Synthesis and Characterization of Mesoporous Hydrotalcite-Alumina Membrane for Carbon Dioxide Enrichment

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Abstract. Hydrotalcite material was incorporated to enhance the carbon dioxide (CO₂) affinity of the alumina membrane for CO₂ separation from different gas mixtures. The crack free mesoporous HT-alumina (~10 µm) porous membranes were successfully synthesized on surface of α-Al₂O₃ disc support using the sol-gel and dip-coating techniques. The unsupported membranes were characterized for the presence of HT, surface functional groups, surface topography and morphology, pore size and CO₂ adsorption capacity. These characterizations were done using X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) spectrometry, scanning electron microscopy (SEM), Brunauer-Emmett-Teller method (BET) and Thermo gravimetric analyser (TGA) techniques. The modification of alumina membrane with HT enhanced CO₂ separation performance. The CO₂ permeance was higher than that of methane and nitrogen. While the permeance of hydrogen was almost same to that of CO₂ even though the hydrogen molecule was smaller than the CO₂ molecule. Indicating that the gas transport through the membrane was predominantly surface adsorption. The mesoporous Hydrotalcite-alumina membrane overcame the Knudsen limitation and produced the highest permselectivity of 2.16 for CO₂/CH₄ system at 30ºC temperature and 100 kPa pressure difference.

1. Introduction
Inorganic mesoporous alumina material have been selected to prepare a membrane for CO₂ gas separation since it is thermally and chemically stable and has good mechanical strength [1]. Generally, the mesoporous alumina membrane provides high gas permeance but low selectivity due to transport of the gases through the pores by Knudsen diffusion mechanism in which the light gases permeate faster than heavy gases [2]. Higher Knudsen separation values are obtained for light gases such as H₂/CO₂ with a separation factor of 4.7. Moreover, mesoporous γ-alumina membranes had an essential function as intermediate layer on macroporous supports in order to provide a smooth pore size transition between the support and the more selective microporous silica membranes [3]. Therefore, to achieve high separation factors, different mechanisms for gas transport through γ-alumina have to be employed.

Separation factors can be enhanced by introducing an interaction between one of the gases in the mixture and the membrane pore surface [4-5]. If the adsorbed gas is mobile along the surface of the pore wall, it will diffuse in the direction of decreasing driving forces. The additional diffusion enhanced the gas permeance and separation factor of the more adsorbed gas. The presence of this type of transport, called surface diffusion, is frequently described in porous materials [6-7].

A few efforts have been reported to improve γ-alumina membranes to facilitate CO₂ surface diffusion. Keirzer et al. [8] and Uhlhorn et al. [9] modified the γ-alumina membrane with magnesia
(MgO) by impregnating technique to improve CO₂ surface diffusion and conform an increase in CO₂ adsorption. However, the modified membrane showed CO₂/N₂ separation factor of only unit nearly to the Knudsen separation factor value, 0.8. They suppose that strong adsorption of CO₂ occurred on the MgO sites, resulting in a decrease in CO₂ permeation rate. Cho et al. [10] improved the CO₂ surface diffusion by doping calcium oxide (CaO) into the γ-alumina membrane. The CO₂/N₂ separation factor was enhanced to be 1.72 at 25 ºC and decreased with increase in the temperature to reach 1.5 at 200 ºC. It was concluded that the separation factor could be enhanced by applying surface diffusion mechanism when the membrane is microporous and the operating temperature is low.

Hydrotalcite (HT) material is a layered double hydroxides (LDH) that has been considered as good CO₂ adsorbent materials at elevated temperature [10-11]. However, researches on the manufacture of HT material as a membrane for CO₂ separation from other gases has been rarely performed [7,12]. In the current study, sol-gel technique was applied to synthesis mesoporous HT-alumina membrane to improve CO₂ permeance and separation. This research also discusses the effect of HT content on the phase composition, pore size, surface morphology and CO₂ adsorption capacity.

2. Experimental

2.1 Support preparation

The home-made porous α-alumina discs of 25 mm in diameter and 2 mm in thickness were prepared using high purity α-alumina powder (>99.99%) with particle size of 45 µm (Sumitomo Co, Japan, AA-04). The alumina powder of 32 g was thoroughly mixed with 2.6 g of de-ionized water prior to pressing. For each support, 3.5 g of the mixture was introduced in a stainless still mold and pressed at 600 kg/cm² for 1 min using hydraulic press pelletizer. The supports were then dried overnight at 80ºC to remove the water binder, and then calcined at 1000ºC for 30 h using a programmable furnace. After calcination, the discs were polished with 800 and 1000 grit sand paper, washed with deionized water and then overnight in oven at 80ºC.

