conducted 3 control experiments to support the hypothesis. Initially, ZIF-8 seeds were separated from its precursor solution and re-dispersed in fresh methanol. Then, α-alumina support was seeded with ZIF-8 seeds in methanol with identical vacuum thermal seeding. The ZIF-8 seed crystals were easily detached through washing indicating the importance of the un-reacted ligands species in the seed suspension. Secondly, two samples of fresh un-reacted ligands in methanol were prepared, they were (1) 2-methyl-imidazole, and (2) zinc chloride. The concentrations of the ligand species in the suspensions were similar with those un-reacted ligands in the solution. After seeding and subjecting to membrane crystallization, only the ZIF-8 seeds with un-reacted ligands precursor resulted in the formation of ZIF-8 intermediate membrane.

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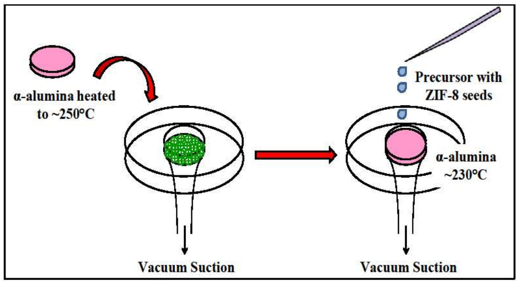

Fig. 1 Schematic diagram for visualization of vacuum thermal seeding of ZIF-8.

The important role of sodium formate has also been presented in this work. A ZIF-8 seeded support was sent for crystallization with similar precursor used except with the absence of sodium formate. The crystallized ZIF-8 microstructures have shown poor intergrown ZIF-8 crystals, with some voids marked with circles as shown in Figure 2a. XRD patterns (Figure 2b) has further confirmed the formation of pure phase ZIF-8 with well defined diffraction peaks of ZIF-8[16-18]. Although pure crystalline ZIF-8 were obtained, these poorly grown ZIF-8 crystals could not contribute to significant CO_2/CH_4 separation. On the other hand, crystallization of ZIF-8 seeded support in the presence of sodium formate has led to formation of continuous ZIF-8 membrane. Figure 2c and 2d show the morphology of crystallized ZIF-8 membrane and ZIF-8 seeded support, respectively. ZIF-8 seeded support showed an excellent adhesion of ZIF-8 seeds and precursor on the α-alumina support while continuous ZIF-8 membrane was formed without any interfacial voids. These results further implied that sodium formate plays a crucial role in the formation of ZIF-8 membrane microstructure. The sodium formate, which co-existed in the un-reacted ligands precursor for seeding and crystallization, acted as a deprotonator at the latter stage in membrane crystallization to promote uniform and well intergrown of ZIF-8 membrane crystals. McCarthy et al. [12] speculated that the 2-methylimidazole linkers at the ZIF-8 crystal surface will be fully deprotonated, due to an increase in pH with the presence of sodium formate, resulting in well intergrowth ZIF-8 crystals. The increase in pH decreases the concentration of protons in solution, thereby shifting the equilibrium and driving the deprotonation of surface linkers. The membrane crystallization solutions were prepared employing $ZnCl_2$, Hmim, sodium formate, and methanol in a molar ratio of approximately 1:5.8:4:180 (details are provided in the Supporting Information). The cross section of the membrane as shown in Figure 2e displayed a continuous grown layer of ZIF-8 membrane on top of the α-alumina support. With application of this exceptional vacuum thermal seeding, we were able to obtain a dense polycrystalline layer of ZIF-8 membrane on α-alumina support.

