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The Effect of Zeolite Imidazole Framework Geometrical Structure on Carbon Dioxide Permeability for Mixed Matrix Membrane

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ABSTRACTS

As the trade-off limitation of polymeric membrane between permeability and selectivity is still the biggest concern, the focus has now diverted into the potential of Mixed Matrix Membrane (MMM). Among the fillers used in MMM, the Zeolitic imidazole framework (ZIF) is one of the metal-organic frameworks (MOF) currently being investigated where findings have shown outstanding performances. Thus, this study aims to investigate the effect of fillers geometry on MMM's gas separation performance. The successful synthesis of ZIF-8 and ZIF-L were confirmed using X-Ray Diffraction (XRD) to measure the crystallinity, Scanning Electron Microscopy (SEM) to observe structure and morphology, and Fourier Transform Infrared (FTIR) to assess the functional groups of the ZIF-L and ZIF-8 particles. The gas permeation test shows that at the highest filler loading of 10wt%, ZIF-L MMM gives higher CO¬2 permeability (271 GPU) as compared to ZIF-8 MMM (121 GPU).

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1. INTRODUCTION

In the past decade, interest has been shifting on the improvement of the performance of polymeric membranes for gas separation due to the trade-off limit (Robenson, 2008). Ever since various types of membranes have been developed including Mixed Matrix Membrane (MMM). MMM comprises of polymer phase and dispersed phase or fillers such as silica particles (Ahn *et al*., 2008), zeolites (Bastani *et al.,* 2013; Poshusta *et al*., 2000), metal-organic framework (Basu *et al*., 2011; Perez *et al*., 2009), and carbon molecular sieve (CMS) (Vu *et al*., 2003). The gas transport mechanism in MMM is usually facilitated by a solution-diffusion mechanism. With the incorporation of inorganic fillers, free fractional volume (FFV) is created allowing the gas molecules to pass through the membrane.

Metal–organic frameworks (MOFs) have been widely integrated into membranes for gas separation studies due to their narrow pore windows and flexibility to be modified according to desired structural and chemical features (Vu *et al*., 2003). Zeolitic imidazole frameworks (ZIFs) in particular have the bright potential to be applied in MMM as they are flexible, chemically, and thermally stable and have been reported to improve the separation performance of polymeric membrane (Melgar *et al*., 2015). The incorporation of zeolites in polymers has been proven to improve the CO2/CH4 selectivity by 2.5 folds (Duval *et al*., 1993). As zeolites have high heat of adsorption with molecules with larger dipole moments, CO2 adsorption is high for zeolites filler. Nordin et al. reported on the improved CO2/CH4 selectivity by up to 72% with the incorporation of 0.5 wt% of modified ZIF-8 (Nordin *et al*., 2015). Meanwhile, the incorporation of ZIF-L in PEBAX MMM has also shown an improved CO2/CH4 selectivity by 5% (Zhu *et al*., 2019). However, there is still little to no research that focuses on the effect of ZIF's geometrical dimension on MMM separation performance.

Therefore, the objective of this work is to investigate the effect of fillers geometry on the CO2/CH4 separation performance of MMM. 2D ZIF-L and 3D ZIF-8 fillers in PSF dense membrane will be fabricated. ZIF-L and ZIF-8 will be synthesized following the methods established from previous literature (Nasir *et al*., 2017; Nordin *et al*, 2014).

2. METHODS

2.1. Materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2 \bullet 6H_2O$), 2-Methylimidazole (2-MeIM), Triethylamine (TEA), Polysulfone (Psf Udel® P-1700), Tetrahydrofuran (THF), Deionized water. All chemicals were used as received from Sigma Aldrich without prior purification.

