Gas Permeation Study Using Porous Ceramic Membranes

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Abstract

A 6000 nm ceramic membrane was repaired with boehmite solution (ALOOH) through the repeat dip-coating technique. The permeance of hydrogen (H_2) and carbon dioxide (CO_2) were obtained through the membrane in relation to average pressure at room temperature for the support membrane and as cracked membrane. A repair process was carried out on the cracked membrane by same dip coating process and results obtained after first and second dips. The permeance of the support membrane obtained ranged between 1.50 to 3.04×10^{-7} mol m^{-2} s^{-1} Pa^{-1}. However, as a result of a crack that occurred during the removal of the membrane from the reactor, the permeance increased from 2.96 to 5.82 10^{-7} mol m^{-2} s^{-1} Pa^{-1}. Further application of boehmite solution on the membrane lead to an improvement on the surface of the membrane with some degree and surface cracks were reduced. This also decreased the permeance to $1.26 - 3.39 \times 10^{-8}$ mol m^{-2} s^{-1} Pa^{-1} after the second dip. Consequently, another silica based modified membrane was used for carbon dioxide and nitrogen (N_2) permeation. The plots show that carbon dioxide permeated faster than the other gases, indicating dominance of a more selective adsorptive transport mechanism. Accordingly, results obtained show an appreciable high carbon dioxide permeance of 3.42×10^{-6} mol m^{-2} s^{-1} Pa^{-1} at a relatively low pressure when compared to nitrogen confirming that the membrane has so far exhibited a high permeability, selectivity and high CO_2 gas recovery. The permselectivities of CO_2 over H_2 at room temperature was also obtained which were higher than the Knudsen selectivity.

Keywords: ceramic membranes, gas permeation, hydrogen selectivity, carbon dioxide selectivity, defect repair

1. Introduction

Carbon dioxide is one of the many greenhouse gases which contribute to global warming. Membrane technology has been suggested as a substitute to the use of conventional separation processes (e.g. dehydration, gas adsorption, distillation among others) due to their unique attributes such as thermal and mechanical stability, as well as harsh chemical resistance (Singh et al., 2004; Anwu et al., 1997). The employment of inorganic membranes in the industry has extended the application of membranes for hydrogen production, CO_2 recovery as well as H_2S removal from associated gas feed streams because of their simplicity and low energy requirement (Yildirim & Hughes, 2002).

There are several methods for porous membrane modification including; dip-coating, chemical vapour deposition (CVD), and pulsed layer deposition (Pejman et al., 2011; Benito et al., 2005; Koutsonikolas et al., 2010). Out of the mentioned modification methods, dip-coating method has many merits over the other methods such as its simplicity, uniform surface and the ability of controlling the pore structure of the membrane (Pejman et al., 2011). However, a lot of research is still needed to examine membrane modification through dip-coating method in order to elucidate the morphological effects of dip-coated membranes. Membranes defects are formed during preparation stages. It can be formed either during dipping, drying, calcination process and sealing (Koutsonikolas et al., 2010) or even during the process of inserting and removing it from the reactor. Any defect on a macroporous membrane (pore diameter > 50 nm) can be regarded as a crack. For example, a defect is considered in the presence of super-micropores (0.7 nm < pore diameter < 2 nm) instead of ultra-micropores (pore diameter < 0.7 nm) (Koutsonikolas et al., 2010). It is known that any amount of defect on the membrane can significantly lower the membrane selectivity.

Lambropoulos et al. (2007) repaired γ-alumina and silica membranes at 573 K by CVD process with a tetraethylorthosilicate (TEOS)/O_3 counter reactant configuration. The defect was characterised with a permeability technique and a novel mercury intrusion. However, Gopalakrishnan et al. (2007) applied a hybrid processing method for hydrogen-selective membrane preparation. They applied a primary sol-gel silica layer for the CVD zone thickness reduction, and a CVD modification with tetramethoxysilane (TMOS) and O_2 at 873 K. After which they only examined H_2/N_2 selectivity to be 2300 at 873 K. Pejman et al. (2011) modified the surface of ceramic supports to facilitate the deposition of defect-free overlying micro and mesoporous membrane. They investigated the effects of dipping time, heating rate, and number of coated layers on microstructure of the modified layers in their study. They have achieved a smoother surface and the cracks size was reduced dramatically after two dip-coating steps.

