Zeolite Imidazole Frameworks Membranes for CO₂/CH₄ Separation from Natural Gas: A Review

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Abstract: Carbon dioxide (CO₂) which exists in natural gas is one of the undesirable impurities that can reduce the caloric power of the natural gas. The implications of CO₂ on the economic loss of the natural gas processing have provoked the development of CO₂ separation technology. In the past decades, membrane technology has emerged as an environmentally friendly, economic feasible and easy-operating method in CO₂ removal. ZIFs membranes presented to be relatively new materials, which possessed high stability and good performance in CO₂ separation under harsh condition. The tunability of the pore apertures and plentiful diversity of the frameworks associated with ZIFs membranes provide massive potential for the researchers to enhance the properties of ZIFs membranes in CO₂ separation. This review attempts to summarize the current performance of the ZIFs membrane in CO₂/CH₄ separation process, considering CH₄ as the main constituents in natural gas. Extensive study on molecular structures, membrane formation and separation mechanism is emphasized on ZIF-8 membranes owing to their exceptionally high CO₂ permeability. To this end, separation performance involved in ZIF-8 membrane is discussed, which affected by the synthesis method, molar composition of the growth solution and modification of the supports.

Key words: CO₂/CH₄ separation, ZIFs membrane, ZIF-8 membrane, molecular structures, membrane formation, separation mechanism

INTRODUCTION

In the past decades, natural gas has played an important role as fuel used in industrial, agricultural and transportation sectors. It is a complex gas mixture containing different kinds of gaseous components, with methane (CH₄) as the main constituent and other impurities such as carbon dioxide (CO₂), hydrogen sulphide (H₂S) and water (H₂O) (Zhu et al., 2006; Scholes et al., 2012). Recently, composition of CO₂ presence in natural gas as high as 70% has been reported (Lin et al., 2006). The presence of high concentration of CO₂ in natural gas can corrode the pipelines mainly due to its acidic behaviour and reduce the caloric power of the natural gas (Zhu et al., 2006). Therefore, separation of CO₂ from CH₄ in natural gas processing is an essential step in order to lessen the economic losses (Drioli and Barbieri, 2011).

Membrane technologies has drawn unprecedented attention of many researchers for CO₂ gas separation owing to its low energy consumption (Zornoza et al., 2013), compact and simple design (Zhu et al., 2006) environmental friendly (Lau et al., 2012), high CH₄ recovery (Basu et al., 2011), smaller capital cost (Chew et al., 2011), ease of operation and easy to scaled-up (Venna, 2010). Among the different types of the existing membranes, Zeolite Imidazolate Frameworks (ZIFs) membrane as the sub-category of metal-organic framework (MOF) membrane has emerged as a relatively new membrane material for CO₂ separation. This was mainly attributed to its remarkable properties such as exceptionally high thermal and chemical stability (Bux et al., 2009; Fairen-Jimenez et al., 2011; Xu et al., 2011; Hu et al., 2012), variety framework diversity with adjustable chemical functionality (Assfour et al., 2010; Fairen-Jimenez et al., 2011), high adsorption capacities, high specific surface areas and high pore volumes (Rosi et al., 2003).

The present review attempts to summarize the current performance of the ZIFs membrane in CO₂/CH₄ separation. Beginning with the brief introduction of ZIF and ZIFs membranes, reported literature on the performance among the ZIFs membranes in CO₂/CH₄ separation were summarized. In this regards, ZIF-8 membrane was chosen for extensive study due to its characteristics which are beneficial for CO₂/CH₄ separation. Subsequently, the...
molecular structures and the mechanisms involved in membrane formation and CO$_2$/CH$_4$ separation of ZIF-8 were presented. Furthermore, the effect of the synthesis conditions on the formation of ZIF-8 membranes including (1) synthesis method, (2) molar composition of the growth solution and (3) modification of the supports, as well as the separation performance of the resultant membranes in CO$_2$/CH$_4$ were discussed. Finally, concluding remarks and future directions were suggested.