2.2. Zif-L Synthesis

ZIF-L is prepared by dissolving 0.59g of $Zn(NO_3)_2 \bullet 6H_2O$ (solution A) in 40mL of deionized water and 1.30g of 2-MeIM (solution B) in 40mL of deionized water. The molar ratio between both is kept at 1:8. As solution B is stirred at a constant speed, solution A is added dropwise and the mixture is stirred for 4 hours. The product is then undergone repeated centrifugation at 10000rpm for 20 minutes with three times washing with fresh methanol. The ZIF-L yield is then dried in the oven overnight at 70ºC. The ZIF-L particles are then grounded into fine particles before being activated at 100 ºC for 12 hours (Nasir *et al*., 2017).

2.3. ZIF-8 Synthesis

ZIF-8 is prepared adopted from previous literature (Nordin *et al*., 2015). Firstly, 2g of $Zn(NO_3)_2 \bullet 6H_2O$ (6.72 mmol), 3.312g of 2-MeIM (40.43 mmol), and a predetermined amount of TEA are dissolved in deionized water. The molar ratio is kept at 1:6:500. The mixture is

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stirred vigorously for 30 minutes until a cloudy solution is formed. The obtained product is washed several times with deionized water to remove excess reactants and dried in the oven at 60 ºC overnight. The ZIF-L particles are undergone an activation process at 100 ºC for 12 hours.

2.4. Membrane fabrication

Dense MMM was fabricated at the constant polymer concentration of 15wt%, adopted from the literature (Jusoh *et al*., 2014). The fillers loading is varied from 2.5 to 10 wt%. **Table 1** shows the membrane abbreviation with each respected filler composition of all fabricated membranes.

Table 1. Prepared membrane with its abbreviation and respective filler loading.

Membrane abbreviation	Filler loading (wt% based on the weight of polymer)
ZL-2.5	2.5
ZL-5.0	5.0
ZL-7.5	7.5
ZL-10.0	10.0
Z8-2.5	2.5
Z8-5.0	5.0
Z8-7.5	7.5
Z8-10.0	10.0

2.5. Characterization

X-Ray Diffraction (XRD) analysis was carried out using Siemens D5000 Diffractometer to measure the crystallinity of ZIF-L and ZIF-8 particles. Scanning ranges between 5º to 40º were employed with copper Kα (λ = 0.1541 nm at 40 kV and 30 mA) was used as the source of radiation. Scanning electron microscopy (SEM, TM3000, Hitachi)) was used to observe the membrane structure and morphology. Fourier Transform Infrared (FTIR) spectra in the range of 4000-400 cm-1 were obtained to test the functional groups of the ZIF-L and ZIF-8 particles.

2.6. Gas Permeation

The gas permeation was conducted using pure CO_2 and CH_4 gas at 2 bar feed pressure and room temperature (25˚C). CH4 was tested first to avoid membrane plasticization by CO2 and the flow rate of gas permeated was measured using a bubble flow meter. The permeance, P/l (unit GPU), is then calculated using the following equation 1:

$$P/l = \frac{Q_{STP}}{A.\Delta P} \quad (1)$$

Where Q_{STP} is the permeate flow rate at standard temperature and pressure. A is the effective surface area of the membrane film, ΔP is the pressure gradient across the membrane. The unit of gas permeance is expressed in GPU (eq. 2).

$$1\ GPU = 1 \times 10^{-6}\ \frac{cm^3(STP)}{sec.cm^2.cmHg} \quad (2)$$

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3. RESULTS AND DISCUSSION

3.1. ZIF-L and ZIF-8 Characterization

Figure 1 shows the XRD spectra of both ZIF-L and ZIF-8. For ZIF-L, diffraction peaks can be observed at {110}, {200}, {211}, {220}, {310}, and {220} planes which were observed at 2θ = 7.40º, 10.47º, 12.78º, 14.80º, 16.74º and 18.08º, respectively. Meanwhile, for prepare ZIF-8 particles, strong peaks at 2θ = 7.30º, 10.35º, 12.70º, 14.80º, 16.40º and 18.00º, which corresponds to the planes at {110}, {200}, {211}, {220}, {310}, and {222}, respectively. Both results show that ZIF-L and ZIF-L were successfully synthesized and shows high crystallinity.