In this paper, we have repaired a crack on a ceramic membrane with boehmite solution (ALOOH), also carbon dioxide separation and the effects of permeation properties such as; permeation pressure was examined.

2. Experimental

The commercial ceramic membrane used was supplied by Ceramiques Techniques et Industrielles (CTI SA) France, consisted of (77% α-alumina + 23% TiO_2) with an average pore diameter of 6000 nm. The membrane has 19.8 mm and 25 mm internal and outer diameter respectively, and a permeable length of 318 mm. The feed pressure applied was between 0.05 to 5 bar at room temperature. Figures 1 and 2 show a SEM image of inside and outside surface of the porous ceramic membranes. The membrane's structure was defect-free before the 1st dip. An SEM of the cross section of the same membrane is also shown in Figure 3. During the removal of the membrane from the reactor; the membrane was cracked Figure 4 i.e. after gas permeation before modification.
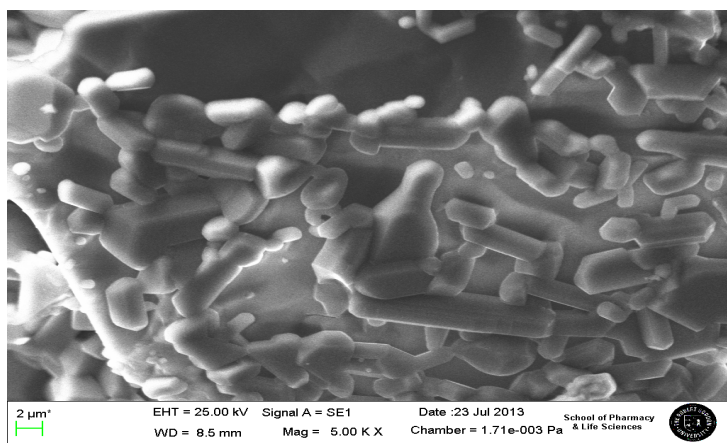

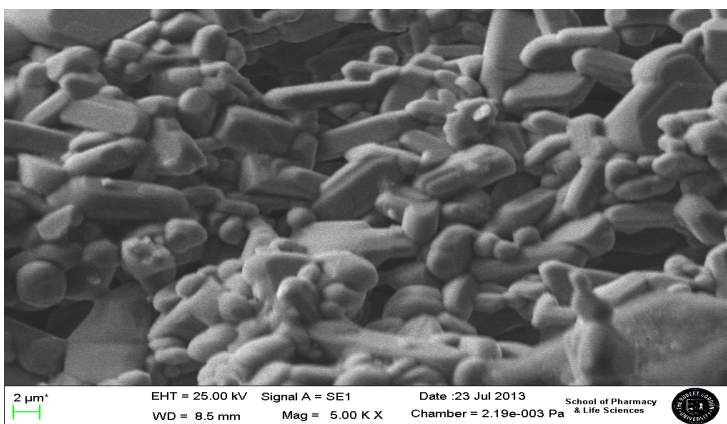Figure 1. SEM image of the inside surface
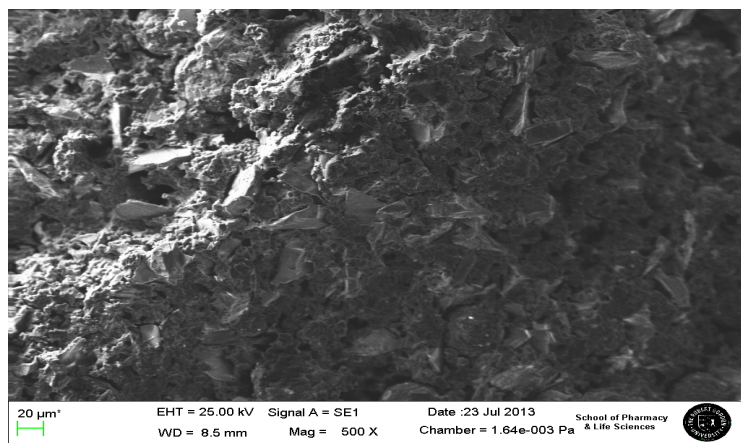