**ZEOLITE IMIDAZOLATE FRAMEWORKS (ZIFs)**

ZIFs presented in formula M(Im)$_n$, where M is the transition metal (Zn$^{2+}$ or Co$^{2+}$) and Im is the imidazolate linker. The transition metal cations are connected by imidazolate anions through N (nitrogen) atoms into tetrahedral frameworks, subtend at an angle of 145° at M-Im-M center that resembling the zeolite topologies (Zhou et al., 2008; Cravillon et al., 2009; McCarthy et al., 2010; Amrouche et al., 2011; Díaz et al., 2011; Huang et al., 2011; Morris et al., 2012). The pores of ZIFs are formed by 4, 6, 8 and 12-membered rings of the ZnN$_x$ and CoN$_x$ clusters (Venema et al., 2010). The plentiful frameworks diversity and tunable pore apertures of the ZIFs promise their potential in gas separation.

**ZEOLITE IMIDAZOLATE FRAMEWORK-8 (ZIF-8) MEMBRANES**

**Introduction to ZIF-8 membranes:** ZIFs crystals that grow continuously on porous support will form thin layer of membrane eventually. The ZIFs membranes exhibit different performance in CO$_2$/CH$_4$ separation as shown in Table 1 (Venema and Carreon, 2009; Huang et al., 2010; Li et al., 2010; Liu et al., 2011; Zhang et al., 2013). Based on the reported results shown in Table 1, ZIF-8 membranes showed the highest CO$_2$ permeance (~240×10$^{-6}$ mol·m$^{-1}$·s$^{-1}$·Pa$^{-1}$) and CO$_2$/CH$_4$ selectivity (~7) as compared to the other types of ZIFs membranes, such as ZIF-7, -69, -90 and -9-67. Apart from its high CO$_2$ permeance and CO$_2$/CH$_4$ selectivity, ZIF-8 membranes show hydrophobic characteristics and resist to some aromatic hydrocarbons such as benzene (Venema and Carreon, 2009) organic solvents and boiling alkaline water (Park et al., 2006). In addition, ZIF-8 membranes exhibit high thermal stability by sustaining the temperature up to 400°C in air and 550°C in N$_2$ (Madhusoodana et al., 2006). The outstanding properties showed by ZIF-8 membranes reveal their advantages over other type of membranes in gas separation application under harsh condition.

**Molecular structures of ZIF-8:** ZIF-8 (Zn(melm))$_n$, melm = 2-methylimidazole) possesses large cavities with the size of 11.6 Å, encompassed by six-membered ring window forming small apertures of 3.4 Å (Venema et al., 2010; Fairen-Jimenez et al., 2011; Xu et al., 2011). It is classified under cubic space group I-43 m with the Zn$^{2+}$ ion connected to the N atoms of melm groups through coordination bond, forming sodalite (SOD) zeolite topology (Hu et al., 2012). Figure 1 shows the three-dimensional structure of ZIF-8 in cubic unit cell at <111> plane, showing large cavity (sphere region) with size 11.6 Å and small apertures (six-membered ring window) with size 3.4 Å. Adapted from (Markov, 2003; Park et al., 2006).

![Figure 1: Three-dimensional structure of ZIF-8 in cubic unit cell at <111> plane, showing large cavity (sphere region) with size 11.6 Å and small apertures (six-membered ring window) with size 3.4 Å. Adapted from (Markov, 2003; Park et al., 2006).](image-url)

