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Mixed Matrix Membranes Comprising of ZIF-8 Nanofillers for Enhanced Gas Transport Properties

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Abstract

In the current research, mixed matrix membranes (MMMs) comprising of 5, 10, 15 and 20 wt% of zeolitic imidazolate framework-8 (ZIF-8) were incorporated into 6FDA-durene polyimide phase. The effect of ZIF-8 loading on the membrane performance of CO_2 and CH_4 separation was investigated. The excellent compatibility and good distribution of ZIF-8 nanofiller in 6FDA-durene polyimide phase even at higher ZIF-8 loading up to 20 wt% has resulted in the increment of CO_2 permeability and CO_2/CH_4 selectivity compared to pure membrane. In this work, 6FDA-durene loaded with 10 wt% ZIF-8 demonstrated impressive CO_2 permeability of 1426.75 Barrer with CO_2/CH_4 selectivity of 28.70, which successfully surpassed the Robeson 2008 upper bound.

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Keywords: ZIF-8; 6FDA-durene; Mixed matrix membrane, CO_2/CH_4 Separation

1. Introduction

Natural gas has been forecasted to be the quickest growing fuel of world energy consumption [1]. The utilization of natural gas is predicted to rise up to 70 percent higher than the amount of natural gas consumed in 2001 by the year of 2025 [2]. The increasing demand of natural gas pushes the energy industries to explore the reservoir with high CO_2 content and impurities. However, the impurities need to be removed in order to prevent a severe corrosion of pipelines and equipments as well as to meet the pipeline specification before being commercialized in the industry [3]. The current technologies used to purify natural gas including absorption, adsorption, cryogenic and

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membrane separations. Among these technologies, membrane is preferable because it requires small space and weight, low labor intensity and maintenance as well as minimum utility requirements [4].

Membrane separation technology has experienced rapidly and continued progress due to its advantages. Gas separation membranes can be generally classified into three categories; polymeric, inorganic and mixed matrix membranes (MMMs) [5]. Polymeric membranes have been widely utilized in industrial application because it is relatively cheap, flexible and easy to fabricate. However, the separation performance of pure polymeric membrane is not able to achieve required selectivity standards and suffer from the upper bound limit, where high permeability and high selectivity cannot be simultaneously attained [6]. On the other hand, inorganic membrane offers higher permeability and selectivity with great chemical and thermal stability. However, it is limited by the fabrication cost and mechanical strength of the membrane material [7].

In order to overcome the above aforementioned drawbacks, MMM has been introduced by incorporating inorganic filler into the polymer phase [8]. The beginning of MMM era have been concentrated on the incorporation of traditional fillers such as zeolites [9-11] and silicas [12, 13] into the commercial type of polymer phase. Even though these materials have shown their promising application in gas separation, the significant problems such as poor compatibility and poor adhesion between the filler and polymer, as well as phase separation are the critical issues found during the fabrication of MMMs [14-16].

Recently, a subclass of metal organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs), has been identified as one of the materials which is capable to enhance the compatibility between inorganic and polymeric materials [17]. Among the ZIFs, zeolitic imidazolate frameworks-8 (ZIF-8) has emerged as an attractive filler for CO_2/CH_4 separation. ZIF-8 is built up from zinc (II) cations and 2-methylimidazole anions, giving a sodalite (SOD) zeolite type structure with two times larger of pore size compared to SOD zeolites [18]. Besides, ZIF-8 consists of six-ring β-cages with aperture pore size of 3.4Å. The characteristics of ZIF-8 such as high surface area, highly porous open framework structure and great chemical and thermal stability, make it an attractive candidate for gaseous separation, especially for CO_2/CH_4 separation [19].

6FDA-durene is a type of polyimide which shows extraordinary gas separation performance as compared to other type of 6FDA-based polyimides. The presence of $–CF_3$- group in its backbone chain inhibits the dense chain packing and reduces local segment mobility and thus, resulted in the increment of permeability and selectivity [20]. Based on the aforementioned advantages, 6FDA-durene polyimide was chosen as a continuous phase for the fabrication of MMM in this study.