Figure 2. Outside surface of ceramic membrane

Figure 3. SEM image of the cross section of the membrane

In order to repair the defected surface of the substrate a 36 g/1000 L boehmite sol was used. A dip-coating method was applied to repair the defected membrane. The internal surface of the coarse alumina tube membrane was exposed to boehmite solution for 30 minutes. After this, the membrane was air-dried overnight and then heat-treated using the temperature profile shown in Figure 5. The dipping-drying firing procedure was repeated in order to achieve the required γ -alumina layer on the coarse support. The prepared membrane glazed at each end was sealed within the stainless steel reactor using graphite seals.
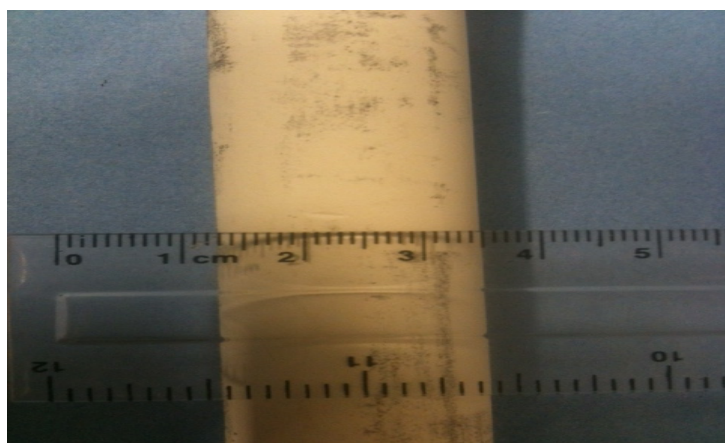

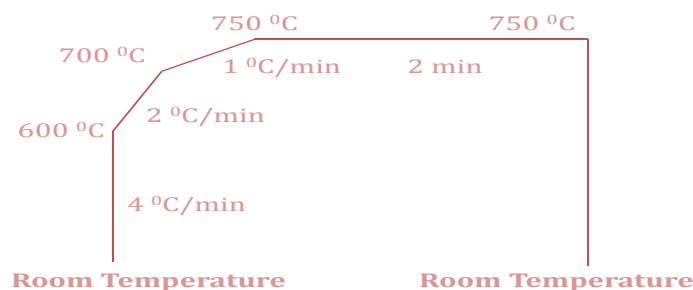Figure 4. Pictorial view of the cracked membrane

Figure 5. Membrane's heat-treatment profile

Single gas permeation measurements were carried out for gas components (H_2 and CO_2) at room temperature using the experimental setup shown in Figure 6 with the retentate valve fully open to the fume cupboard. The

permeate flow tube was connected to the flowmeter to record gas flow rate. Gas permeance was obtained from the following expression;

$$Q = \left(\frac{q}{A.\Delta P} \right) \tag{1}$$

Where Q is the Permeance (mol m^{-2} s^{-1} Pa^{-1}); q is the molar flow (mol/sec); A is the membrane area (m^{2}); and ΔP is the pressure difference (Pa) across the membrane.

Figure 6. Experimental arrangement for the membrane reactor

The permselectivity of the membrane was also obtained using Equation (2);

$$S_{ij} = Q_i/Q_j \tag{2}$$

Where S_{ij} is the permselectivity of i to j; Q_i is the permeance of i (mol m^{-2} s^{-1} Pa^{-1}); Q_j is the permeance of j (mol m^{-2} s^{-1} Pa^{-1}).