<table>
<thead>
<tr>
<th>Types of ZIFs membranes</th>
<th>Feed pressure (kPa)</th>
<th>Temperature (°C)</th>
<th>CO$_2$ permeance ($10^{-6}$ mol·m$^{-1}$·s$^{-1}$·Pa$^{-1}$)</th>
<th>CO$_2$/CH$_4$ selectivity</th>
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<tr>
<td>ZIF-8</td>
<td>139.5</td>
<td>298</td>
<td>249</td>
<td>7</td>
<td>Venema and Carreon (2009)</td>
</tr>
<tr>
<td>ZIF-7</td>
<td>100.0</td>
<td>493</td>
<td>0.035</td>
<td>1.13**</td>
<td>Li et al. (2010)</td>
</tr>
<tr>
<td>ZIF-69</td>
<td>101.3</td>
<td>298</td>
<td>1.0</td>
<td>4.6*</td>
<td>Liu et al. (2011)</td>
</tr>
<tr>
<td>ZIF-90</td>
<td>101.3</td>
<td>473</td>
<td>0.348</td>
<td>2.22**</td>
<td>Huang et al. (2010)</td>
</tr>
<tr>
<td>ZIF-9-67</td>
<td>N/A</td>
<td>298</td>
<td>15.8</td>
<td>0.3**</td>
<td>Zhang et al. (2013)</td>
</tr>
</tbody>
</table>

*CO$_2$/CH$_4$ = 50:50, **Ideal selectivity
Mechanism for ZIF-8 membrane formation: ZIF-8 membrane is formed through the continuous nucleation and crystallization process of ZIF-8 crystals on the porous supports. Initially, building unit of ZIF-8 emerges when Zn$^{2+}$ cation attacks the melamin anion which is rich in electron. Nucleation process happens when each of the building unit of ZIF-8 is linked to the other building units through N atoms forming ZnN$_6$ clusters, which connect together and form the unit cell of ZIF-8 with the window cages. After nucleation process, ZIF-8 starts to grow through the collision and particle-monomer attachment process, indicating the occurrence of crystallization. The porous supports used for synthesizing ZIF-8 membrane to date include alumina (Verna and Carecen, 2009; Bux et al., 2011; Tao et al., 2013), titania (Bux et al., 2009) and YSZ ceramic fiber (Pan et al., 2012). Those selected porous supports possess inert characteristics and did not influence the growth of the membrane. Comprehensive schematic diagram on the ZIF-8 membrane formation is presented in Fig. 2 (Banerjee et al., 2008; Friscic et al., 2013).

Mechanism for CO$_2$/CH$_4$ gas separation in ZIF-8 membranes: In ZIF-8 membranes, CO$_2$ molecules permeate over the membrane through adsorption–desorption and diffusion mechanism (Chmelik et al., 2012) as displayed in Fig. 3. First, CO$_2$ molecules are selectively attracted by ZIF-8 membrane. Then, the molecules will diffuse through the matrix of the membrane owing to the gradient of chemical potential based on Maxwell-Stefan diffusion theory (Kapteijin et al., 2000). Finally, the CO$_2$ molecules are described from the membrane to achieve equilibrium with the surrounding. Schematic diagram of the mass transfer of CO$_2$ molecules through ZIF-8 membrane in steady state is shown in Fig. 4 (Bux, 2011). Gas phase A and B existed at the feed and permeate sides of the membrane corresponding to constant pressure and respectively. The adsorption and desorption of CO$_2$ molecules on both sides of membrane at different pressure resulted in different concentration and chemical potentials of the molecules.

CO$_2$ molecules are preferentially adsorbed by ZIF-8 as compared to CH$_4$ molecules. This was due to the presence of the electrostatic potential (ESP) at the three methyl rings and the six imidazole rings of ZIF-8 (Liu et al., 2012). Existence of ESP favours the attraction of CO$_2$ molecules with larger quadrupolar moment ($13.4 \times 10^{-30}$ Cm$^2$) as compared to CH$_4$ molecules, which are non-polar with the absence of quadrupolar moment (D'Alessandro et al., 2010). Besides, the diffusivity of CO$_2$ is larger than CH$_4$ under the same amount of molecules loading. This was due to the larger size of CH$_4$ molecules ($>3.8 \AA$) than CO$_2$ molecules ($>3.3 \AA$) that contributed to higher steric hindrance during the interaction with the window cage of ZIF-8 ($>3.4 \AA$).

