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GAS PERMEATION STUDY OF H_2 AND N_2 THROUGH ZEOLITIC IMIDAZOLATE FRAMEWORKS-8 MEMBRANE SYNTHESIZED VIAMICROWAVE-ASSISTED SECONDARY SOLVOTHERMAL GROWTH

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ABSTRACT

In the present work, a continuous and well-intergrown zeolitic imidazole framework (ZIF)-8 membrane was synthesized using microwave-assisted secondary solvothermal growth method. The resultant membrane was characterized through scanning electron microscopy and EDX mapping. The performance of ZIF-8 membrane in the permeation of H_2 and N_2were performed at different pressure differences ranging from 100 kPa to 700 kPa. Results showed that, the membrane was highly robust with sustainable permeation performance up to 700 kPa. Furthermore, the resultant membrane exhibited high ideal H_2/N_2 selectivity of 10.25.

Keywords: ZIF-8 membrane, microwave-assisted secondary growth, H_2 and N_2 gas permeation, high pressure.

INTRODUCTION

In recent years, hydrogen (H_2) separation has provoked a great interest among researchers due to its potentialin addressing environmental issues, such as eliminating carbon emission with water as the by-product (Huang *et al*., 2014; Cacho-Bailo *et al*., 2014; Li *et al*., 2010). It can be an alternative energy with the highest energy content per unit of weight as compared to the other known fuels(Adhikari and Fernando, 2006). Zeolitic imidazolate frameworks-8 (ZIF-8) is one of the widely studied materials for gas separation owing to its excellent chemical and hydrothermal stability, high surface area, microporosity and frameworks flexibility (Park et al., 2006). It possesses large pore sizes of 11.6 Å and small apertures of 3.4 Å with the zinc metal center coordinated by the imidazole-type of organic linkers and resembles neutral zeolitic sodalite (SOD) topology (Huang *et al*., 2006). To date, in situ synthesis method is hard to obtain continuous ZIF-8 membrane due to the poor interfacial bonding between crystals and the substrate(Shah et al., 2012). Secondary seeded growth has been widely studied with several seeding method reported, such as rubbing(Venna and Carreon, 2009), dip-coating (Bux *et al*., 2011; Liu *et al*., 2014), slip-coating (Pan *et al*., 2012), microwave seeding (Kwon and Jeong, 2013), vacuum seeding (Yeo *et al*., 2014) and etc. Nonetheless, the technique required for the seeding methodsremains challenging. The condition of the seeds suspension and the method of preparation can affect the membrane growth significantly. In this paper, a simple seeding method through evaporation of solvent is used. The method causes a strong adherence of ZIF-8 seeds layer on the porous support without any support modification. This is attributed to the exceptionally high concentration of reactant ions formed under the reduction of solvent. On the other hand, since last decade, microwave technology has provoked a great interest in chemical synthesis of nanoporous materials (Tompsett and Conner, 2006) and membranes (Li and Yang, 2008). Microwave irradiation with uniform, rapid heating and controllable ramp rate (Schanche, 2003), has successfully reduced the synthesis duration and inhibited the formation of impurities (Li and Yang, 2008). Besides, ZIF-8 membranes have been mostly studied at low pressure differences so far (Zhang *et al*., 2014; Cacho-Bailo *et al*., 2014; Dumee *et al*., 2013; Isaeva *et al*., 2015). Therefore, in the current study, the ZIF-8 membrane was synthesized through microwave-assisted solvothermal growth with the solvent evaporation seeding method. The resultant membrane was then tested under different pressure differences up to 700 kPafor H_2 and N_2single gas permeation.

METHODOLOGY

Preparation of seeded support

For the solvent evaporation seeding method, the solution was prepared by dissolving 1.06 g of zinc chloride ($ZnCl_2$, >97%, Fisher brand), 0.99 g of 2-methylimidazole (Hmim, 99%, Fisher brand) and 0.54 g of sodium formate (HCOONa, 99%, Acros brand) in 80 mL of methanol (MeOH, >95%, Merck). Then, the polished α-alumina porous support (Nishimura Porcelain) with the thickness of 2 mm and diameter of 18 mm was placed horizontally at the bottom of a 100 mL vessel. The solution was then poured into the vessel and covered with aluminum foil. After that, the solution was subjected to heating at 65 °C to 70 °C for theslow evaporation of the solventfor 3 hours. Lastly, the seeded support was dried in the desiccator at room temperature overnight prior to the solvothermal synthesis.

