



Innovative layer by layer and continuous growth methods for synthesis of ZIF-8 membrane on porous polymeric support using poly(ether-*block*-amide) as structure directing agent for gas separation



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ABSTRACT

Poly(ether-*block*-amide) (Pebax grade 1657) was utilized as structure directing agent for fabrication of ZIF-8 membranes on polyphenylsulfone (PPSU) by layer-by-layer and continuous methods of growth. N₂ adsorption, SEM, XRD, TGA and FTIR tests were applied to characterize the synthesized membranes. Polydimethylsiloxane (PDMS) was utilized to cover the possible surface defects of ZIF-8 membranes by dip coating method. The ideal performances of uncoated and coated synthesized ZIF-8 membranes were evaluated in separations of CO₂/CH₄, CO₂/N₂, H₂/CH₄ and H₂/N₂. The results showed that: 1- The coating of membranes by PDMS significantly enhanced the selectivity and decreased the permeance in almost all separation tests. 2- Higher numbers of cycles of solution changing in layer-by-layer method resulted in less permeable and more selective membranes. 3- Continuous growth method with PDMS coating lead to observation of maximum separation factors in many permeation tests: In permeances of 2.5×10^{-7} mol m⁻² s⁻² Pa⁻¹ for H₂ and 1.9×10^{-7} mol m⁻² s⁻² Pa⁻¹ for CH₄, exceptional ideal selectivities of 22.8, 20.8, 17.3 and 15.8 were obtained for H₂/CH₄, H₂/N₂, CO₂/CH₄ and CO₂/N₂, respectively.

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1. Introduction

CO₂ emission is a threat to environment. Global warming and ocean acidification can be enumerated as the most serious consequences of CO₂ emission [1–3]. The rate of CO₂ emission in atmosphere is rapidly increasing mainly due to raised consumption of oil and gas mostly originating from significant drop in price of these fuels in recent years. Therefore, the need for effective and energy efficient methods of CO₂ capture was realized by industries [2,3]. One of the key solutions to CO₂ emission crisis is to utilize more environmental friendly fuels instead of fossil fuels. Hydrogen is a fuel with zero-emission burning product [4]. The product of H₂ burning is water, which is a precious substance to human these days. H₂ is also a key element in many industrial processes such as in refinery processes, methanol production, etc [5]. Hence, the separation of this gas from mixture of other industrial gases by a safe and efficient method is also exigent.

Membrane-based separation processes with their low energy consumption and ease of operation show more promises than other traditionally used technologies such as adsorption and cryogenic operations in gas separation [6]. Among all different types of membranes materials used for gas separation, metal organic frameworks (MOFs) which consist of metal clusters or cations joined by organic ligands showed notable promises. Remarkable progresses were observed in development of MOFs in recent years especially in CO₂ and H₂ separations [6,7].

MOF membranes supported by a porous inorganic support are the most widely used types of these membranes for gas separation [6–10]. The reason for selection of porous inorganic support was mainly due to the higher mechanical and thermal stability of these materials compared to polymers. However, inorganic materials often need functionalization in order to be used as support of membrane and they often have to be seeded for fabrication of selective layer on their top [8–17]. These drawbacks motivated the researchers to look for another type of support. In recent studies, utilization of polymeric materials for support of membranes has been reported [18–21]. The main reason for selection of polymers as support was the good compatibility between MOFs and

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polymers at selective layer-support interface resulted from the organic nature of polymers.

Nylon was used by Yao et al. as support of ZIF-8 [21]. Polyethersulfone and Polysulfone were used as support of ZIF-8 by Ge et al. [19] and Nagaraju et al. [20] respectively in separate works. Polyimide was used as substrate for ZIF-8 in a work by Jin et al. [22] for catalytic purposes. Brown et al. [23] used polyimide/polyamide as support in synthesis of hollow fiber ZIF-90 membrane and recently Cacho-Bailo et al. [18] used Psf as substrate for ZIF-8 to enhance H₂ separation performance of membranes. Although, different types of supports have been used by these researchers, however the gas separation properties obtained in their works were not satisfying at least compared to the membranes synthesized on inorganic supports.

It is certain that there are advantages using polymers as support, as was reported by several researchers, however, low thermal stability of polymers is a problem because MOFs tend to grow on the surface of support at high temperatures and many of polymers cannot withstand high temperatures and consequently deform. Therefore, both the temperature of synthesis environment and the selection of support material for that temperature are critical in fabrication of functional MOF membranes.

In order to fabricate MOF membranes in higher temperatures, a polymeric support with high thermal resistance (high T_g) with satisfying mechanical stability and processability is required. Polyphenylsulfone (PPSU), a member of sulfone polymers, with high processability and remarkable thermal resistance (does not deform until near 500 °C) is a superior membrane support candidate compared to Psf and PES [24].