2.2 Mesoporous HT-alumina membrane preparation

The alumina membrane was prepared using sol-gel method. Aluminum tri-sec butoxide (ATB) was used as a precursor. The sol was prepared by heating 90.47 ml of de-ionized water on a heating mantle at 90ºC, followed by slow addition of 12.38 g aluminum tri-sec butoxide and stirred vigorously for 1 h at 90ºC. 2.1 ml of PVA solution (4 g PVA/100 ml H₂O) was then added to the mixture as a binder. 7.5 ml of 1 M HCl acid was then added drop-wise to the solution while stirring at 90ºC to peptize the sol and form a stable solution. The mixture was subsequently heated at 90ºC for 24 h under reflux condition to ensure complete mixing and hydrolysis. Finally, the sol was cooled down slowly to room temperature for a few hours. The molar ratios of ATB, HCl and water used in the experiment to prepare the boehmite sol were 1:100:0.07 using the sol gel method as developed previously [13-14]. After reflux, small amount of the resulting sol mixture, approximately 2-3 ml, was poured into a 10 mm diameter petri-dish for further analysis of the unsupported membrane. The sol was flatten and left to dry at room temperature for 24 h to obtain gel. The resulting gel was transferred into a porcelain crucible for sintering at 500ºC for 3 h using a programmable furnace and then was characterized. For supported membrane, the resulting sol was coated on the α-alumina pellet support. The α-alumina pellet was held using a forceps and the support surface was dipped in the alumina sol for 10 sec and then removed from the solution and dried at room temperature for 24 h before it was sintered. During sintering process, low heating and cooling rate of 0.5-1ºC /min was applied to produce crack free γ-Al₂O₃ membrane. The dipping, drying and sintering processes are repeated once, to produce crack free γ-Al₂O₃ membrane.

2.3 Characterization of membrane

The XRD analysis of the powder samples was carried out to identify phase structures of the synthesized membranes. The XRD measurements were obtained using wide scattering angles XRD (10º ≤ 2θ ≤ 90º) with a step size of 0.03º 2θ and step time of 72.4 s. The analysis was performed using
Cu Kα radiation over a Bruker X-ray diffractometer (Bruker D2 Phaser Germany, 2011). The changes of the covalent chemical bonding in molecules for the powder samples were analyzed using FTIR spectroscopy using Perkin Elmer spectroscope (Perkin Elmer System FT-IR 2000, USA). The CO₂ adsorption capacity of the unsupported membranes was conducted using Thermal Gravimetric Analysis (Perkin Elmer STA 6000). The surface textural characteristics of the membranes were analyzed using nitrogen adsorption–desorption isotherms. The isotherms for the unsupported membranes were collected from Micromeritics instrument (model ASAP 2020). The surface morphology and the film thickness of the supported membranes were analyzed using the images obtained from QUANTA FEG 450 scanning electron microscope (SEM).

2.4 Gas permeation and separation testing

A single gas permeation experiments through the membrane was performed with CO₂, H₂, N₂ and CH₄ at 30°C and 100 kPa of the pressure difference across the membrane. A bubble flow meter was used to measure the gas flow rates of feed, retentate and permeate streams. The gas permeance of gas i through the membrane, \( K_i \) (mol/m².s.Pa), was calculated as below:

\[
K_i = \frac{N_i}{\Delta p}
\]

Where: \( N_i \) is the mole flux of the gas i permeate through the membrane and \( \Delta p \) is the pressure difference between retentate and permeate streams (Pa). The permselectivity was used to measure the single gas separation performance of the membrane. The permselectivity of the membrane, \( \alpha_{i/j} \), was calculated from the ratio of single gas permeances, \( K_s \), as shown below:

\[
\alpha_{i/j} = \frac{K_i}{K_j}
\]

Where: i refers to CO₂ gas and j refer to another gas species (H₂, N₂ and CH₄).

3. Results and Discussion

3.1 Structure and phases present

Figure 1 depicts the XRD patterns of pristine γ-alumina membrane as well as 3 and 6 vol. % of HT in γ-alumina membranes. Figure 1(a) shows the XRD pattern of γ-alumina membrane sintered at 500 °C with three diffraction peaks obtained for pure crystalline γ-Al₂O₃ phase. These reflections were associated with 2θ = 37.68°, 45.85° and 66.85°, respectively. These peaks matched with peaks reported for γ-Al₂O₃ phase [15-16]. The crystallite size of γ-Al₂O₃ was 4.49 nm with cubic structure and unit cell (a=7.906 Å). Figure 1 (b and c) shows the XRD patterns for the HT-alumina membranes with HT vol. % of 3 and 6%, respectively. As it can be seen, the crystal phase of HT was enhanced in the alumina material and interpreted by the peak centered at 2θ = 23.42° [17].
3.2 Surface chemistry