ZIF-8 membrane synthesis

The synthesis precursor was prepared by dissolving 2.12 g of $ZnCl_2$, 1.98 g of Hmimand 1.08 g of HCOONain 160 mL of MeOH. The seededα-alumina

porous support was placed vertically in the Teflon-lined vessel using a PTFE holder. The synthesis precursor was then poured into the vessel and heated in a microwave oven (MARS 6, CEM Corporation) at 140 ºC and 5 hours, with the ramping rate of 14 °C/min. After heating, the membrane was washed with freshMeOH. The other side of the membrane was polished with the fine sand paper to avoid the deposition of ZIF-8 crystals. Then, the resultant membrane was dried in the desiccator at room temperature overnight.

Membrane characterization

The surface morphology of the ZIF-8 membrane and the seeded porous support were observed through scanning electron microscopy (SEM, Hitachi TM3030). The elements content of the membrane were determined using Energy-Dispersive X-ray Spectroscopy (EDX) and the distribution of the elements was scanned through EDX mapping.

Gas permeation testing

Gas permeation testing was studied using membrane permeation testing rig. The membrane was mounted in a stainless steel module with silicone gasket as seal. The total feed flow rate was set to 200 ml/min. The feed pressure was set accordingly with the pressure differences ranging from100 to 700 kPa. The permeate side was maintained at atmospheric pressure. The temperature of the testing was maintained at 298 K. The gas permeance was measured by using bubble flow meter after attaining steady state condition. The system was vacuumed before each testing to evacuate all the impurities.

Permeance, P_i (mol/m^2·s·Pa) of component i was calculated using equation (1) as follows:

$$P_i = \frac{J_i}{\Delta p_i} \quad (1)$$

Where J_i is the flux of component i (mol/m^2·s) andΔp_i is the pressure difference of component i (Pa) in the feed and permeate side.In this study, component i is H_2 or N_2.

The ideal selectivity $H_2/N_2$was calculated as the ratio of the single gas permeance using equation (2) as follows:

$$\propto_{H_2/N_2} = \frac{P_{H_2}}{P_{N_2}} \quad (2)$$

RESULTS AND DISCUSSIONS

Scanning electron microscopy

The morphologies of the seeded support and ZIF-8 membrane were examined by SEM and the images are shown in Figure-1. Referring to Figure-1 (a), a well-distributed ZIF-8 seeds layer with very small particles size is obtained through the solvent evaporation seeding method. The coverage of seeds is found to be uniform on the surface of the porous support. Figure-1 (b) shows the ZIF-8 membrane grew on the seeded support after microwave-assisted solvothermal synthesis. It can be seen that, the ZIF-8 seeds have grown into larger grains and thus forming continuous and well-intergrown ZIF-8 membrane on the seeded support.

