Current Perspectives and Mini Review on Zeolitic Imidazolate Framework-8 (ZIF-8) Membranes on Organic Substrates

P D Sutrisna¹, E Savitri¹, N F Himma², N Prasetya³ and I G Wenten⁴

¹Department of Chemical Engineering, University of Surabaya, Jl Raya Kalirungkut, Surabaya, 60293, Indonesia
²Department of Chemical Engineering, Universitas Brawijaya, Jl Mayjen Haryono 167, Malang 65145, Indonesia
³Barrer Centre, Department of Chemical Engineering, Imperial College London. Exhibition Road, London SW7 2AZ, United Kingdom
⁴Department of Chemical Engineering, Institut Teknologi Bandung, Jl Ganesha 10, Bandung 40132, Indonesia

E-mail: pudod@staff.ubaya.ac.id

Abstract. Zeolitic Imidazolate Framework (ZIF) membranes have been considered as promising membrane for gas separation processes due to their robustness and good separation capabilities. The separation of hydrogen (H₂) from larger gases is one of their potential applications. Among the different types of ZIF, ZIF-8 is considered as potential candidates for H₂ separation owing to its small aperture size and excellent chemical stability. In recent years, ZIF-8 membranes have been fabricated on both inorganic and polymeric substrates. The fabrication of the ZIF-8 layer on polymeric substrates is more challenging than its inorganic counterpart because of the incompatibility issue between organic substrates and ZIF-8. However, the flexible nature of polymeric substrates offers better mechanical stability at high pressure than inorganic substrates. The purpose of this mini-review is to present the state of the art and challenges of research on ZIF-8 membrane synthesis on different polymeric substrates. These challenges include the formation of cracks and defects due to compatibility issues and membrane stability at different operating conditions. Current research results showed excellent gas separation properties of ZIF-8 membranes on polymeric substrates that can surpass the trade-off line of gas permeability and selectivity.

1. Introduction

Carbon Capture and Storage (CCS) is indispensable to enable the ongoing utilization of fossil fuels while reducing the emissions of CO₂ to the atmosphere. CCS is a three-step process including CO₂ capture from other gases in the gas emission source; CO₂ transport to a storage location, and the permanent storage of CO₂. The considerable cost of capture, more than 60 % of the total cost for CCS, is slowing down the implementation of commercial CCS. It is reported that the cost for the capture process already consumes energy up to 40 % of the overall energy cost [1]. The key to reduce the CO₂ capture cost is to increase the separation efficiency of capture material and technique. Therefore, the discovery of new materials with excellent capture of CO₂ develops into the greatest challenge in this field. There are three options available to capture CO₂, i.e. (i) post-combustion, (ii) pre-combustion, and (iii) air separation followed by oxy-fuel combustion captures [2]. Post-combustion capture deals mainly with the separation of CO₂ from flue gas. Pre-combustion capture consists of the production of
carbon monoxide (CO) – hydrogen (H₂) mixture by combusting fuel with air, and then the CO is supplied into a catalytic reactor to be converted into H₂ and CO₂. Oxy-fuel combustion involves pure oxygen to burn fuels that can produce pure CO₂ [1]. Until recently, chemical absorption and adsorption are considered as mature technologies to separate gas mixture that contains carbon dioxide [3-4]. However, chemical absorption consumes large amount of chemical solvent especially when treating huge amount of gases [2]. In addition, the simplicity of adsorption in operation and wide option for adsorbent material make adsorption technology developed as a good option for gas separation technique. In spite of these advantages, there are still much research needed to find the best adsorbent material to capture CO₂ from gas mixture. Besides chemical absorption and adsorption, membrane technology achieves a growing interest in gas separation processes by many researchers. This is because membrane can offer very high surface areas for gas separation in a small footprint as well as easy to scale up. However, membrane available today for gas separation processes still cannot achieve the desired separation performance, thus its realization in industrial operation is still limited.

