Synthesis and Performance of Deca-Dodecasil 3 Rhombohedral (DDR)-Type Zeolite Membrane In CO₂ Separation—A Review

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CO₂ capture technologies including absorption, adsorption, and cryogenic distillation are reported. Conventional technologies for CO₂ separation from natural gas have several disadvantages including high cost, high maintenance, occupy more space and consume high energy. Thus, membrane technology is introduced to separate CO₂ due to their several advantages over conventional separation techniques. Inorganic membranes exhibit high thermal stability, chemical stability, permeability and selectivity for CO₂ and CH₄ separation as compared to other type of membranes. Zeolite membranes are potential for CO₂ separation due to their characteristics such as, well define the pore structure and molecular sieving property. Among the zeolite membranes, DDR membranes exhibit highest selectivity for CO₂ and CH₄ separation. DDR membranes are synthesized by conventional hydrothermal and secondary growth methods. These methods required very long synthesis duration (25 days) due to extremely low nucleation and crystal growth rate of DDR zeolite. In this review, synthesis and performance of DDR membrane in CO₂ separation from CH₄ reported by various researchers are discussed. Challenges and upcoming guidelines related to the synthesis DDR membrane and performance of DDR membrane also included.

Keywords: Carbon dioxide separation, Natural Gas, DDR membrane, Synthesis

INTRODUCTION

Worldwide consumption of natural gas is increasing day by day, which reaches over 3.1 trillion cubic meters per year (1-2). It is estimated that the consumption of natural gas will be increased to 185 trillion cubic feet in 2040 (1). CO₂ in natural gas can be varies from 4% to 50% depends on the gas source. The presence of CO₂ in natural gas decreases the heating value
and acid environment due to the reaction of \( \text{CO}_2 \) with water and therefore resulted in pipeline corrosion (3). Generally, \( \text{CO}_2 \) concentration in natural gas should be less than 2% to 3%. Thus, various technologies have been introduced to remove \( \text{CO}_2 \) from natural gas (4). Adsorption, physical absorption, chemical absorption and physical-chemical absorption are the conventional methods used for \( \text{CO}_2 \) removal. In 2012, 1297 patents published on \( \text{CO}_2 \) capture technologies as shown in Figure 1(5).

![Fig. 1: Number of patents published through March 2012 (5).](image)

Physical absorption is usually preferred, when high \( \text{CO}_2 \) contents are present in the feed gas and low purity product is required (4). But this method required high capital cost. Chemical absorption is the most mature technology for the \( \text{CO}_2 \) removal from natural gas. However, these techniques possess several drawbacks including high energy consumption and cause corrosion (6). Adsorption process is not a smart approach because the current adsorbents exhibit low \( \text{CO}_2 \) loading capacity (4). Thus, membrane technology is introduced in \( \text{CO}_2 \) separation in order to overcome these drawbacks (7). Among the inorganic membrane zeolite membranes showed better performance in \( \text{CO}_2 \) separation. Thus DDR zeolite membrane has highest selectivity among all zeolite membrane at room temperature. In this review, synthesis and performance of DDR membrane in \( \text{CO}_2 \) separation from \( \text{CH}_4 \) reported by various researchers are discussed.

**MEMBRAN TECHNOLOGY IN \( \text{CO}_2 \) SPEARATION**

\( \text{CO}_2 \) removal from natural gas through membrane separation has become a favorable approach as compared to conventional processes. This is due to the advantages of membranes such as high reliability, operational simplicity, low capital cost, low operating cost, environmentally friendly, light weight and high space efficiency, low maintenance and low energy consumption (7).