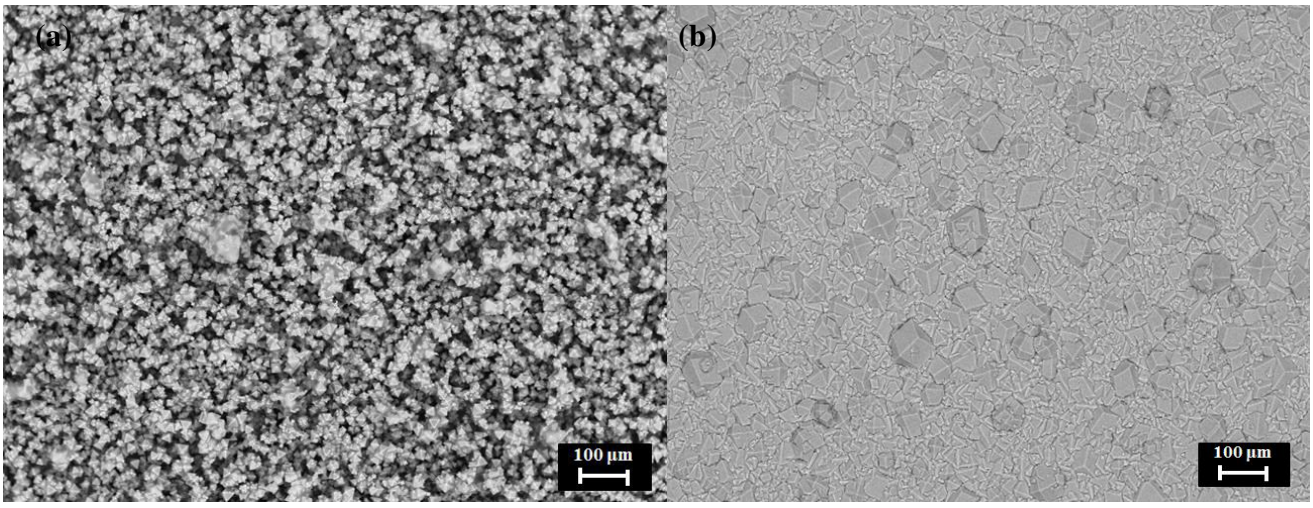

Figure-1. SEM images of (a) seeded supportand (b) ZIF-8 membrane growth on the seeded support.

Figure-2 shows the EDX mapping and the elemental composition of the ZIF-8 membrane. As shown in Figure-2, the membrane is fully covered with ZIF-8 grains which confirmed by the presence of C, N and Zn elements in EDX mapping (Figure-2 (a)). Besides, quantification of EDX results shown in Figure-2 (b)exhibits that 39.32 % of C, 31.71 % of N and 26.64% of Zn has been obtained, which is consistent with the reported EDX result for ZIF-8 (Cravillon *et al*., 2009).

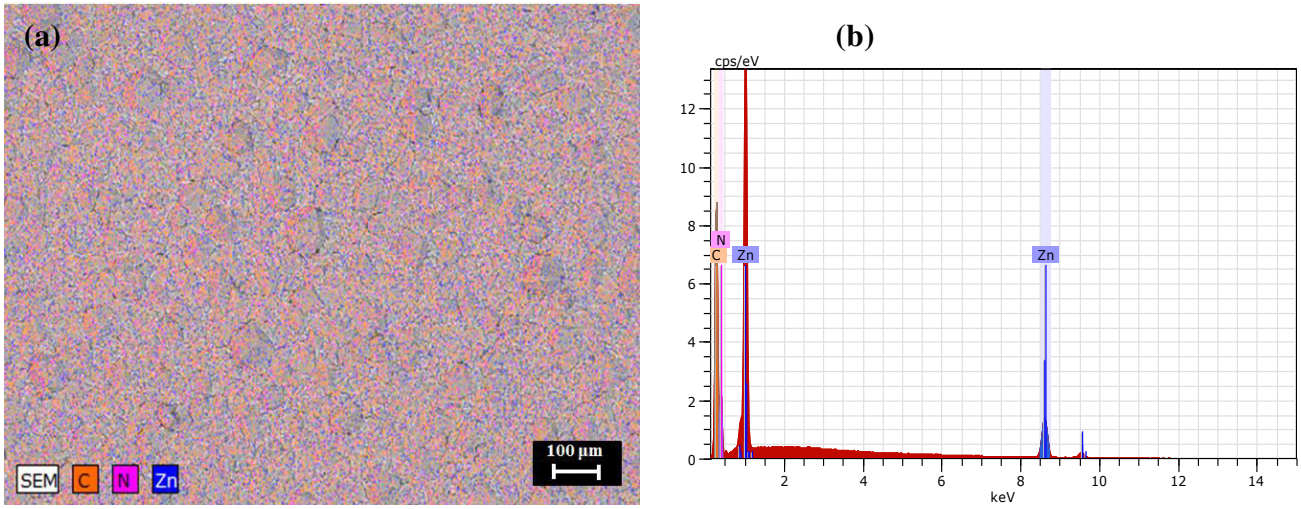

Figure-2. (a) EDX mapping and (b) EDX spectrum of the ZIF-8 membrane.