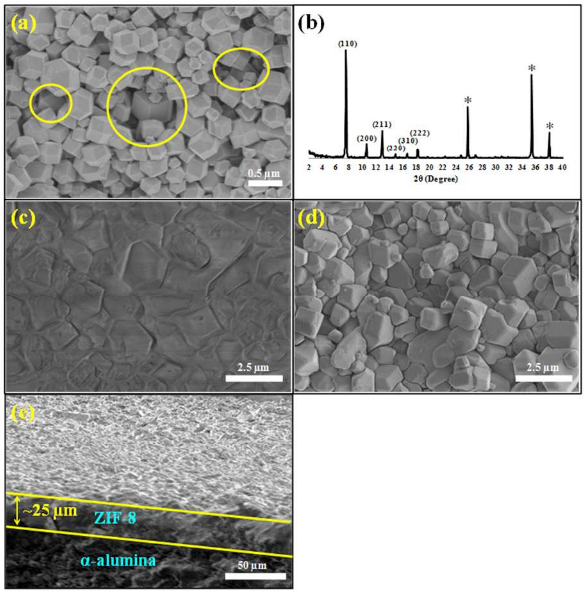

Fig. 2 (a) Surface morphology of ZIF-8 without sodium formate, (b) XRD pattern of ZIF-8 (*α-alumina peaks), (c) Surface morphology of ZIF-8 seeded support, (d) Surface morphology of ZIF-8 membrane prepared with sodium formate, and (e) cross section of ZIF-8 membrane prepared with sodium formate.

Secondary seeded growth was used for the preparation of zeolite T membrane on both α-alumina support and supported ZIF-8 membrane. Milky aluminosilicate precursor were prepared by mixing sodium hydroxide, potassium hydroxide, sodium aluminate, and fumed silica in deionized water with molar composition of $SiO_2:Al_2O_3:Na_2O:K_2O:H_2O=1:0.05:0.26:0.09:14$. The zeolite T seeded support was placed in the hydrothermal gel at 110°C for 45 hours for the formation of zeolite T membrane. FESEM micrographs in Figure 3a show the surface morphology of zeolite T membrane with the presence of rod shaped crystals and its membrane cross section is shown in Figure 3b. The XRD patterns in Figure 3c show that pure phase zeolite T membrane (Figure 3c(ii)) was obtained from zeolite T seeds (Figure 3c(i))[13-15]. Following the fabrication of hybrid membrane, the cross section was shown in Figure 3d revealing fine surface compatibilization between the ZIF-8 and zeolite T membranes.

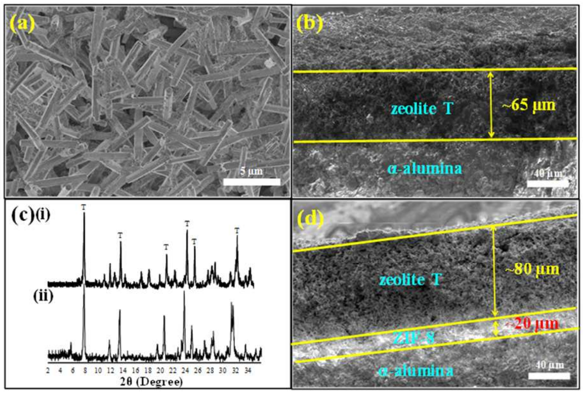

Fig. 3 (a) Surface morphology of zeolite T membrane, (b) cross section of zeolite T membrane, (c) XRD patterns of (i) zeolite T seeds, (ii) zeolite T membrane, and (d) cross section of hybrid membrane.

The permeation studies of the CO_2 and CH_4 gases were investigated for both single and binary gases. The binary gas permeation was performed with gas chromatographic control of a 1:1 (v/v) CO_2/CH_4 gas mixture at 298K and 1 bar. Each type of membrane was measured at least 3 times to provide reliable error estimates, which is smaller than 8%. Table 1 shows the tabulated data for CO_2 permeability and selectivity for all three membranes. A lack of macroscopic cracks and defects in ZIF-8 membrane was confirmed by transmembrane pressure dependent permeation measurements. This indicates that the synthesized ZIF-8 membrane after secondary growth of vacuum thermal seeded ZIF-8 with sodium formate was compact. The ideal selectivity of ZIF-8 resulted in ~4.1 with CO_2 and CH_4 permeance of 1.18 x 10^{-7} and 0.29 x 10^{-7} mol/s.Pa.m^2, respectively. On the other hand, the ZIF-8 membrane exhibited a moderate binary selectivity of 3.0 *via* binary gas permeation. The apparent surface area of the ZIF-8 nanocrystals was measured to be 1552 m^2/g, using BET method. As shown in Figure 4i, ZIF-8 displays a preferential adsorption of CO_2 over CH_4. Though CO_2 serves to be a non-polar molecule, the polar nature of the carbon oxygen bonds favours the binding and preferential adsorption on the ZIF-8 walls [19]. In addition, density functional theory simulation shows that the smaller pores are the preferential adsorption sites for CO_2 molecules [20]. The achieved CO_2/CH_4 selectivity could be explained by a combination of stronger CO_2 adsorptions as compared to CH_4 together with molecular sieving through the ZIF-8 pores.

