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Synthesis and Performance of Deca-Dodecasil 3 Rhombohedral (DDR)-Type Zeolite Membrane In CO_2 Separation– A Review

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CO_2 capture technologies including absorption, adsorption, and cryogenic distillation are reported. Conventional technologies for CO_2 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 CO_2 due to their several advantages over conventional separation techniques. Inorganic membranes exhibit high thermal stability, chemical stability, permeability and selectivity for CO_2 and CH_4 separation as compared to other type of membranes. Zeolite membranes are potential for CO_2 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 CO_2 and CH_4 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 CO_2 separation from CH_4 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). CO_2 in natural gas can be varies from 4% to 50% depends on the gas source. The presence of CO_2 in natural gas decreases the heating value and acid environment due to the reaction of CO_2 with water and therefore resulted in pipeline corrosion (3). Generally, CO_2 concentration in natural gas should be less than 2% to 3%. Thus, various technologies have been introduced to remove CO_2 from natural gas (4). Adsorption, physical absorption, chemical absorption and physical-chemical absorption are the conventional methods used for CO_2 removal. In 2012, 1297 patents published on CO_2 capture technologies as shown in Figure 1(5).

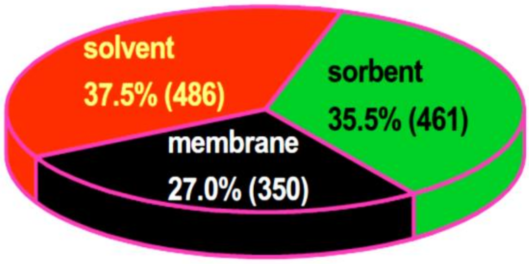

Fig. 1: Number of patents published through March 2012 (5).

Physical absorption is usually preferred, when high 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 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 CO_2 loading capacity (4). Thus, membrane technology is introduced in CO_2 separation in order to overcome these drawbacks (7). Among the inorganic membrane zeolite membranes showed batter performance in 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 CO_2 separation from CH_4 reported by various researchers are discussed.

MEMBRAN TECHNOLOGY IN CO_2 SPEARATION

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 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

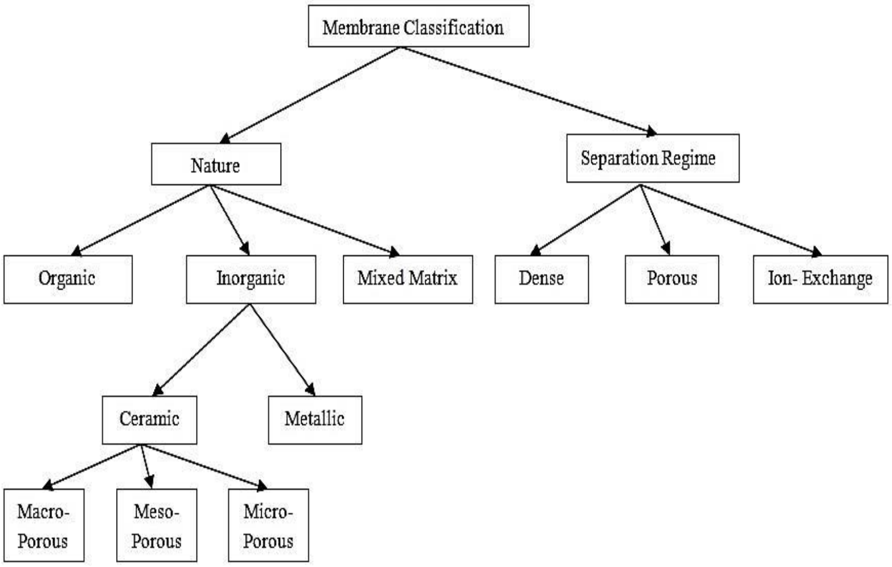

Fig.2 : General classification membrane

into the polymeric matrix in order to increase the mechanical strength, stability and performance of the membranes in CO_2 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 polymeric and mixed matrix membranes. Among all inorganic membranes, silica membranes, carbon membranes and zeolite membranes are widely reported. Among all inorganic membranes, zeolite membranes showed 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, insitu 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).