FT-IR spectra of the pristine γ-alumina membrane as well as 3 and 6 vol. % of HT in γ-alumina membranes after sintering are shown in figure 2. The pristine alumina material typically exhibits major IR bands assigned at 480, 625, 931, 1089, 1120, 1385, 2360, 3250, 3415, 3484 and 3552 and large band in the range 3200-3700 cm\(^{-1}\) with notable intensities. The IR band at around 480 cm\(^{-1}\) can be attributed to Al–O bending vibration [18] and the band at 625 cm\(^{-1}\) is due to Al–OH bending vibration [19]. It was suggested that the band at 930 cm\(^{-1}\) was due to vibration of OH groups coordinated to Al-Al pairs [20]. The band at 1120 cm\(^{-1}\) was attributed to asymmetric Al–O stretch [21]. The characteristic absorption bands at 1385 and 1638 cm\(^{-1}\) were due to the bending vibration of –OH group bonded with Al\(^{3+}\) [22]. All the samples show a wide band at about 3200-3700 including the small peaks at 3250, 3415, 3471 and 3553 for alumina sample due to the O-H stretching vibration of water and hydroxyl groups [23]. For HT-alumina materials, the bands at 480, 625 and 930 cm\(^{-1}\) disappeared as the HT vol. % increase in alumina matrix, and new wide band at round 470-630 cm\(^{-1}\) was formed, attributed to defective Al–OH and Al-O groups. Also, it can be observed that HT-alumina materials exhibited higher intensity of the 1635 cm\(^{-1}\) band and the bands between 3200-3700 cm\(^{-1}\) due to the increase of O-H band and inter layer water molecules with increase in HT content.

3.3 Textural properties

![Figure 1. XRD patterns of the HT-alumina membranes containing different HT vol. %: (a) 0% (pure alumina); (b) 3 % and (c) 6 %, sintered at 500ºC.](image1)

![Figure 2. FT-IR spectra of HT-alumina membranes containing different HT vol. %: (a) 0% (pure alumina); (b) 3 % and (c) 6 %, sintered at 500ºC.](image2)
The nitrogen adsorption–desorption isotherms for the pristine $\gamma$-alumina, 3 and 6 vol. % of HT in $\gamma$-alumina membranes, are shown in figure 3(a–d). They are indexed as type IV with H2 hysteresis loop by IUPAC classification, which is characteristic of mesoporous materials. This hysteresis arises from monolayer and multi-layer condensation of nitrogen within ill-defined mesopores between 2 and 50 nm [24]. It can be seen that the incorporation of HT into the alumina matrix did not affect the textural properties of the $\gamma$-alumina membranes, where the shape of hysteresis loop of HT-alumina membranes was the same as the pristine $\gamma$-alumina material.

![Figure 3. Nitrogen adsorption–desorption isotherms of HT-alumina membranes containing different HT vol. %: (a) 0% (pure alumina); (b) 3 % and (c) 6 % and (d) 100 % HT, sintered at 500ºC.](image)

Figure 4 shows the pore size distribution of pristine $\gamma$-alumina, 3 and 6 vol. % of HT in $\gamma$-alumina membranes sintered at 500ºC. The pore size distribution for all the membranes was estimated by the Barrett, Joyner, and Halenda (BJH) method. It is observed that the pore size distribution of the pristine $\gamma$-alumina and HT are narrow with an average pore diameter of 35.0 and 37.5 Å, respectively, which is in agreement with the adsorption isotherm results and also with the alumina and HT prepared previously [14, 25]. The incorporation of HT into the alumina membrane shifted the pore diameter of alumina membrane to 36.9 Å and widened the pore distribution.
3.4 CO₂ adsorption/desorption measurements

The CO₂ adsorption capacities of alumina, HT and HT-alumina samples at 30 °C under pure CO₂ gas were evaluated using thermal analysis techniques and are given in figure 5 and Table 1. The adsorption capacity of HT powder was the largest at 56.82 mg CO₂/g sorbent. While the pure alumina sintered showed the smallest adsorption capacity at 22.33 mg CO₂/g sorbent. The adsorption capacity of the HT-alumina samples increased with increasing HT content. The incorporation of 6 vol. % HT material inside the alumina membrane enhanced the CO₂ adsorption capacity of about 83 % from 22.33 to 40.78 mg CO₂/g sorbent. Higher CO₂ adsorption capacity of the synthesized HT-alumina composite membrane containing 6 vol. % HT (0.927 mmol CO₂/g sorbent) is observed when compared with that of the mesoporous alumina material modified with tertiary alkanolamine (0.39 mmol CO₂/g sorbent) or with 2-amino-2-methyl-1,3-propanediol (0.57 mmol CO₂/g sorbent) [26].