Polymeric membrane gas separation process gains much interest in the current trend on gas separation research because it is believed that this technique has not been explored into its optimum capacity. The application of pure polymeric membrane in the gas separation field is limited by the trade-off phenomenon between membrane permeability and selectivity. A logarithmic correlation between membrane permeability and selectivity for different gas mixtures from the data available in the literature has been developed by Robeson (2008) [5]. The correlation indicates that there is an upper bound line exists in which recent polymeric membrane cannot surpass. It means that until now one main challenge for researchers in the field of gas separation membrane is to find the best membrane that can provide permeability and selectivity that exceed Robeson’s upper bound line [6]. In current years, Metal-Organic Frameworks (MOFs) has received a growing interest from many researchers as potential fillers in mixed matrix membranes (MMMs) as well as pure MOFs membranes. MOFs contain metal cations connected by an organic linker. MOFs have coordination network and bonding, which make them less stiff and brittle than zeolite. Thus, it is considered that MOFs are able to show flexibility in terms of gate opening and linker dynamics [7]. There are more than hundreds of MOFs structure that have been synthesized and it is a big challenge to choose suitable MOFs that will be used as membranes.

Zeolitic Imidazolate Framework (ZIF) materials are investigated more widely by many researchers as gas separation membranes or filler for mixed matrix membranes than any other MOFs because of their framework flexibility and high chemical and thermal stability [8]. The bonding in ZIF is a coordination bonding that is weaker than covalent bonding in the zeolite. This means that the bonding between the metal node and organic linker is not kinetically stable. This instability means that substitution by other ligands such as water might happen. However, for some ZIF such as ZIF-8, ZIF-11 and ZIF-69 the stability of their structures can be maintained even in boiling solvents like benzene and water [9]. Hydrophobic ZIF-8 with sodalite (SOD) topology connecting Zn⁺⁺ metal and organic imidazolate linker is reported has 3.4 Å aperture diameters and it can retain their structure at the temperature up to 400°C. ZIF-8 has properties that make it considered as the most hydrolytically stable porous coordination polymer [10]. However, in the recent report by Zhang, et al. the effective aperture size of ZIF-8 particles is reported as 4.0 to 4.2 Å [11]. Because of this flexibility, ZIFs are considered able to increase the permeability of the polymeric membrane in separating gas mixtures. ZIF-8 emerges as one type of ZIF that are studied and employed widely as membranes in gas separation processes. Due to the simple fabrication process, use of an environmental-friendly solvent, high gas permeance, and its open structure, have attracted many researchers to explore this material. The number of publications related to ZIF-8 used as filler in MMMs and as pure membranes show an increasing trend as shown in Figure 1. There are also a number of reviews on MOFs membranes [12-13], but a review on ZIFs membrane on the polymeric substrate is still required to present the current trend on this membrane.
3. The number of published papers related to the search term of “ZIF membrane”, “ZIF membrane gas separation”, and “ZIF-8 membrane gas separation” indexed by Web of Science (23 July 2018). The insert is the distribution of ZIF-8 use for gas separation membrane.

2. The Synthesis of ZIF-8 membranes

The fabrication of excellent ZIF membranes, such as ZIF-8 membranes, on the surface of porous substrates for the gas separation process is relatively difficult. The challenges in the ZIF-8 membrane fabrication include the incompatibility issue between ZIF-8 and substrate materials and the flexibility of ZIF-8 materials. In addition, the issue on the reproducibility of the synthesis procedures of ZIF-8 membranes remains a challenging topic recently [12]. The techniques employed to fabricate ZIF-8 membranes can be classified into two techniques, i.e. in situ growth technique and secondary growth technique. In addition, inorganic and organic porous supports have also been utilized as the platform to grow ZIF-8. Figure 2A-B present the schematic diagram of in situ and secondary growth techniques to fabricate ZIF-8 membranes.

Figure 2. Schematic diagram of ZIF-8 membrane preparation by: (A) in situ growth method; (B) secondary growth method, and (C) counter diffusion method.

2.1 The In situ growth of ZIF-8 membrane on the porous support

Compared to the secondary growth, in situ growing technique does not require seed particles. During the synthesis, the porous support is soaked or immersed in the ZIF-8 precursor solution either at room temperature or at elevated temperature [12-13]. In terms of support, unmodified and modified supports have been employed for in situ grow ZIF-8 particles. In addition, both flat sheet and hollow fibre supports have been used to grow ZIF-8 particles.