In the present work, a series of MMMs were fabricated by incorporating different loadings of nano-sized ZIF-8 into 6FDA-durene polymer matrix. The physical and chemical properties of the resultant membranes were characterized using different analytical tools such as XRD, FESEM and EDX. Subsequently, the permeation properties of ZIF-8/6FDA-durene MMMs in CO_2/CH_4 separation were studied in order to investigate the effect of ZIF-8 loading in 6FDA-durene towards the separation performance.

2. Methodology

2.1. Chemicals and gases

For the fabrication of mixed matrix membrane, 6FDA-durene polymer and 50nm of ZIF-8 crystals were synthesized from our laboratory. Dichloromethane (DCM, ≥ 99.8% purity) solvent was obtained from Sigma Aldrich and used as received. Gases for permeation experiments, such as carbon dioxide (≥ 99.995 % CO_2) and methane (99.995 % CH_4) were purchased from Gas Walker Sdn Bhd and used as received.

2.2. Fabrication of Pristine and ZIF-8/6FDA-durene Mixed Matrix Membrane

6FDA-durene and ZIF-8 particles were dried in a vacuum oven at 60°C overnight prior to use. 6FDA-durene flat sheet membrane was prepared by dissolving 2% w/v solution of polymer in DCM before cast on a Petri dish. The cast film was dried and annealed at 250°C in a vacuum oven. On the other hand, MMMs contained different inorganic fillers loadings (5, 10, 15 and 20 wt%) were fabricated by using DCM as solvent. Two solutions of polymer and ZIF-8 were prepared in two separate vials. 6FDA-durene polymer was added into DCM and stirred until dissolved. Then, 5, 10, 15 and 20 wt% of ZIF-8 crystals were added into DCM, stirred and sonicated for 1 h to disperse ZIF-8 in DCM. Then, the ZIF-8 nanocrystals were primed by adding a small amount of polyimide solution to the ZIF-8 solution, which it was further stirred and sonicated for another 1 h. After thorough mixing, the remaining bulk polymer solution was added and the mixture was again further stirred and sonicated for 1 h. Lastly, the mixture was stirred vigorously for 1 h before cast on a Petri dish. The cast film was then dried in an oven at 60°C followed by annealing at 250°C for 24 h.

2.3. Characterization of pristine 6FDA-durene membrane and ZIF-8/6FDA-durene MMM

The elemental compositions and the distribution of the fillers in the resultant membranes were verified using an energy-dispersive X-ray spectroscopy (EDX) apparatus equipped with the FESEM via the EDX data analysis and mapping image, respectively.

2.4. Gas Permeation Measurements

Single gas permeation measurements were conducted using custom-built gas permeation test rig at 30°C and 3.5 bar for CO_2 and CH_4 gases. The detailed explanation on the testing setup and procedure can be found elsewhere [21]. The permeability of CO_2 and CH_4 were calculated as follows [22]:

$$P_A = \frac{V_p t}{A_m (p_h - p_l)} \qquad (1)$$

Where P_A is the permeability of membrane, V_p is the permeate flow rate, t is the thickness of membrane, A_m is the membrane area , p_h and p_l are the pressure in feed side and permeate side respectively, A is CO_2 or CH_4. The permeability of the membranes were reported in the unit of Barrer (1 Barrer $=1\times10^{-10}$ cm^3(STP).cm/s.cm^2.cmHg).

The ideal selectivity of the membrane can be obtained by dividing permeability of CO_2 over permeability of CH_4.

3. Results and Discussion

3.1. Characterization of pristine and MMM

Fig. 1 displays the dispersion of ZIF-8 particles in polymer phase by mapping the Zn element in the MMM using EDX. It can be observed from Fig.1 that ZIF-8 particles are homogenously distributed in the polymer matrix without agglomeration even at higher loading up to 20 wt%. As ZIF-8 particles are primarily consists of Zn element, well distribution of Zn element indicates the uniform dispersion of ZIF-8 particles in polymer matrix.