Now looking at standing free zeolite T membrane, it has shown selectivity of 68 with CO_2 and CH_4 permeance of 6.08 x 10^{-8} and 0.09 x 10^{-8} mol/s.Pa.m^2, respectively, and CO_2/CH_4 binary selectivity of 49. With zeolite T possessing pore aperture of 0.36 x 0.51 nm, the significant decrease of CH_4 (0.38 nm) permeance is due to molecular sieving effect with CH_4 kinetic diameter of more than 0.36 nm. This is an affirmation on our finding with CH_4 having lower permeance as compared to CO_2. The sandwiched hybrid membrane which consisting of zeolite T on ZIF-8 gave the selectivity of 229 with CO_2 and CH_4 permeance of 7.33 x 10^{-9} and 0.032 x 10^{-9} mol/s.Pa.m^2, respectively. Moreover, the hybrid membrane has also achieved the binary gas selectivity of 193. Although zeolite T has a far lesser surface area of 397 m^2/g as compared to ZIF-8, it has shown a higher CO_2 uptake as compared to ZIF-8. This could be driven by the high Al content in zeolite T resulting in large cationic density leading to larger adsorption of CO_2. Furthermore, the huge decrease (96%) of CH_4 permeance as compared to standing free zeolite T resulted in ~3.4 times increase in the overall selectivity. This is likely due to the double multiplying effect of hybrid membrane whereby the CH_4 molecules have been partly sieved out through ZIF-8 membrane followed by further molecular sieving through zeolite T membrane. The differences in adsorption strength and the diffusivity between CO_2 and CH_4 represent the main mechanisms for the significant separation achieved in the hybrid membrane. The separation performance maintained its quality even though with 3 days of testing which further implied that the prepared membrane was stable and had high potential for natural gas purification.

Figure 4ii compares the CO_2/CH_4 separation performance for the membranes developed in the present work with ZIF-8 and zeolite T reported in literature. The upper bound of polymeric membranes in the selectivity versus permeability (Barrers) was obtained from the latest Robeson's trade off line [21]. It is distinct that the hybrid membrane is well above the present upper bound and even better than those of thermally rearranged polymeric membranes, mainly attributed to their precise size-selective molecular sieving with adsorption strength. This is a promising result as the superior hybrid properties can be exploited in the membrane area.

Table 1 Tabulated gas permeation results for ZIF-8, zeolite T, and hybrid membranes at room temperature with 1 bar feed pressure.

Membrane	**CO_2 Permeability**		**Ideal**	**Binary**
	10^8 mol/m^2.s.Pa	**Barrers**	**Selectivity**	**Selectivity**
ZIF-8	11.80	8811	4.1	3.0
Zeolite T	6.08	11804	68.0	49.0
Hybrid	0.73	2189	229.0	193.0