3. Results and Discussion

Figure 7 shows the results of carbon dioxide permeance through the multilayered alumina membrane against average pressure at room temperature for the support membrane, cracked membrane, first and second dip repaired with boehmite solution stages. It can be seen that the permeance of the support is between 1.50 to 3.04 $\times$ 10^{-7} mol m^{-2} s^{-1} Pa^{-1}. However, due to the crack which occurred during the removal of the membrane from the reactor, the permeance increased to 2.96 – 5.82 10^{-7} mol m^{-2} s^{-1} Pa^{-1}. After exposing boehmite solution to the membrane, the surface was improved to some degree, surface cracks are also lowered, and the permeance decreased to 1.26 – 3.39 $\times$ 10^{-8} mol m^{-2} s^{-1} Pa^{-1} after the second dip which is almost parallel to the x-axis which indicates the applicability of Knudsen diffusion mechanism.
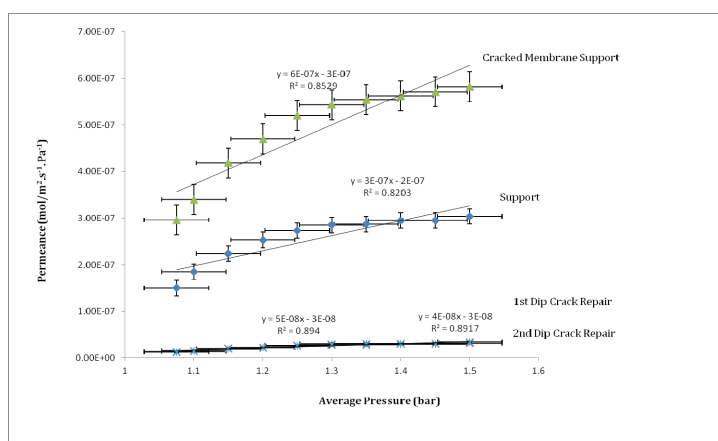

Figure 7. Permeance against average pressure for carbon dioxide at room temperature

Silica layer membrane was also prepared using the repeated dip-coating method (Gobina, 2006) which allows CO_2 to permeate faster from flue gas by maintaining a pressure drop across the membrane due to surface diffusion despite its higher molecular weight. It can be seen in Figure 8 that the graph showing the effect of feed pressure on CO_2 and N_2 permeance. From a feed pressure of about 1.4 bar, the permeance of CO_2 was quite higher than that of N_2, which indicates the presence of surface diffusion while that of N_2 reduced drastically which indicates the presence of Knudsen diffusion mechanism.
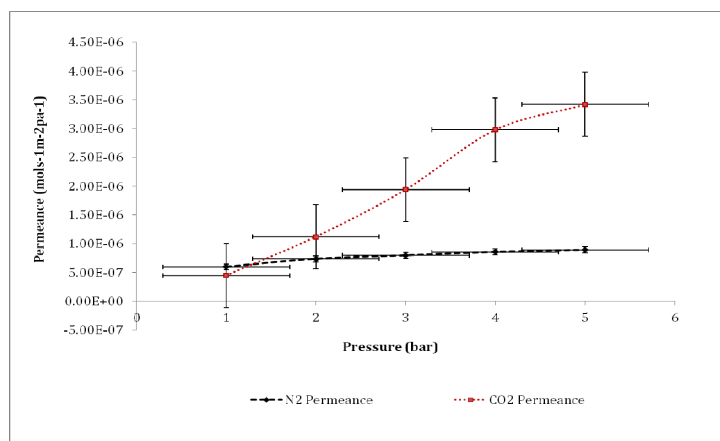

Figure 8. Effect of pressure on CO_2 and N_2 permeance

The permselectivities of CO_2 over H_2 at room temperature is shown in Figure 9. It can be seen that the selectivities obtained are higher than the Knudsen selectivity. After exposing the support to the boehmite solution, it was observed that a significant increase in the selectivity to CO_2 had occurred for the first dip crack repair as shown in Figure 9. Subsequent dips however reduced the CO_2 selectivity. This behaviour is related to the transport regime in the membrane. Transport owing to the combination of diffusion through the gas phase in the pores of the membrane and surface diffusion is a combination of mechanisms. The total transport in the absence of a pressure difference over the membrane of i owing to the combination of diffusion through the gas phase in the pores of the membrane and surface diffusion is described by Equation (3);

$$J_{i, tot} = J_{i, gas} + (4/d_p) J_{i, surf} \tag{3}$$

Where $J_{i, tot}$ = total molar flux owing to both transport mechanisms (mol-m^{-2}-s^{-1}), $J_{i, gas}$ = molar flux owing to transport in the gas phase in the pores (mol-m^{-2}-s^{-1}), and d_p = average pore diameter (m).