In general, the growing of ZIF-8 by using this technique involves high temperature and long fabrication time due to the incompatibility issue. To reduce temperature and time, several researchers employed microwave heating and sodium formate to enhance the heterogeneous nucleation of ZIF-8.
Bux et al. (2009) have been successfully fabricated defect-free ZIF-8 membranes using this technique [14]. The ZIF-8 membranes resulted in a good H$_2$ separation performance. Unmodified porous α-alumina supports were also used as support for the growth of ZIF-8 crystals in the presence of sodium formate [15]. A similar technique was employed into porous polymeric polysulfone support to produce a ZIF-8 membrane with a micrometre and nanometre sized crystals on the support surface [16]. On another line of research, the combination of in situ growth and layer-by-layer techniques was applied on the polysulfone membrane to produce ZIF-8 membranes with low synthesis temperature [17]. In recent years, the growing of ZIF-8 on hollow fibre porous supports has also been started to produce membranes with larger surface area compared to flat sheet membranes. ZIF-8 membrane from concentrated synthesis gel was successfully prepared on the surface of ceramic hollow fibre supports [18]. In situ growth on modified support was carried out to create a more efficient ZIF-8 growing process. ZIF-8 film was grown on the inner surface of the APTES modified ceramic hollow fibre using a modified seeding process [19].

2.2 The secondary growth method of ZIF-8 on porous support

Besides its advantages such as the simple fabrication technique, the in situ growing technique of ZIF-8 membranes faces some challenges. Such challenges include the difficulty to control the growth of particles on the surface of the substrate as the nucleation and crystal growth occur at the same time [12]. To enhance the performance of the ZIF-8 membrane, several studies have been successfully employed a secondary growth method to produce defect-free ZIF-8 membranes. The secondary growth technique discriminates the nucleation and growth steps, thus offers a better control on the microstructure of the membrane. Rubbing of seed particles on the surface of porous substrates is a relatively common technique used as a precursor during the secondary growing of ZIF-8 crystals. Ge et al. (2012) fabricated ZIF-8 thin film on the surface of polyethersulfone by firstly rubbed the support surface with ZIF-8 seed particles followed by secondary growing technique. Other techniques for seeding are dip-coating and slip coating. One study employed dip-coating to seed YSZ tubular support [20]. Slip coating to seed alumina support was also carried out to synthesize ZIF-8 membrane. Produced membrane showed very good olefin/paraffin separation performance [20-21]. In addition to dip-coating and slip coating, another technique, i.e. reactive seeding, was also used as a precursor before the secondary growth of ZIF-8 membranes [22]. In this technique, microwave-assisted seeding was carried out to enhance the attachment of the ZIF-8 seeding layer to α-alumina support with a rapid nucleation process.

Despite its attractiveness in producing defect-free ZIF-8 membranes, the membranes produced using secondary growth technique experience delamination due to the weak interaction between the ZIF-8 layer and porous support [23]. Hence, support surface modification started to be employed to improve the adhesion of ZIF-8 particles on the surface of porous support [24-26]. A study to improve the attachment of ZIF-8 particles on the surface of porous supports utilized vapour phase modification to add amine functional groups and reduce the pore size of support. This technique could produce the ZIF-8 membrane with a relatively continuous structure [26]. Another technique to improve the attachment of nano-ZIF-8 particles is by using polyethyleneimine (PEI) as a coupling agent. This coupling agent forms hydrogen bonds with ZIF seed crystals and free hydroxyl groups of ceramics (α-Al$_2$O$_3$) porous substrate. PEI may also form Zn – N coordination bonds with Zn cations on the surface of the ceramic. The crystal seeds were attached to the porous substrate using dip-coating method [27].

2.3 Novel methods to synthesize ZIF-8 membranes on porous support

In addition to in situ and secondary growth methods, several studies offer new and innovative techniques to grow the ZIF-8 layer on the surface of the porous support. Such techniques include counter diffusion technique [28]. The experimental set up of the contra diffusion technique to grow ZIF-8 on nylon support is presented in Figure 2C. ZIF-8 layer on the zinc nitrate with cubic structure was more uniform than fibre-like structure of ZIF-8 crystals grown on the 2-methyl imidazolate surface. ZIF-8 membranes with relatively good gas separation performances could be synthesized in one cycle of crystallization process thus reduce the synthesis time. Another observation from this
experiment suggested the different crystal structure formed by changing the position of zinc nitrate and 2-methyl imidazole in the contra diffusion apparatus. Gas separation performance of such membranes could produce gas selectivity higher than Knudsen selectivity, which indicated the formation of defect-free ZIF-8 membranes. Each technique presented above has its own benefits considering the ease of fabrication, reproducibility, and the uniformity of the produced membrane. In general, it can be mentioned that in situ growth offers a simpler technique compared to other methods. However, in terms of reproducibility and the uniformity of the membranes, by employing the in situ technique will be very hard to produce dense and uniform membrane.