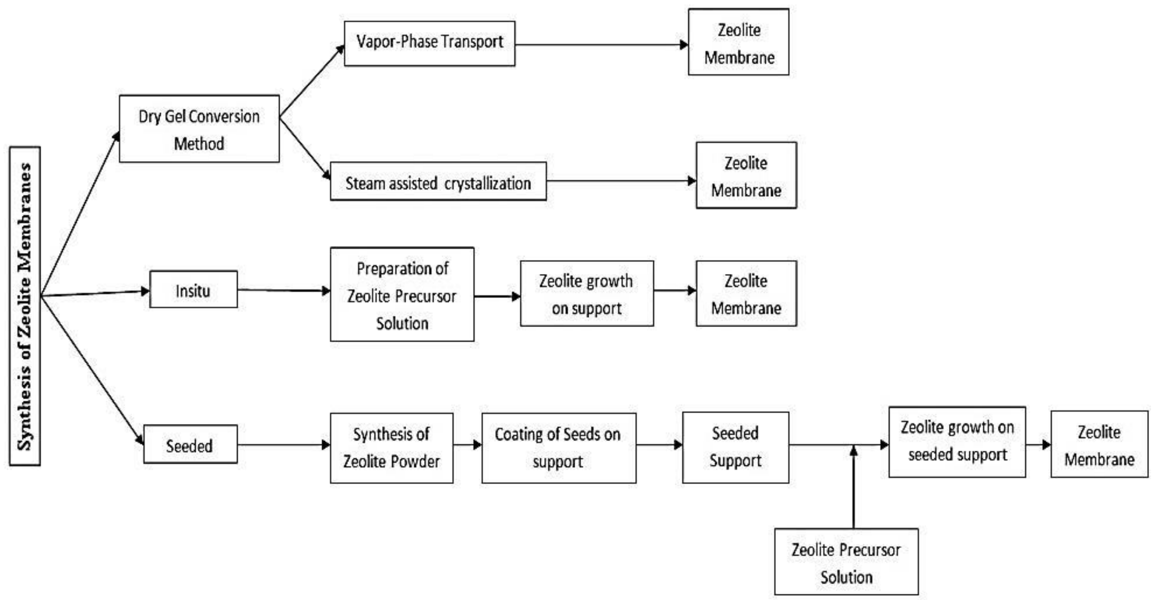

Fig.3 : Different methods and steps for synthesis of zeolite membrane (12)

Performance of Zeolite Membranes in CO_2 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 CO_2 separation from natural gas. Zhu et al. (13) studied the performance of silicate-1 zeolite membrane in CO_2 separation. They found that CO_2 permeance of 1.98 x 10^{-9} mol/m^2 s Pa and CO_2/CH_4 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 CO_2/CH_4 selectivity of 14.2 and CO_2 permeance of 6.1 x 10^{-9} mol/m^2 s Pa. Hasegawa and his coworkers (15) reported the performance of KY zeolite membrane in CO_2 separation. They found that the range of CO_2 permeance was varied from 7.5 x 10^{-7} mol/m^2 s Pa to 9.0 x 10^{-7} mol/m^2 s Pa, while the CO_2/ CH_4 selectivity of 25 to 40 were obtained at temperature of 35 ˚C. On the other hand, low CO_2/CH_4 selectivity was observed by Kusakabe et al. 1997 (16) using Y-type zeolite membrane. They found that the CO_2 permeance of 4.0 x 10^{-8} mol/m^2 s Pa and CO_2/CH_4 selectivity of 2 were obtained at temperature of 30 °C.

Recently, T-type zeolite has been reported in CO_2 separation from CH_4. Zeolite T membrane can easily separate CO_2 from CH_4 based on molecular sieving effect (17). CO_2 permeance of 7.03 x 10^{-9} mol/m^2 s Pa and CO_2/CH_4 selectivity of 70.8 were obtained by Mirfendereski et al. 2008 (18) using a zeolite T membrane. But this CO_2/CH_4 selectivity is not high. SAPO-34 is another type of zeolite membrane which has been widely reported in CO_2 separation. Venna et al. 2011 (19) reported the performance of SAPO-34 membrane in CO_2 separation. They found that CO_2 permeance of 5.0 x 10^{-7} mol/m^2 s Pa and CO_2/CH_4 selectivity of 245 were obtained at 22 ˚C. But, SAPO-34 exhibits poor

Table 1. Performance of Inorganic Zeolite Membranes in CO_2 Separation from Natural Gas Reported by Various Researchers.

Membranes	Temperature (◦C)	CO_2/CH_4 Selectivity	CO_2 Permeance (mol/m^2 s Pa)	Ref.
Silicate-1	30	4.3	1.98×10^{-9}	(13)
ZSM-5	27	14.2	6.1×10^{-9}	(14)
KY-Type	35	25-40	$(7.5 - 9.0) \times 10^{-7}$	(15)
Y-type	30	2	4.0×10^{-8}	(16)
Zeolite-T	-	70.8	7.0×10^{-9}	(18)
SAPO-34	22	245	5.0×10^{-7}	(19)
Ba-SAPO-34	30	103	37.6×10^{-8}	(21)
DDR	30	400	0.65×10^{-7}	(22)