In the present study, it was assumed that the pores could be regarded as ideally cylindrically shaped although this assumption is questionable for alumina membranes. Another complicating factor is the homogeneity of the distribution of the γ-alumina over the α-alumina surface inside the membrane. As the main objective of the present study was to demonstrate the occurrence of surface diffusion effects in ceramic membrane reactors no special attention has been paid to the actual pore configuration. Moreover, pore shape only affects the value of the constants of the denominator of the term for $J_{i, surf}$ in Equation (3), e.g. rectangular pores have a value of 4. The geometric factor $4/d_p$ in Equation (3) arises from the fact that transport owing to diffusion through the gas phase in the pores is proportional to the cross-sectional area of the pores, therefore proportional to d_p^2 whereas transport owing to surface diffusion is proportional to the circumference of the pores, therefore proportional to d_p. The molar flux of component i through the gas phase in the pores of the membrane is described by Fick's law using the Bosanquet formula for the combination of Knudsen and continuum diffusion by the principle of resistances in series.

It is demonstrated experimentally that during the 1st dip repair surface diffusion of CO_2 in an alumina membrane impregnated with γ-Al_2O_3, can contribute substantially to the transport rate. Moreover, for this system it is of almost the same order of magnitude as the transport caused by ordinary diffusion through the gas phase in the pores. Subsequent dipping result in continuum diffusion and the molar flux is therefore independent of pressure. Surface diffusion however is linearly proportional to the pressure provided the fraction of the adsorption sites covered is very low. It is demonstrated that the resulting difference in pressure dependence of both transport mechanisms can be used to distinguish between diffusion through the gas phase in the pores and surface diffusion.
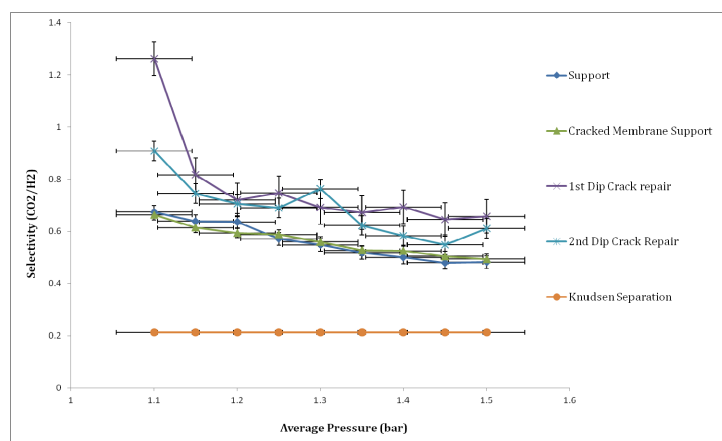
Figure 9. Selectivity of CO_2/H_2 against average pressure at room temperature

4. Conclusions

A simple but effective technique to modify nanostructure ceramic membranes which involves dip-coating method was studied and involved the use of boehmite solution to modify the membrane. Several parameters such as dipping time, number of coating, heating rate on the nanostructure were investigated. A high temperature heat-treatment was applied in order to repair defects on the commercial membranes, and to improve the permselectivity of these membranes above Knudsen regime selectivity. Single gas permeation tests were used to examine the permeance of the membrane. After the first and second modifications with boehmite solution, permeance decreased significantly which indicates the presence of Knudsen diffusion mechanism.

The silica membrane is thought to exhibit higher CO_2 permeance from flue gas N_2 by maintaining a pressure drop across the membrane due to surface diffusion mechanism. In general, inorganic membranes would exhibits an improved performance on carbon dioxide separation from flue gases.

Acknowledgements

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