Separability of carbon dioxide from methane using MFI zeolite–silica film deposited on gamma-alumina support

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A B S T R A C T

Silicalite-1, Na-ZSM-5 and B-ZSM-5 zeolite crystals were grown on a mesoporous silica layer to form MFI zeolite asymmetric layer for separation of CO_2 from CO_2/CH_4 binary mixture. Silicalite-1 demonstrated the highest crystallinity followed by B-ZSM-5 and Na-ZSM-5. The cubical and rectangular MFI zeolite crystal structures exhibited random orientation. The crystals appeared to interlock and entwine with each other to form a continuously polycrystalline film covering the surface of the silica support. Results from the permeation test indicated that the selectivity and permeation flux of CO_2 decreased as the temperature was increased but they increased with increase in pressure. B-ZSM-5 showed the highest CO_2/CH_4 selectivity of 8.17 followed by Na-ZSM-5 and silicalite-1 crystals with selectivity of 6.28 and 2.23, respectively.

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1. Introduction

Carbon dioxide separation from CH_4 is important in natural gas processing because CO_2 reduces the energy content of natural gas. CO_2 is acidic and corrosive in the presence of water within the transportation and storage systems. Pipeline specifications for natural gas require a CO_2 concentration below 2–3%. The technology most widely used for CO_2 reduction or removal is amine adsorption, but amine plants are complex and costly [1]. Membrane plants using CO_2 selective cellulose acetate membranes installed in 1980s are currently the largest membrane facility for CO_2 removal with 700 million scfd capacity. The poor performance and stability at high temperature and high pressure, however, limit polymeric membranes for use in CO_2/CH_4 separation. Another factor that limits the use of polymeric membrane is due to the fact that the high partial pressures of CO_2 can plasticize the polymer material, causing the separation ability to decrease [2].

Zeolite membranes were employed [3–5] to separate CO_2 from CH_4 with separability factor ranging from 2.5 to 5.5 using silicalite-1 MFI membrane [6,7], 20 using Y-type zeolite [8], 36 using SAPA-34 zeolite membrane [9], 40 using KY-type zeolite membrane [10], 55 using SAPO-35 [3] and 220 using DDR type zeolite membrane [5]. The interestingly high selectivity of DDR zeolite membrane was attributed to the molecular sieving mechanism of zeolite DDR since the zeolite membrane pore diameter was in between the kinetic diameter of CO_2 and CH_4.

Silicalite-1 is a MFI zeolite crystal containing aluminum free atom in its SiO_4 tetrahedral structure that is important for use as a catalyst in the processes such as methanol to gasoline conversion, syngas production, Fischer-Tropsch synthesis, xylene isomerization, steam reforming and various other applications including gas separations. In this work, three types of MFI zeolite membranes (silicalite-1, Na-ZSM-5 and B-ZSM-5) were synthesized to explore their potentials for use in carbon dioxide enrichment from a binary gas mixture containing methane. The three membranes prepared in this work were chosen because they were known to exhibit significant fluxes through non-zeolitic pores [11], which, zeolite DDR might be deficient in. While the highest separation ability was reportedly achieved at 5.5 for MFI zeolite [7], higher CO_2/CH_4 selectivity of 8.17 was achieved from this work. The in situ crystallization method was used to synthesize Na-ZSM-5 and B-ZSM-5 zeolite membrane while secondary growth method was employed to synthesize silicalite-1 membrane. Disc type α-alumina with diameter of 25 mm and thickness of 3 mm was used as a core substrate. The surface of the alumina substrate was coated with a mesoporous silica layer to enhance the development of zeolitic crystals.

2. Materials and methods

The porous membrane support was made by dry pressing of α-alumina powder followed by sintering of the compact disc at 1200 °C for 4 h. In preparing the macroporous alumina support, 35 g of α-alumina powder was first mixed with 2.8 g of double distilled deionized (DDI) water. About 3.5 g of the mixture was

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transferred to a 25 mm diameter stainless steel die and dry pressed at 12 metric tons pressure for 1 min. The compact disc was later dried at 40 °C for 8 h before sintering process ensued. During sintering process, the rate of heating and cooling was selected at 1 °C/min. The sintered α-alumina disc was later polished using a 1000 grit sand paper and cleaned ultrasonically in DDI water for 3 min for three times to remove the loose alumina powder. Finally the washed support was dried at 100 °C for 8 h.

In order to reduce the risk of crack formation due to thermal stress, all the alumina discs were coated with a thin layer of mesoporous silica. The presence of silica layer was desired because it not only prevented leaching of aluminum oxide from the support, but it also assisted in the formation of distinguish zeolite thin layer by preventing the infusion of zeolite synthesis solution into the support pores. The mesoporous silica layer was prepared using a sol–gel dip-coating technique following the procedure from the previous work [12–15]. The development of zeolite crystals was achieved following a secondary growth procedure [16]. The silica precursor was obtained by mixing 63 ml ethanol, 60 ml tetraethyl orthosilicate (TEOS) with 4.87 g DDI water, followed by addition of 0.2 ml of 0.07 M HCl to adjust the pH to ca. 4. The mixture was hydrolyzed under reflux and vigorous stirring conditions at 60 °C for 1.5 h. Then, 4 g of cetyltrimethylammonium bromide (CTAB surfactant) was added to 40 ml of the hydrolyzed sol. The pH of the sol was adjusted to 2 by adding 7 ml of 0.07 M HCl until all the surfactant was dissolved. The clear sol was aged at 50 °C for 2.5 days until it became viscous. The viscous sol was diluted two times using anhydrous ethanol to decrease the film thickness prior to dip-coating on the alumina support by immersing the support in the sol for 1 min, removing the support from the sol at a speed of 0.5 cm/s and holding the support vertically for 1 min to let the solvent evaporate. The support was dried at 100 °C for 8 h. Finally the dip-coated support was calcined at 500 °C for 8 h with ramping rate of 1 °C/min to remove the surfactant.