3.2. Gas Permeation Properties

Separation performance of the resultant membranes were conducted using pure gases; CO_2 and CH_4. Fig. 2 shows the CO_2 and CH_4 permeability of pristine membrane and ZIF-8/6FDA-durene MMMs. All the resultant MMMs demonstrate higher CO_2 permeability as compared to pristine membrane. At ZIF-8 loading of 5, 10, 15 and 20 wt%, the MMMs show CO_2 permeability of 693.5 Barrer, 1426.8 Barrer, 1466.1 Barrer and 1462.8 Barrer, respectively as compared to pristine membrane, with CO_2 permeability of only 468.0 Barrer.

It can be seen from Fig. 2 that the increment of ZIF-8 loading in the MMM increases the CH_4 permeability from 49.71 Barrer for 5 wt% ZIF-8/6FDA-durene MMM to 163.11 Barrer for 20 wt% ZIF-8/6FDA-durene MMM. The increment of CO_2 and CH_4 permeability with the increase in ZIF-8 loading is mainly due to the good compatibility between the inorganic filler and polymer phase and well dispersion of ZIF-8 in the polymer phase as shown in EDX mapping [23]. The good compatibility between ZIF-8 material and 6FDA-durene phase could be explained due to the nano-sized of ZIF-8 particles used in the present work and ability of ZIF-8 particles to remain in a suspension

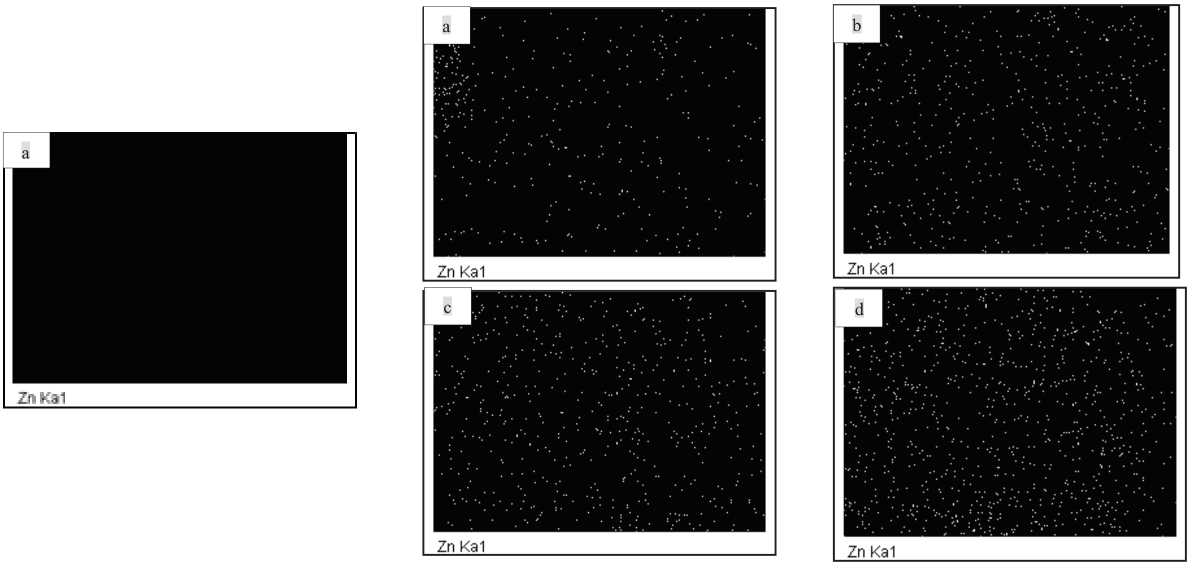

Fig. 1: EDX mapping of ZIF-8/6FDA-durene MMM at different ZIF-8 loading of (a) 0 wt% (b) 5 wt% (c) 10 wt% and (d) 15 wt% (e) 20 wt%

state before cast [24]. The improvement of permeability might be also due to the presence of inorganic filler that interrupted the polymer chain packing which might be able to increase the free volume and the diffusion pathways for gas penetration [25]. In addition, the combined effects of the pore aperture sizes of ZIF-8 and strong quadrupolar interaction of CO_2 with the imidazolate linker in the ZIF-8 particles framework facilitates the transport of gases [26]. Besides that, the presence of $C(CF_3)_2$- and bulky methyl group in 6FDA-durene polyimide also plays the role in resulting higher permeability due to the steric bulk hindrance which contributes to the chain stiffness and reduction of the chain packing [27]. As a result, the gas permeability increases.