![Figure 4. Pore size distribution of HT-alumina membranes containing different HT vol. %](image)

![Figure 5. Isothermal adsorption-desorption of HT-alumina membranes containing different HT vol. %, at 30°C.](image)

| HT vol.% | Adsorption capacity (mg CO₂/g sorbent) | Adsorption capacity (mmol CO₂/g sorbent) |
|----------|----------------------------------------|-----------------------------------------|
|          |                                        |                                         |

Table 1. Summarized isothermal adsorption result of HT-alumina membranes containing different HT vol. %, at 30°C.
3.5 Surface morphology

Figure 6 shows the SEM micrographs presenting the surface and the cross-section of mesoporous HT-alumina membrane containing 6 vol. % HT. Figures 6 (a) and (b) show that the mesoporous HT-alumina layer had good adhesion and good uniformity with a clear boundary with the α-alumina support. The thickness of the 2 coated layers of HT-alumina on the α-alumina support was about 10-11 µm, as shown in Figure 6 (c) and (d). The higher thickness of HT-alumina membrane compared to alumina membrane (9 µm) was probably due to the change of the sol's viscosity or inconsistent coating.

![Figure 6. SEM images of HT-alumina membrane containing 6 vol. % HT: (a) surface measures at 50 µm, (b) surface measures at 5 µm (c) cross sectional view measures at 100 µm and (d) cross sectional view measures at 30 µm.](image)


table

|   | µm |   |
|---|----|---|
| 0 (pure alumina) | 22.33 | 0.508 |
| 3 | 37.65 | 0.856 |
| 6 | 40.78 | 0.927 |
| 100 (pure HT) | 56.82 | 1.291 |

3.6 Permeation and separation measurements

The synthesized of alumina as well as HT-alumina composite membranes containing 3 and 6 vol. % HT were subjected to single gas permeation with H₂, CO₂, N₂ and CH₄ at 30°C and 100 kPa pressure difference across the membrane. Figure 7 shows the effect of the vol. % of HT in the composite membrane on the CO₂ permeance and permselectivities of CO₂/CH₄, CO₂/N₂ and CO₂/H₂, at 100 kPa pressure difference and 30°C. It was observed that the incorporation of HT in the composite membrane improved the CO₂ permeance. The increase in CO₂ adsorption capacity with increase in HT vol. % in composite membrane enhanced the CO₂ affinity along the membrane wall and favoured its transport through the membrane. The pure alumina membrane exhibited the lowest permselectivities (less than 1) for CO₂/CH₄ > CO₂/N₂ > CO₂/H₂ systems. The permeation of gases through mesoporous
alumina membrane with pore size of 3.5 nm governed by Knudsen diffusion mechanism, which separates the gases based on molecular weight [27]. The mesoporous HT-alumina composite membrane with pore size of 3.7 nm exhibited new mechanism for gas permeation that combined the Knudsen diffusion and surface diffusion. The mesoporous HT-alumina composite membrane with 6 vol. % of HT showed the highest permselectivities of 2.16, 1.65 and 0.98 for CO₂/CH₄, CO₂/N₂ and CO₂/H₂, respectively, compared to the other membranes. The increase in permselectivities far from Knudsen diffusion was due to the incorporation of HT which improved the adsorption diffusion of CO₂. However, the HT-alumina membrane containing 6 vol. % of HT showed high CO₂ permeance (2.16×10⁻⁶ mol·m⁻²·s⁻¹·Pa⁻¹) but relatively low permselectivity due to large pore size (3.7 nm).

![Figure 7. Permselectivities of CO₂/H₂, CO₂/N₂, CO₂/CH₄ and CO₂ permeance at 100 kPa pressure difference and 30°C for HT-alumina composite membranes containing different HT vol. % sintered at 500°C.](image)

5. Conclusions

Mesoporous HT-alumina composite membrane with 10.5 µm thickness was successfully prepared on the surface of 2 mm thick α-alumina supports using sol-gel method. The mesoporous HT-alumina membrane exhibited good pore size distribution with pore size of 37 Å. The HT-alumina membrane containing 6 vol. % HT and sintered at 500°C was found to combine the Knudsen diffusion characteristic of pristine alumina material with the high CO₂ adsorption capacity of HT. It yielded the highest permselectivities of 2.16, 1.65 and 0.98 for CO₂/CH₄, CO₂/N₂ and CO₂/H₂, respectively due to its high CO₂ affinity.

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