A secondary growth method was employed in the synthesis of silicalite-1 (Si/Al = ∞) membrane. Fine zeolite seeds (precursor) were first prepared according to the method proposed in the previous work [17,18], by adding 0.85 g NaOH to 60 ml 1 M tetrapropylammonium hydroxide (TPAOH), stirred until dissolved. Fifteen grams of fumed silica was then added to the solution to form slurry having composition $SiO_2:TPAOH:NaOH:H_2O$ of 10:2.4:1:110. The solution was placed in a teflon-lined stainless steel pressure reactor for hydrothermal synthesis at 125 °C for 8 h under stirring. The seed was recovered by repeated washing and centrifuging at 4500 rpm for 15 min until pH of the seed solution was neutral. The seeds were dried at 100 °C for 8 h. The stable aqueous suspension was prepared by dispersing 4 g zeolite seeds into 200 ml DDI water (20 g/L) in ultrasonication for 3 min. The zeolite seeds were deposited on the support by a vacuum seeding method [19–21]. The apparatus used in the vacuum seeding method is illustrated schematically in Fig. 1. The support was sealed vertically inside a cell, one side of it was immersed in the seed solution and the other side was connected to a vacuum pump. When the vacuum pump was switched on, pressure difference was created between the two sides of the support wall. The water passed through the pore of the support and was removed by the action of vacuum force. Consequently, the zeolite seeds were transported and coated on the support surface along with the flow of water. The vacuum seeding was operated under the pressure differences of 0.0025 MPa for 4 min. After the vacuum seeding, the seeded support was dried in air at 100 °C for 8 h and calcined at 450 °C for 8 h.

In preparing Na-ZSM-5 (Si/Al = 25) and boron substituted B-ZSM-5 (Si/B = 100) membrane, in situ crystallization method was employed. Na-ZSM-5 membrane precursor was synthesized by dissolving 0.4 g $Na_2Al_2O_3$ and 0.94 g NaOH in 83.45 g DDI water. About 1.18 g tetrapropylammonium bromide (TPABr) was

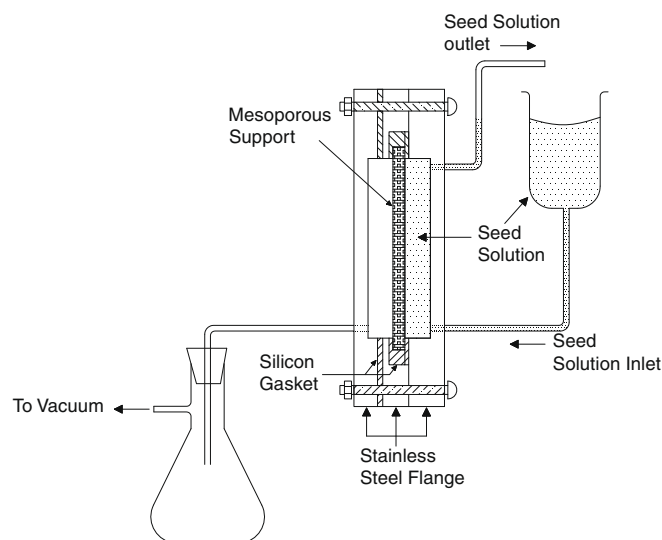**Fig. 1.** Vacuum seeding apparatus.

dissolved in 83.45 g DDI water separately and added slowly into the solution containing in $Na_2Al_2O_3$, stirred for 5 min until a homogenous solution was obtained. About 15.38 g TEOS was added into the solution and aged for 2 h prior to deposition on the support during hydrothermal synthesis.

B-ZSM-5 (Si/Al = 100) membrane precursor was prepared by dissolving 0.10 g boric acid (BOH) in 53.58 g DDI water. About 12.63 g TPAOH was mixed with 53.58 g DDI water and slowly added into the solution containing boron element under vigorous stirring. About 33.78 g TEOS was added into the solution mixture and aged for 2 h prior to deposition on the support and hydrothermal synthesis under autogenous pressure inside a high pressure reactor that has a capacity of 51.7 MPa (750 psig).

The gas permeation was obtained using a permeation cell that was fabricated following the previous work [22] with some modifications such as shown in Fig. 2. The permeance and selectivity are defined as:

Permeation Flux

$$= \frac{\text{amount of components permeate pass the membrane}}{\text{time}}$$

$$= \frac{cm^3}{min} \tag{1}$$

$$\text{Selectivity}, \alpha_{A/B} = \frac{y_A}{y_B} \Big/ \frac{x_A}{x_B} \tag{2}$$

where y_A, y_B are the molar fraction of component A and B in the permeate, respectively. x_A, x_B are the molar fraction of component A and B in the retentate, respectively.

The molar fractions of the component at permeate and retentate were obtained from the analysis of the samples using HP 5890 Series II gas chromatograph (GC). The GC unit was equipped with thermal conductivity detector, capillary column and Agilent Chemstation software (Revision A.09.03). The GC unit was operated at isothermal conditions with helium as carrier gas flowing at 25 ml/min. The separation of binary gas mixture was achieved using HP-PLOT Q capillary column (0.55 i.d. × 30 m, 40 μm film thickness).

The flow rate of two inlet gases were controlled by two mass flow controllers (MKS type M100 series) connected to a two channels digital set point/readout unit (MKS PR4000). The flow range of the control valves were 0–100 SCCM (cm³/min) with an accuracy of ±5%. At the permeate side, the flow of sweep gas was controlled