Currently, removal of \( \text{CO}_2 \) from natural gas using membrane based process has been practiced on a large scale; more than 200 plants have been installed (8). Synthetic membranes for gas separation fall into three categories based on their materials of manufacture including, polymeric, mixed matrix and inorganic membranes. Figure 2 shows the general classification of synthetic membranes. Generally, the separation efficiency of polymeric membranes decreases with time due to membrane swelling (9). Besides, polymeric membranes showed low stability at high temperatures and high pressure (4). To overcome the limitations of polymeric membranes, mixed matrix membranes was introduced. In mixed matrix membranes; inorganic fillers like silica, zeolites or carbon were introduced
into the polymeric matrix in order to increase the mechanical strength, stability and performance of the membranes in CO₂ separation. Although the separation performance of mixed matrix membrane is better than polymeric membranes, (9) fabrication of mixed matrix membranes remains a difficult task (10) mainly due to the incompatibility between the inorganic filler and the polymer matrix. Inorganic membranes have high chemical stability, thermal stability, high resistance to harsh environments and high resistance to high pressure drops. Besides, these membranes exhibit high compatibility to organic solvents and free from swelling. Inorganic membranes showed better performance (higher selectivity) as compared to silica membranes and carbon membranes.

**ZEOLITE MEMBRANES**

The term zeolite, which was introduced in 1756, describes the variety of hydrated and crystalline aluminosilicates in the framework structure. Zeolite membranes consist of ultra large structures with 14-, 18- or 20 membered rings, large pore structures with 12-membered rings (FAU, MOR), medium pore frameworks with 10-membered rings (MFI, MEL, FER) and small pore structures with six, eight or nine tetrahedral membered ring (LTA, CHA and DDR) (11). Generally, there are three methods used to synthesize zeolite membranes including, in situ hydrothermal synthesis, secondary growth hydrothermal synthesis and dry gel conversion method. Figure 3 shows the different methods and steps for synthesis of zeolite membranes (12).
Performance of Zeolite Membranes in CO₂ Separation from Natural Gas

Zeolite membranes such as Silicate-1, ZSM-5, KY-type, Y-type, Zeolite-T, SAPO-34, Ba-SAPO-34 and DDR (13, 14, 15, 16, 18, 19, 21 and 22) were reported in CO₂ separation from natural gas. Zhu et al. (13) studied the performance of silicate-1 zeolite membrane in CO₂ separation. They found that CO₂ permeance of 1.98 x 10⁻⁹ mol/m² s Pa and CO₂/CH₄ selectivity of 4.3 were obtained at 30 °C, which was too low as compared to ZSM-5 zeolite membrane. As reported by Banihashemi et al. (14), ZSM-5 exhibited CO₂/CH₄ selectivity of 14.2 and CO₂ permeance of 6.1 x 10⁻⁹ mol/m² s Pa. Hasegawa and his coworkers (15) reported the performance of KY zeolite membrane in CO₂ separation. They found that the range of CO₂ permeance was varied from 7.5 x 10⁻⁷ mol/m² s Pa to 9.0 x 10⁻⁷ mol/m² s Pa, while the CO₂/ CH₄ selectivity of 25 to 40 were obtained at temperature of 35 °C. On the other hand, low CO₂/CH₄ selectivity was observed by Kusakabe et al. 1997 (16) using Y-type zeolite membrane. They found that the CO₂ permeance of 4.0 x 10⁻⁸ mol/m² s Pa and CO₂/CH₄ selectivity of 2 were obtained at temperature of 30 °C.