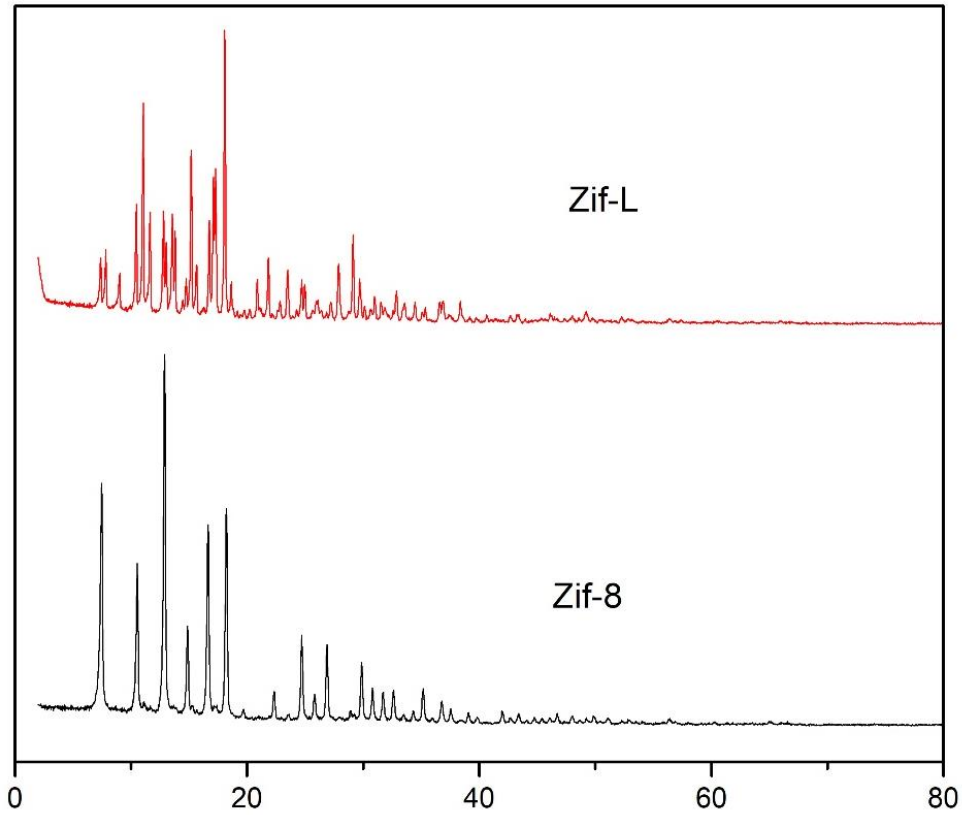

Figure 1. XRD spectra of ZIF-L and ZIF-8.

FTIR analysis was conducted to study the functional group of both ZIF-L and ZIF-8 particles and the spectra are plotted in **Figure 2**. ZIF-8 functional groups were defined in the peak band at 3433.02 cm−1 which attributes to the N-H stretching vibration. Both peaks at 3134.84 cm−1 and 2971.92 cm−1 can also be attributed to the aromatic and aliphatic C-H asymmetric stretching vibrations, respectively while the peak at 1585 cm-1 was associated with the C=N stretch vibration. Meanwhile, bands at 1310.19-1458.45 cm−1 were for the entire ring stretching, and the signal at 1146 cm−1 is for aromatic C-N stretching mode. The peaks at 996 and 759 cm−1 were for C-N bending vibration and C-H bending mode, respectively. For ZIF-L, corresponding characteristic peaks can be observed at 1600 cm−1 which represents the C=N stretch in the imidazole ring, while at 1300 cm−1 associated with the C-N stretching band.