Fig. 3 demonstrates the CO_2/CH_4 ideal selectivity of the MMM with respect to the ZIF-8 loading. All the MMMs demonstrate higher CO_2/CH_4 selectivity as compared to pure membrane. The CO_2/CH_4 selectivity of 5 wt% ZIF-8/6FDA-duren f only 7.03.

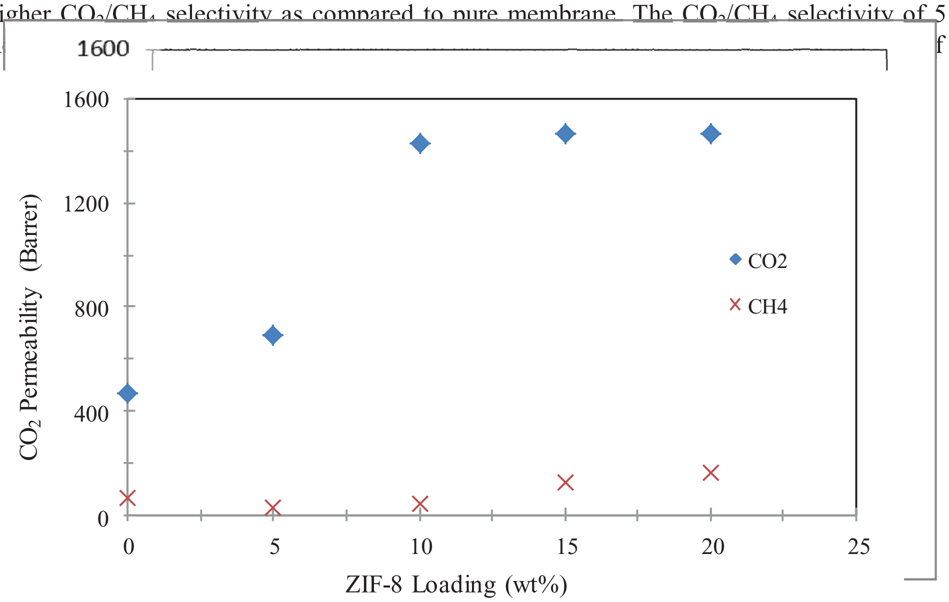

Fig.2: Effect of ZIF-8 loading on CO_2 and CH_4 permeability

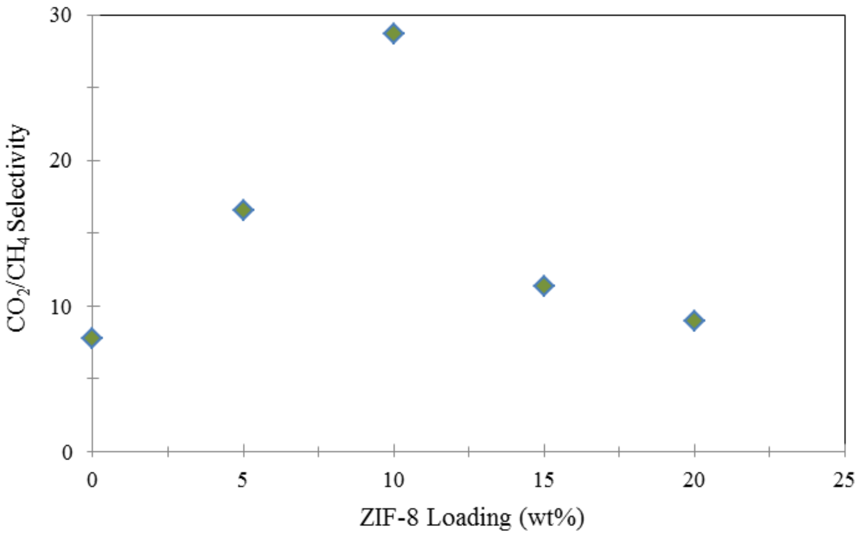

Fig.3: Effect of ZIF-8 loading on CO_2/CH_4 selectivity

Meanwhile, at loading of 10 wt% ZIF-8 in 6FDA-durene polymer matrix, the highest CO_2/CH_4 selectivity (28.70) with the increment of 250% as compared to pristine membrane is obtained. This result could be due to the small pore size of ZIF-8 (3.4Å) that able to separate smaller gas molecule, CO_2 (3.3 Å) from CH_4 (3.8 Å) through the interior cavities of ZIF-8 [28]. However, as the loading of ZIF-8 further increases to 15 and 20 wt%, CO_2/CH_4 selectivity decreases to 11.3 and 9.0, respectively. This may due to the presence of unselective voids at higher loading of ZIF-8. Overall, in this work, all the MMMs demonstrate the improvement in gas permeability and gas pair selectivity.

3.3. Performance Comparison with Robeson Upper Bound

Fig. 4 shows the Robeson plot for CO_2/CH_4 separation and the position of the data points for the MMMs synthesized in the present work. Based on Fig. 8, MMM with loading of 5 wt% and 15 wt% of ZIF-8 are successfully surpassed the 1991 Robeson upper bound. On the other hand, 10% ZIF-8/6FDA-durene MMM is able to improve the performance of the membrane in CO_2/CH_4 separation and surpasses the 2008 Robeson's upper bound line.