Recently, T-type zeolite has been reported in CO₂ separation from CH₄. Zeolite T membrane can easily separate CO₂ from CH₄ based on molecular sieving effect (17). CO₂ permeance of 7.03 x 10⁻⁹ mol/m² s Pa and CO₂/CH₄ selectivity of 70.8 were obtained by Mirfendereski et al. 2008 (18) using a zeolite T membrane. But this CO₂/CH₄ selectivity is not high. SAPO-34 is another type of zeolite membrane which has been widely reported in CO₂ separation. Venna et al. 2011 (19) reported the performance of SAPO-34 membrane in CO₂ separation. They found that CO₂ permeance of 5.0 x 10⁻⁷ mol/m² s Pa and CO₂/CH₄ selectivity of 245 were obtained at 22 °C. But, SAPO-34 exhibits poor
moisture-stability, which is the major drawback of this membrane (20). In order to remove this problem, Ba ion was introduced in SAPO-34. Chew et al. 2011 (21) reported the performance of Ba-SAPO-34 zeolite membrane in CO₂ separation. CO₂ permeance of 37.6 x 10⁻⁸ mol/m² s Pa and CO₂/CH₄ selectivity of 103 were obtained at 30 °C. DDR zeolite membrane is a relatively new type of zeolite membrane having aperture of 0.36 nm x 0.44 nm. van den Bergh et al. 2006 (22) reported the performance of DDR membrane in CO₂ separation at 30°C. They found that the CO₂ permeance of 0.65 x 10⁻⁷ mol/m² s Pa and CO₂/CH₄ selectivity of 400 were obtained at 30 °C. Table 1 shows the performance of inorganic zeolite membranes in CO₂ separation reported by various researchers.

As shown in Table 1, it can be observed that various researchers (13, 14, 15, 16, 18, 19, 21 and 22) studied the performance of different zeolite membrane (Silicate-1, ZSM-5, KY-type, Y-type, Zeolite-T, SAPO-34, Ba-SAPO-34 and DDR) in CO₂ separation from natural gas. The DDR zeolite membrane has potential in CO₂ separation due to their characteristics such as; well defined pore structure, molecular sieving property and high selectivity. It is observed that among all zeolite membranes, DDR zeolite membrane showed highest CO₂/CH₄ selectivity at lower temperature which was 400 and comparable CO₂ permeance obtained by van den Bergh and his coworkers (22).

**DDR ZEOLITE MEMBRANE**

Deca-dodecasil 3 Rhombohedral (DDR) zeolite is a member of the group of clathrasils with the chemical formula of \((\text{C}_{10}\text{H}_{17}\text{N})_6(\text{N}_2)_9[\text{Si}_{120}\text{O}_{240}]\) (23). The crystal structure of DDR have 4, 5, 6 and 8 Si...
items in rings formed by combining decade hadron with dodeca hadron cages, resulting 19 hadron cage (24). DDR zeolite exhibits high thermal stability and stable in water (25). DDR zeolite contains aperture of 0.36 nm x 0.44 nm; which can easily separate CO$_2$ from natural gas based on molecular sieving effect. Figure 4 shows the framework of DDR crystals (26).

**Fig. 4:** Framework of DDR crystals (26)

DDR membrane is a relatively new type of zeolite membrane having DDR crystals layered on micro-porous alumina support. The micro-porous support provides the required mechanical strength to the membrane. In 2004, Tomita et al. firstly, reported the synthesis of DDR membrane in 27 days using secondary growth method (27). Figure 5 shows the surface morphology and cross sectional view of DDR membrane reported by Kuhn et al. 2008 (28).

**Synthesis of DDR Zeolite Membrane**

In 2004, Tomita et al. (27) reported the synthesis of DDR membrane in 27 days by using secondary growth method. They synthesized DDR crystals in 25 days and membrane in 2 days using conventional heating method. In subsequent years, NGK Corp (29) also synthesized DDR membrane in 30 days to improve membrane performance in CO$_2$ separation. Recently, Bose et al. 2014 (30) successfully reduced the synthesis duration of DDR zeolite membrane from 25 days to 7 days by using sonochemical coupled with conventional heating method. Firstly, they reported DDR crystals at room temperature in 5 days. After that, they repeated the same procedure and synthesized DDR crystals in 2 days and membrane in 5 days. Table 2 shows the synthesis of membranes by using

**Fig. 5:** Surface and cross sectional view of DDR membrane (28)
Synthesis and Performance of Deca – Dodecasil 3 Rhombohedral (DDR) – Type Zeolite Membrane in CO$_2$ Separation – A Review