Single gas permeation experiments

The resultant ZIF-8 membrane was tested for its H_2 and N_2 gas permeance under pressure differences ranged from 100 to 700kPa as shown in Figure-3. These experimental data exhibits repeatability with the error of ± 10%. In the pressure range studied, H_2 permeance is higher than N_2 permeance. This result is mainly attributed to the molecular sieving effect of ZIF-8 membrane with pore apertures of 0.34 nm(Huang *et al.*, 2006), which enables a higher permeance of H_2 with smaller kinetic diameter of 0.28 nmas compared to N_2 with larger kinetic diameter of 0.36 nm. Nonetheless, although the kinetic diameter of N_2 is larger than the pore aperture of ZIF-8, N_2 still can permeate through the ZIF-8 pore mainly due to the flexibility of ZIF-8 pore frameworks (Zhang *et al.*, 2012; Fairen-Jimenez *et al.*, 2011).

It is also observed from Figure-3 that both of the gas permeances are nearly independent of the effect of pressure differences. H_2 permeance of $7.642\pm0.029\times10^{-8}$mol/m^2·s·Pais obtained at pressure difference of 100kPa and increases slightly to $7.704\pm0.015\times10^{-8}$mol/m^2·s·Pa at700kPa. Meanwhile, N_2 permeance has also slightly increased from $0.746\pm0.014$to $0.801\pm0.015\times10^{-8}$mol/m^2·s·Pa. Although further increase in the pressure difference increases the flux of the gases, the chemical potential gradient of the membrane decreases at the same time due to the saturation of the surface coverage by the gas molecules (Li *et al.*, 2004). Therefore, both of these factors which happen simultaneously have resulted in almost constant H_2 and N_2 gas permeance through ZIF-8 membrane when the pressure difference increases.

On the other hand, Figure-4 shows the H_2/N_2ideal selectivity obtained in the present study under different pressure differences.H_2/N_2ideal selectivity of $10.25\pm0.17$is obtained at pressure difference of 100kPa, which is largely exceeding Knudsen selectivity of 3.7(Cacho-Bailo *et al.*, 2014). The selectivity decreases slightly to 9.63 ± 0.16 when the pressure difference increases to 700kPa. This result shows that the ZIF-8 membrane obtained in the present work has demonstrated high pressure stability up to 700 kPa.

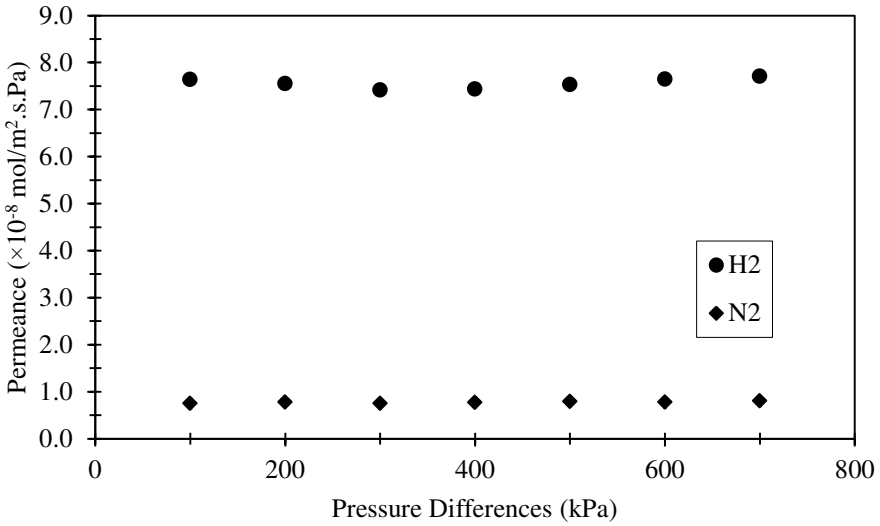

Figure-3. Singlegas H_2 and N_2 permeance for ZIF-8 membrane at pressure differences ranged from 100 to 700 kPa.