3. Future perspectives and conclusions
Table 1 presents literature data of ZIF-8 membranes that have been synthesized recently. The data compiled the gas separation performance of ZIF-8 membranes fabricated on organic and inorganic supports to compare the performances of these two membranes. Gas permeance and selectivity data for ZIF-8 membrane in Table 1 indicate the roles of ZIF-8 layer thickness and size of ZIF-8 crystals on the gas separation performance of membranes. A thin layer of ZIF-8 on the surface of the substrate ensures high gas permeance through the membrane. Up to now, the ZIF-8 membranes that have been synthesized could achieve H$_2$ permeance of more than 60,000 Gas Permeation Unit (GPU), which is very high compared to pristine polymeric membranes. On the other hand, the gas selectivity of the membrane should be maintained as high as possible before the membrane can be applied in real applications. In terms of organic support, there is still a possibility to improve the performance of ZIF-8 membranes to produce high gas permeance with good separation capability. In addition, a study on the mechanical strength of ZIF-8 membranes on polymeric supports is still relatively new and indispensable before the membrane can be applied in the industrial scale. Other challenges in the fabrication of ZIF-8 membranes include developing a single-step synthesis method that can be produced in a large scale and tackling the reproducibility issue in the synthesis of the membrane [12]. Thus, the development of pure MOFs membrane, especially the ZIF-based membrane, offers promising performance to surpass the gas permeability-selectivity trade-off. However, some challenges in membrane fabrication, such as method reproducibility and relatively long preparation time, still need to be addressed [34]. Several techniques can be considered to tackle the problems, such as surface modification and post-treatment of the membranes.

**Table 1.** Selected ZIF-8 membranes synthesized at various substrates and synthesis conditions.

| Support         | Modification approach   | Thickness (µm) | H$_2$ permeance$^*$ | Selectivity H$_2$/CO$_2$ | H$_2$/N$_2$ | Ref. |
|-----------------|-------------------------|----------------|---------------------|--------------------------|------------|------|
| PD/SWCNT        | Contra diffusion         | ~0.55          | 6.31                | 43                       | NA         | [29] |
| PVDF hollow fibre | TiO$_2$ functionalised | ~1             | 201                 | 7                        | 7.8        | [30] |
| PVDF-hollow fibre | Ammoniation             | ~40            | 24.43               | 12.18                    | 14.31      | [24] |
| PAN hollow fibre | Dehydrogenation         | <1             | 3.05                | 6.85                     | N/A        | [25] |
| Nylon hollow fibre | Contra-diffusion         | ~2.5           | 11.3                | N/A                      | 4.6        | [31] |
| Nylon hollow fibre | Contra-diffusion         | ~16            | 126.2               | N/A                      | 3.7        | [28] |
| Porous polysulfone | Micro-nanosized growth   | ~50            | 2.0                 | N/A                      | 12.4       | [16] |
| BPPO hollow fibre | Chemical modification    | 0.2            | 20.5                | 12.8                     | 9.7        | [26] |
| Poly(amide–imide) | Interfacial microfluidic | ~0.9           | 1.23                | NA                       | NA         | [32] |
| BPPO flat sheet | Contra diffusion         | ~2             | 7.5                 | 5.1                      | 8.3        | [23] |
| Porous AAO      | PDA-modified            | <0.2           | 287                 | 14                       | 18         | [26] |
| Titania (flat sheet) | Microwave-assisted      | ~30            | 0.6                 | 4.61                     | 11.5       | [14] |
| YSZ hollow fibre | Secondary seed growth    | ~2             | 15.4                | 3.85                     | 11         | [20] |
| SS-nets (flat sheet) | PDA-coated surface    | ~30            | 266                 | 8.8                      | 15.4       | [33] |

*) Permeance unit is in (x10$^{-7}$ mol.m$^{-1}$.s$^{-1}$.Pa$^{-1}$)

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