Table 2. Synthesis of DDR Membrane Reported by Various Researchers

<table>
<thead>
<tr>
<th>Synthesis Method</th>
<th>Synthesis Duration (Days)</th>
<th>Total Duration (Days)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal seeds + Membrane</td>
<td>25</td>
<td>2</td>
<td>27</td>
</tr>
<tr>
<td>Secondary Growth</td>
<td>25</td>
<td>2</td>
<td>(27)</td>
</tr>
<tr>
<td>Secondary Growth</td>
<td>25</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>Sonochemical</td>
<td>5</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>Sonochemical</td>
<td>2</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>Secondary Growth</td>
<td>25</td>
<td>1</td>
<td>26</td>
</tr>
</tbody>
</table>

Table 3. Performance of DDR Membrane in CO$_2$ Separation Reported by Various Researchers

<table>
<thead>
<tr>
<th>Method</th>
<th>Temperature (°C)</th>
<th>CO$_2$/CH$_4$ Selectivity</th>
<th>CO$_2$ Permeance (mol/m$^2$ s Pa)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tomita et al. 2004</td>
<td>25</td>
<td>200</td>
<td>$3.0 \times 10^{-7}$</td>
<td>(27)</td>
</tr>
<tr>
<td>NGK Corp. 2005</td>
<td>26</td>
<td>670</td>
<td>$48.0 \times 10^{-9}$</td>
<td>(29)</td>
</tr>
<tr>
<td>Van den Bergh et al. 2006</td>
<td>30</td>
<td>400</td>
<td>$0.65 \times 10^{-7}$</td>
<td>(22)</td>
</tr>
<tr>
<td>Uchikawa et al. 2010</td>
<td>-</td>
<td>10</td>
<td>$2.0 \times 10^{-7}$</td>
<td>(32)</td>
</tr>
</tbody>
</table>

conventional heating method.

**Performance of DDR membrane CO$_2$ separation**

Tomita et al. 2004 (27) reported for the first time DDR membrane performance in CO$_2$ and CH$_4$ separation. It was found that the CO$_2$ permeance of the membrane was $3.0 \times 10^{-7}$ mol/m$^2$ s Pa and CO$_2$/CH$_4$ selectivity was 200 at room temperature. In 2005, NGK Corp (29) synthesized DDR membrane to improve the membrane performance in CO$_2$ separation. They found that the CO$_2$ permeance of $48.0 \times 10^{-9}$ mol/m$^2$ s Pa and CO$_2$/CH$_4$ selectivity of 670 were obtained at 26 °C. CO$_2$ permeance was $0.65 \times 10^{-7}$ mol/m$^2$ s Pa while CO$_2$/CH$_4$ selectivity was 400 at 30 °C using DDR membrane reported by van den Bergh et al. (22). In contrast, CO$_2$ permeance of $2.0 \times 10^{-7}$ mol/m$^2$ s Pa and CO$_2$/CH$_4$ selectivity of 10 were observed by Uchikawa et al. 2010 (32) using DDR membrane. Table 3 shows the performance of DDR membrane in CO$_2$ separation from natural gas at different temperatures.

**Issues with performance of DDR membrane in CO$_2$ separation**

i. DDR membrane is not perfectly hydrophobic. So, DDR membrane performance can be affected in presence of water.
ii. Using DDR membrane with increase in temperature CO₂ flux decreases.

**Issues with synthesis of DDR membrane**

i. Synthesis of DDR membrane requires very long duration (25 days) using conventional hydrothermal heating method (27).

ii. Method to synthesis DDR membrane with minimum defect remains a challenging task.

**CONCLUSIONS and FUTURE DIRECTIONS**

i. This paper reviews the performance of zeolite membranes in carbon dioxide separation from natural gas. From the literature, it is found that among all inorganic zeolite membranes, DDR membrane demonstrated the highest selectivity for CO₂ and CH₄ separation, which was up to 670 at room temperature.

ii. Synthesis duration of DDR membrane is very long (25 days) using conventional heating method. From literature study, it is expected that by applying the microwave heating method, synthesis duration of DDR membrane could be reduced.

iii. A reproducible synthesis method needs to be developed in order to minimize the defects of the DDR membrane.

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**REFERENCES**