Effect of synthesis conditions on the formation and CO$_2$/CH$_4$ gas separation of ZIF-8 membranes: There are several factors affecting the quality of ZIF-8 membranes formed such as the synthesis method, molar composition of the synthetic solution and modification of the supports through the seeding methods. Correlation between those factors and the gas separation performance (CO$_2$/CH$_4$, selectivity) of the membranes was compared and listed in Table 2 (Bux et al., 2009; Verna and Carecen, 2009; Bux et al., 2011; Pan et al., 2012). ZIF-8 membrane which showed highest selectivity was reported by Verna and Carecen (2009). Secondary seeded growth method was used for the synthesis with the molar composition of the synthesis solution of Zn$^{2+}$: HIm: MeOH of 1:8:700. The thickness of the resultant membrane was ~5 to 9 µm. CO$_2$/CH$_4$ selectivity of ZIF-8 membranes reported by Pan et al. (2012) and Bux et al. (2009) was relatively low.

<table>
<thead>
<tr>
<th>Types of ZIF membranes</th>
<th>Molar composition</th>
<th>Synthesis method and duration</th>
<th>Membrane thickness (µm)</th>
<th>CO$_2$/CH$_4$ selectivity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIF-8</td>
<td>Zn$^{2+}$; HIm: MeOH 1:8:700</td>
<td>In situ crystallization with solvothermal synthesized seeds and secondary seeded growth (rubbing) with α-alumina tubular support; 5h</td>
<td>~5-9</td>
<td>~7*</td>
<td>Verna and Carecen (2009)</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>Zn$^{2+}$; HIm: H$_2$O 1:70:1238</td>
<td>Secondary seeded growth method (dip-coating for 10s) with hollow YSZ ceramic fiber; 6h</td>
<td>~2.5</td>
<td>~3.33**</td>
<td>Pan et al. (2012)</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>Zn$^{2+}$; HIm: MeOENACOOH 1:1.5:250:1</td>
<td>Microwave-assisted solvothermal with asymmetric titania disc; 4h</td>
<td>~30</td>
<td>~2.77**</td>
<td>Bux et al. (2009)</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>Zn$^{2+}$; HIm: MeOENACOOH 1:1.5:250:1:5</td>
<td>Microwave-assisted solvothermal secondary seeded growth (dip-coating) with porous PEI polyethyleneimine modified α-alumina support; 0.5-4h</td>
<td>~12</td>
<td>N/A</td>
<td>Bux et al. (2011)</td>
</tr>
</tbody>
</table>

*CO$_2$/CH$_4$ = 50:50, **Ideal selectivity, 'polyethyleneimine
Fig. 2: Schematic diagram of ZIF-8 membrane formation involved nucleation and crystallization processes, adapted from (Banerjee et al., 2008; Frisco et al., 2013)

regardless of their thickness and different molar composition of the synthesis solution (using water (Zn$^{2+}$: Hmim: H$_2$O of 1:70:1238) or sodium formate (Zn$^{2+}$: Hmim: MeOH:NaCOOH of 1:1.5:250:1)). However, microwave-assisted solvothermal synthesis process reported by Bux et al. (2009) required less synthesis duration of 4 h as compared to the other methods such as in situ crystallization and secondary seeded growth (5-6 h). On the other hand, by using microwave-assisted solvothermal secondary seeded growth, Bux et al. (2011) successfully produced a thinner membrane (~12 µm) as compared to their previous work (~30 µm) using in situ crystallization (Bux et al., 2009). However, the CO$_2$/CH$_4$ separation performance of the resultant ZIF-8 membranes was not reported by Bux et al. (2011). Hence, the CO$_2$/CH$_4$ gas separation performance for ZIF-8 membrane is still in
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