Zeolite imidazolate frameworks (ZIF), a subclass of MOFs consisting inorganic metal clusters coordinated with organic imidazole ligands have been extensively used as membrane in gas separation applications [8,13–15,23,25–30]. ZIF-8, the most studied member of this family, with a SOD topology and ring pore apertures of 3.4 Å has intrinsic affinity for CO₂ and widely investigated for separation of this gas from different gases [10,11,14–16,19,30–35]. Moreover, owing to unique pore size (0.34 nm) and structure of this microporous material, H₂ separation with molecular sieving mechanism has been also an extensively investigated field of research in recent years [7,9–11,14–16,19,21,25–27,29–36].

Recently ZIF-8 particles with enhanced porosity were synthesized using Pebax 1657 as structure directing agent [37]. The porosity and gas sorption capacity of ZIF-8 synthesized by this method was notably enhanced due to the change in the pore size of ZIF-8 from microporous to near mesoporous regime. A similar approach was applied in this study to use the enhanced porosity of ZIF-8 membrane for separation of H₂ and CO₂ with a novel synthesis method explained hereafter in this report.

The thermal stability of PPSU enabled us to perform fabrication of ZIF-8 membrane in higher temperatures compared to most of reported synthesis procedures in literature. The performance of prepared ZIF-8 membranes was investigated for separation of CO₂ and H₂ from CH₄ and N₂.

2. Experimental

2.1. Materials

2-methyl Imidazole (99%, MeIm), Zinc nitrate hexahydrate (99%, Zn(NO₃)₂·6H₂O), Ethanol (99.99%, EtOH), *N*-Methyl-2-pyrrolidone (99.99%, NMP), *n*-hexane (99.99%) and Deionized Water (H₂O) were all purchased from Merck Inc. and used as received without further purification. Poly(phenyl sulfone) (PPSU) and Polydimethylsiloxane (PDMS) were both provided by Sigma Aldrich Inc.

and Pebax 1657 purchased from Arkema Inc. and used as received without any modification.

2.2. Synthesis of PPSU support

To synthesize a porous PPSU support, 40 g of PPSU powder was dissolved in 200 ml of NMP. The stirring continued for 12 h. To remove the trapped bubbles in polymeric solution, aging for about 5 h was needed. The polymeric solution was then casted on glass substrate using a casting knife with adjusted gap of about 200 μm. The casted PPSU layer was then placed in coagulation bath of water. After 24 h for phase separation and solvent exchange the coagulated film of PPSU was placed in air at ambient temperature to dry for about 24 h.

2.3. Synthesis of ZIF-8 membrane on PPSU support

The synthesis of ZIF-8 membrane on PPSU support was performed by in situ crystallization method in the presence of Pebax 1657. For comparison purposes, two different method of ZIF-8 membrane synthesis were applied. In the first method (layer-by-layer growth), the PPSU film was placed and stuck to the bottom of a vessel with stickers made of indissoluble material in water to avoid growth of crystal at both sides of support. The solution containing 140 ml of ethanol, 60 ml of water, 4 g of Pebax 1657 granules and 2 g of zinc nitrate hexahydrate (Zn(NO₃)₂·6(H₂O)) was prepared under vigorous stirring. This solution was transferred to the vessel containing PPSU support then aged for 24 h. This solution which contains Zn²⁺ above PPSU film was then replaced by 200 ml of 70 vol%–30 vol% of ethanol-water solution containing 27.6 g of 2-methyl Imidazole (MeIm) while the PPSU film was kept there for another 24 h. This sequence was repeated several times with the same but fresh solutions to help the growth of formed ZIF-8 crystals at surface of PPSU. After the ZIF-8 membranes have passed predetermined cycles of solutions replacements, it was placed in a furnace with a temperature progression of 10 °C/min from ambient temperature to 450 °C. The sample was remained in furnace at 450 °C for 24 h to ensure the complete removal of Pebax 1657 from the structure.

In the second method (continuous growth) of ZIF-8 membrane synthesis, the PPSU film was placed and stuck to the bottom of a Teflon lined autoclave. Both of first and second prepared solutions in previous method were poured on PPSU film gently and simultaneously along with stirring for 1 h. The autoclave was placed in oven for 72 h at 150 °C boosting the assembly reaction of ZIF-8 particles formation. After this duration, the resulted ZIF-8 membrane was separated from the bottom of autoclave, placed in a furnace, heated with the exact heating conditions explained for previous method.

The schematic diagram of brief synthesis procedures of ZIF-8 membranes are provided in Fig. 1.

2.4. Coating of synthesized ZIF-8 membrane

Each of ZIF-8 membrane samples prepared by layer-by-layer and continuous growth methods were split into two similar parts. One of those parts was coated by PDMS to investigate the effectiveness of coating in covering the possible surface defects. The PDMS is a highly permeable polymer. The applications of thin layers of this polymer on the surface of a membrane as defect covering layer have been previously reported [38].

To prepare coating solution, 10 ml of PDMS was diluted in 40 ml of *n*-hexane to adjust its viscosity for coating purpose. The prepared ZIF-8 membrane stuck to the bottom of petri dish and the coating solution was poured gently over the ZIF-8 membrane surface until

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