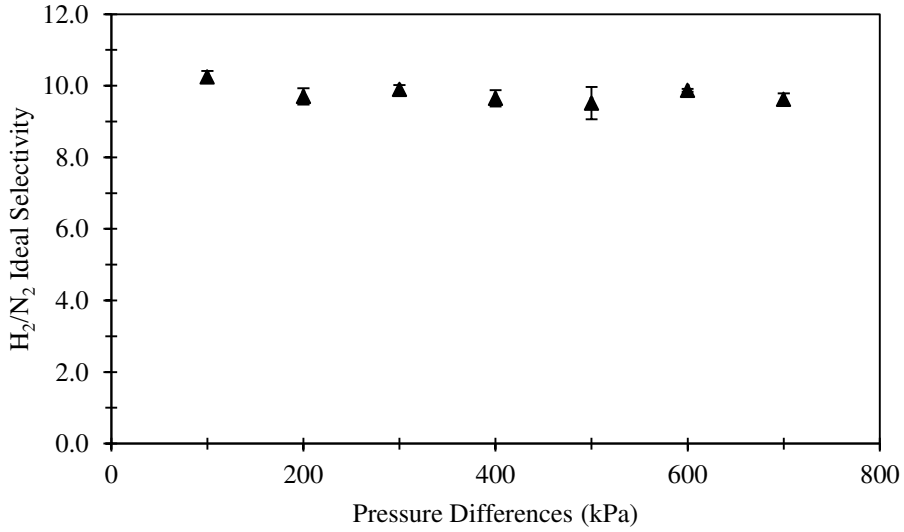

Figure-4. H_2/N_2ideal selectivity for ZIF-8 membrane at pressure differences ranged from 100 to 700 kPa.

Figure-5 shows the comparison of the ZIF-8 membrane synthesized in the present work with the other ZIF-8 membranes reported in the literatures (Bux *et al.*, 2009; McCarthy *et al.*, 2010; Pan and Lai, 2011; Shah *et al.*, 2013). The performance of the ZIF-8 membrane in terms of its H_2 permeance and H_2/N_2 ideal selectivity is comparable to the other reported data. It can be concluded that the solvent evaporation seeding method used in the present work is feasible and able to produce high quality and robust ZIF-8 membrane.

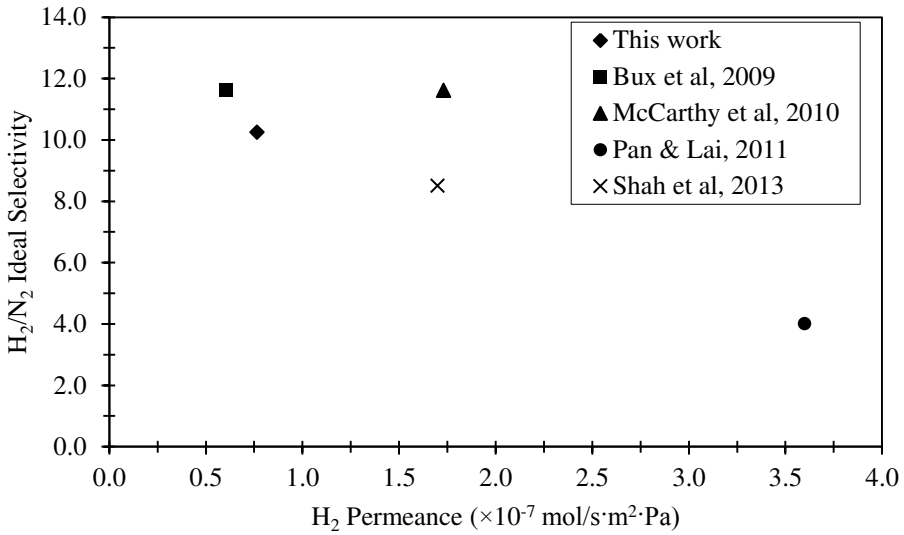

Figure-5. Comparison of H_2 permeance and H_2/N_2ideal selectivity among ZIF-8 membranes reported in the literatures.

CONCLUSIONS

In conclusion, a continuous and well intergrown ZIF-8 membrane was successfully synthesized viamicrowave-assisted secondary growth method with the feasible and reproducible solvent evaporation seeding method. The resultant membrane shows fully coverage of pure phase ZIF-8 grains based on the SEM image and EDX mapping, with the comparable gas permeation results shown. The molecular sieving property of themembrane is exhibited with H_2/N_2ideal selectivity of 10.25at pressure difference 100kPa. Meanwhile, negligible pressure effect on the performance of ZIF-8 membrane has been observed at higher pressure difference of 700 kPa, with only slight lowerideal H_2/N_2 selectivity of 9.63, demonstrating the high pressure stability of the ZIF-8 membrane. Therefore, the membrane shows its potential for the gas separation application in the industry.

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