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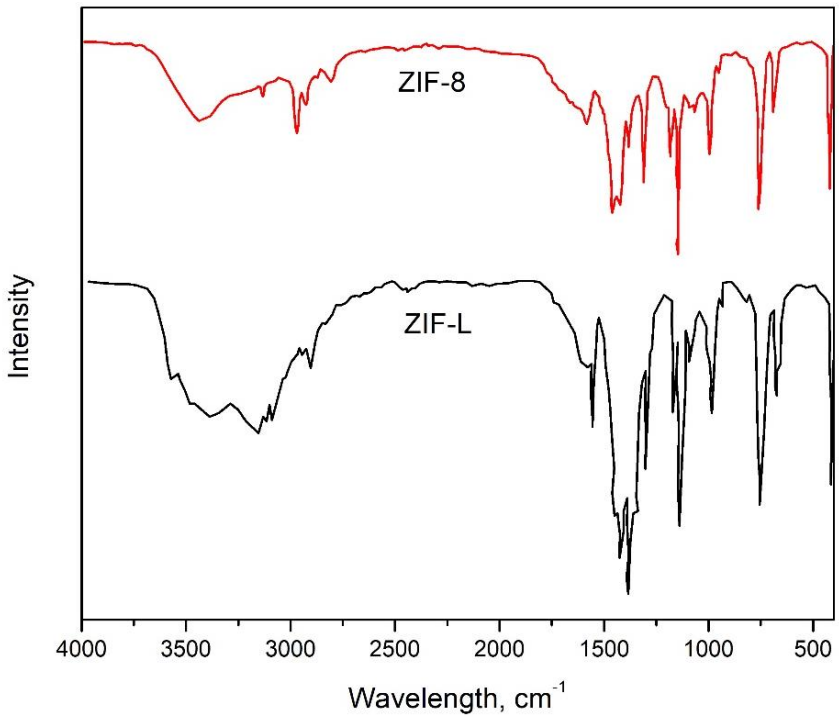

Figure 2. FTIR spectra of ZIF-L and ZIF-8

SEM analysis was also conducted to observe the morphology of the prepared ZIF-L and ZIF-8 particles at a magnification of 10kx and the result is shown in **Figure 3**. From the result, ZIF-L shows the leaf-like shape while ZIF-8 shows a hexagonal-like shape in line with literature (Khan *et al*., 2018).

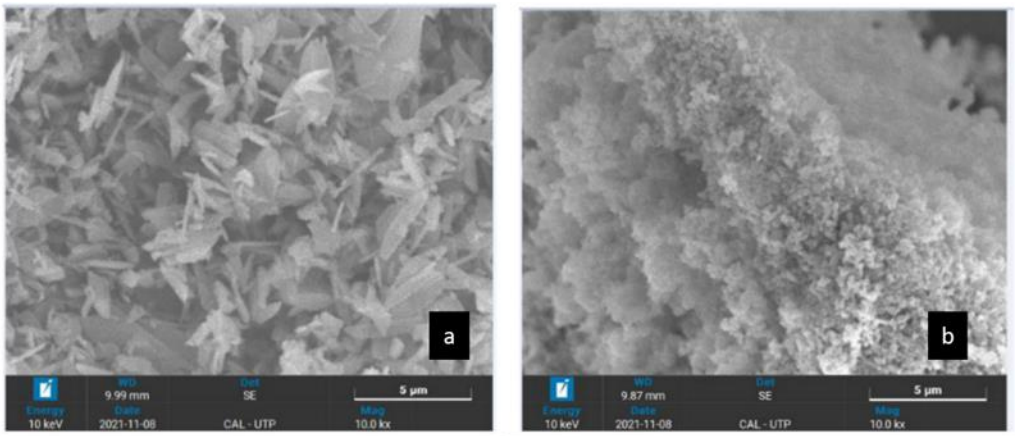

Figure 3. SEM images of a) ZIF-L and b) ZIF-8 at a magnification of 10kx.