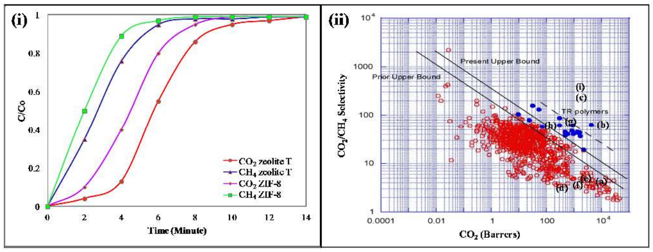

Fig.4 (i) Breakthrough curves of ZIF-8 and zeolite T crystals; (ii) The essential properties of (a) ZIF-8, (b) zeolite T and (c) hybrid membranes from our experimental values were plotted in CO_2/CH_4 Robeson plot [21]. Other reported membranes of the ZIF-8 ((d) Bux et al. [22], (e) McCarthy et al. [12], (f) Pan et al. [23]) and zeolite T ((g) Zhang et al. [24], (h) Mirfendereski et al. [25], (i) Cui et al. [26]) are listed for comparisons in the Robeson plot. (The dashed line represents the upper bound of the thermally rearranged (TR Polymers) polymeric membranes).

Conclusions

We have obtained a gas separating ZIF-8 membrane with selectivity of ~4.1 for CO_2 with respect to CH_4 *via* a novel vacuum thermal seeding. The membrane achieves a good balance between the permeance and selectivity relative to other ZIF-8 membranes reported up to date [11, 23]. On the other hand, the standing free zeolite T has achieved CO_2/CH_4 selectivity of 68. Nonetheless, with ZIF-8 forming as an intermediate membrane, the hybrid membrane has demonstrated highest selectivity of 229, which is likely due to the double multiplying effect of CH_4 sieving through the sandwiched membrane. This work has provided a positive lead with hybrid membrane consisting of MOF and zeolite serving to have a high CO_2 and CH_4 separation performance.

Notes

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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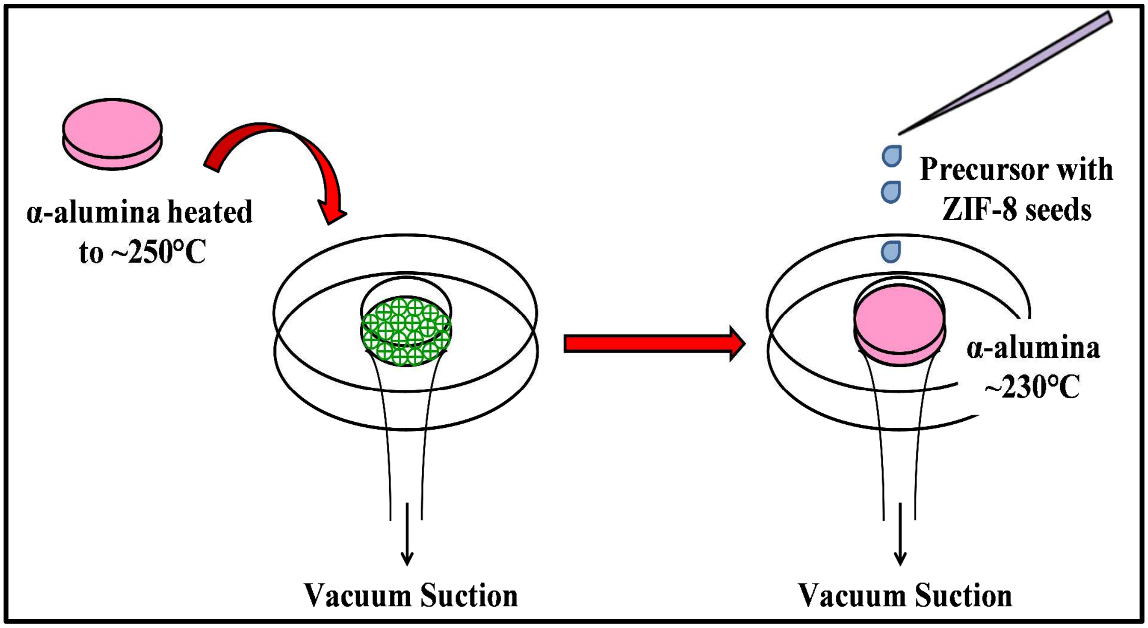
Graphical Abstract



Vacuum thermal seeding was performed to synthesize ZIF-8 membrane, followed by fabrication of zeolite T on the ZIF-8 layer. The synergistic effect of both materials in the gas separation mechanism has resulted in high CO_2/CH_4 selectivity.