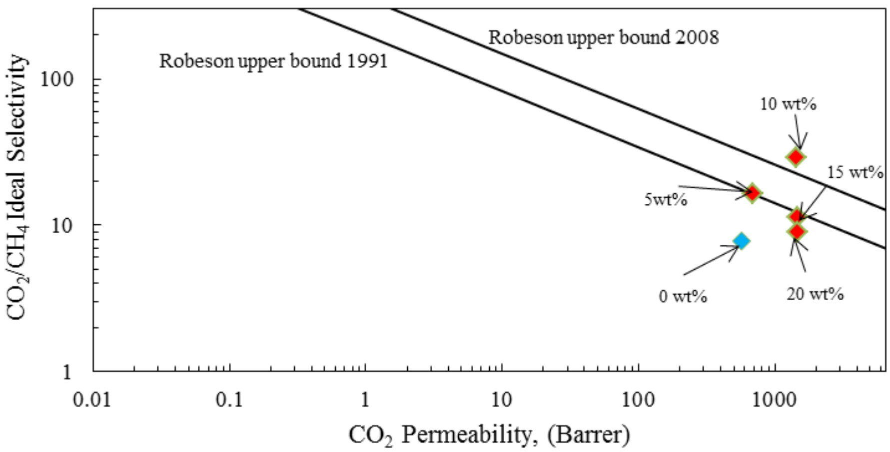

Fig. 4: Gas separation performance of ZIF-8/6FDA-durene MMM at different loading compared with CO_2/CH_4 Robeson's upper bound

4. Conclusion

In this research, ZIF-8/6FDA-durene MMMs with ZIF-8 loadings up to 20 wt% were fabricated and tested for CO_2/CH_4 separation. The effects of ZIF-8 loading in 6FDA-durene phase on the structural properties and gas separation performance have also been studied. Well dispersed of particles with no sign of agglomeration is observed in EDX mapping images for all the resultant MMMs.

Experimental results showed that the increase in CO_2 permeability with increasing ZIF-8 loading was mainly due to the great compatibility between the filler and polymer phase. Besides, it also could be due to the increment of free volume for gas penetration. The incorporation of ZIF-8 into polymer chains led to significant changes in ideal CO_2/CH_4 selectivity because of the molecular sieving characteristics of ZIF-8 particle which enhanced the separation of CO_2 from CH_4. An increment as high as 250% (28.70) in CO_2/CH_4 selectivity is achieved by using 10wt% ZIF-8/6FDA- durene MMM. This membrane has been successfully surpassed the Robeson's upper bound trade-off curves. From these results, it can be concluded that the membranes developed in the present research demonstrated a superior performance in CO_2/CH_4 separation and potential to be utilized in natural gas purification process.

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