3.2. Gas

Figure 4 shows the CO_2 permeability of all prepared ZIF-L and ZIF-8 MMM at different filler loading. Firstly, for ZIF-L MMM, ZIFL-2.5 shows CO_2 permeability of 40.18 GPU. With increasing loading, ZIFL-5.0, ZIFL-7.5, ZIFL-10.0 shows a significant increase of 27.5%, 210.0%, 577.5%, respectively. Meanwhile, for ZIF-8 MMM, the CO_2 permeability of ZIF8-2.5 starts at 11.71 GPU. With increasing loading to ZIF8-5.0, the CO2 permeability drops a little by 1.75 folds but increases with ZIF8-7.5 and ZIF8-10 by 2.47 folds and 10.41 folds, respectively. Overall, for all filler loading, ZIF-L MMM displays a higher CO2 permeability compared to ZIF-

8 MMM. By configuration, ZIF-8 promotes higher CO_2 permeation due to having pore openings of 3.4Å equivalent to the kinetic diameter of CO_2. The decrease in CO_2 permeability in ZIF-8 MMM is probably due to (1) polymer chain rigidification which would hinder the CO_2 permeation across the membrane hence low permeability or (2) due to pore blockage induced by the polymer during membrane fabrication. Therefore, as an initial observation, it can be postulated that ZIF-L MMM gives higher CO_2 permeability compared to ZIF-8 MMM.

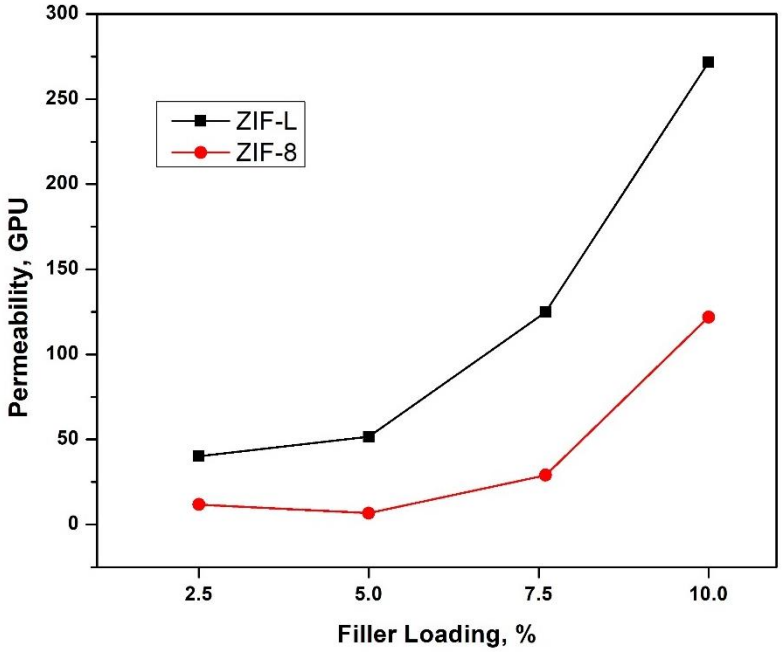

Figure 4. CO2 permeability of ZIF-L and ZIF-8 MMM at different filler loading.

4. CONCLUSION

The effects of MOF's geometrical structure on the gas separation performance of MMM are investigated. PSF membrane incorporated with different loadings of ZIF-L and ZIF-8 particles were successfully fabricated as indicated by the characteristic peaks shown from XRD and FTIR analysis. The CO2 permeability test shows that ZIF-L MMM gives higher CO2 permeability as compared to ZIF-8 MMM. At the highest filler loading of 10wt%, ZIF-L MMM gives an almost 123% increment in CO2 permeability compared to that of ZIF-8 MMM. Although the dimensional structure of ZIF-L and ZIF-8 MMM has shown significant findings in the CO2 permeability, further study on the filler's distribution across the membrane and its effect on gas solubility and diffusivity would be beneficial to further understand this topic.

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6. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. Authors confirmed that the paper was free of plagiarism.

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