moisture-stability, which is the major drawback of this membrane (20). In order remove this problem, Ba ion was introduce in SAPO-34. Chew et al. 2011 (21) reported the performance of Ba-SAPO-34 zeolite membrane in CO_2 separation. CO_2 permeance of 37.6×10^{-8} mol/m^2 s Pa and CO_2/CH_4 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 CO_2 separation at 30°C. They found that the CO_2 permeance of 0.65×10^{-7} mol/m^2 s Pa and CO_2/CH_4 selectivity of 400 were obtained at 30 °C. Table 1 shows the performance of inorganic zeolite membranes in CO_2 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 CO_2 separation from natural gas. The DDR zeolite membrane has potential in CO_2 separation due to their characteristics such as; well defined pore structure, molecular sieving property and high selectivity. It is observed that the among all zeolite membranes, DDR zeolite membrane showed highest CO_2/CH_4 selectivity at lower temperature which was 400 and compare able CO_2 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 $(C_{10}H_{17}N)_6(N_2)_9$ $[Si_{120}O_{240}]$ (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).

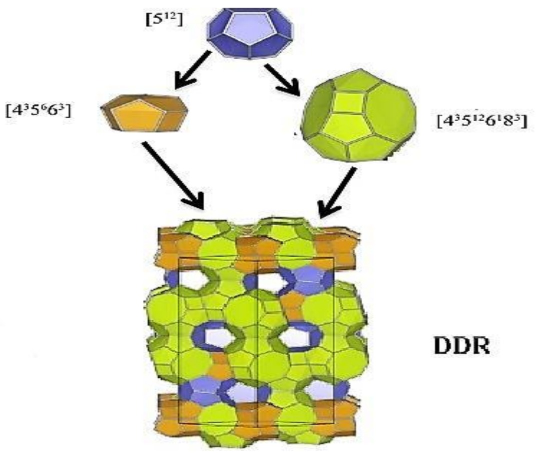

Fig. 4: Framework of DDR crystals (26)

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

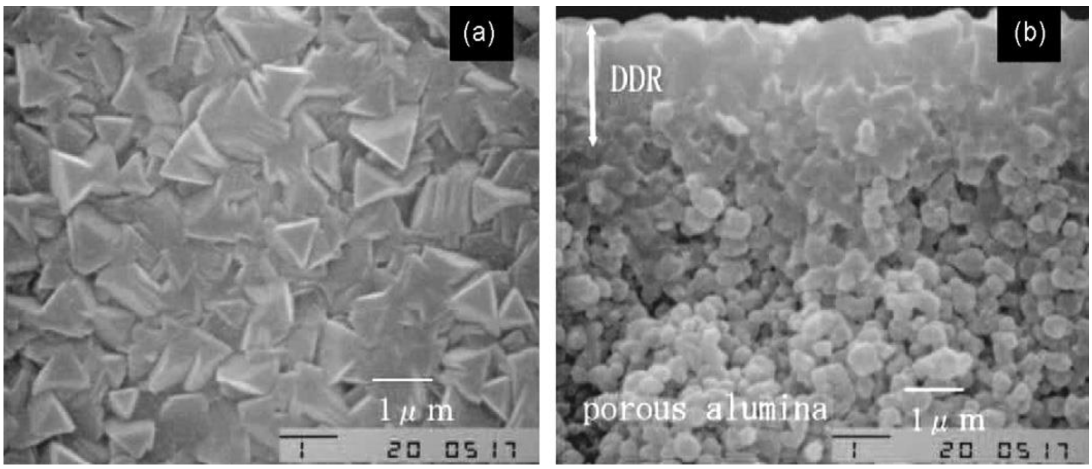

Fig.5 : Surface and cross sectional view of DDR membrane (28)

Table 2. Synthesis of DDR Membrane Reported by Various Researchers

Synthesis Method	Synthesis Duration (Days)		Total Duration (Days)	Ref.
	Crystal seeds	Membrane		
Secondary Growth	25	2	27	(27)
Secondary Growth	25	5	30	(29)
Sonochemical	5	2	7	(30)
Sonochemical	2	5	7	
Secondary Growth	25	1	26	(31)

Table 3. Performance of DDR Membrane in CO_2 Separation Reported by Various Researchers

Method	Temperature (◦C)	CO_2/CH_4 Selectivity	CO_2 Permeance (mol/m2 s Pa)	Ref.
Tomita et al.2004	25	200	3.0×10^{-7}	(27)
NGK Corp.2005	26	670	48.0×10^{-9}	(29)
Van den Bergh et al. 2006	30	400	0.65×10^{-7}	(22)
Uchikawa et al. 2010	-	10	2.0×10^{-7}	(32)

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 3.0×10^{-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 48.0×10^{-9} mol/m^2 s Pa and CO_2/CH_4 selectivity of 670 were obtained at 26 °C. CO_2 permeance was 0.65×10^{-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 2.0×10^{-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 spearation

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 CO_2 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 CO_2 and CH_4 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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