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High Molecular Permeance Dual-Layer Ceramic Membrane for Capturing CO_2 from Flue Gas Stream

Ngozi C. Nwogu, Mohammed N. Kajama, Ifeyinwa Orakwe, Edward Gobina[*]

Centre for Process Integration and Membrane Technology, (CPIMT), School of Engineering, The Robert Gordon University, Aberdeen, United Kingdom
Email: [*]e.gobina@rgu.ac.uk

Abstract

With the objective to create technologically advanced materials to be scientifically applicable, dual-layer silica alumina membranes were molecularly fabricated by continuous surface coating silica layers containing hybrid material onto a ceramic porous substrate for flue gas separation applications. The dual-layer silica alumina membrane was prepared by dip coating technique before further drying in an oven at elevated temperature. The effects of substrate physical appearance, coating quantity, cross-linking agent, number of coatings and testing conditions on gas separation performance of the membrane have been investigated. Scanning electron microscope was used to investigate the development of coating thickness. The membrane shows impressive perm selectivity especially for CO_2 and N_2 binary mixture representing a stimulated flue gas stream.

1. Introduction

Constrained by the increasing reliance on fossil fuels, the rising utilization of coal-burning power plants discharges huge amounts of carbon dioxide and other greenhouse gases into the atmosphere resulting in global warming, a worldwide environmental concern. Flue gas from fossil fuel power plants has been identified as the main contributor to carbon dioxide emission. The major human related sources of CO_2 are burning of fossil fuels and cement manufacture. Some uses of fossil fuel are in the generation of energy, transportation and heating

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[*]Corresponding author.

system. The bulk of greenhouse gases in the atmosphere can be curtailed by regulating the rate at which gases are being emitted [1]. In addition, development of advanced techniques to mitigate these emissions has been suggested by some researchers [2]-[4]. A number of methods have been acknowledged to separate the CO_2 from flue gas mixture. This includes absorption, adsorption, cryogenic distillation and membrane technology. Absorption of carbon dioxide via amine based solvent remains the leading process, particularly in large scale processes. However, membrane is a developing technology and holds great potentials for bulk gas separation [2] [5]. CO_2 separation by absorption using monoethanolamine (MEA) solvent is well known to be too costly. In addition, cryogenic separation of CO_2 is energy intensive due to reheating and cooling [6]. Membrane separation of CO_2 from flue gas however offers excellent separation due to its inherent features which are favourable in gas separation [1]. In order to contend with other technologies, a membrane with good power-driven strengths and gas separation performance is necessary. Excessive interest in membrane-based gas separations, refining and catalytic application has been investigated [7]-[10]. Most of the separation applications have focused on the Knudsen region, however, it is necessary to improve the pore structure due to the low gas selectivity in the Knudsen region. In this study, the design of single and binary gas selectivity and permeability characteristics of a multi-layer silica alumina ceramic membrane were investigated as a novel separation tool for a stimulated flue gas stream at room temperature [11].

2. Basic Gas Separation Theory

In IUPAC commendations and categorizations, gas transport and pore diameter of porous ceramic membranes are closely interrelated [11]. Notably, micro-porous membranes have pore diameter less than 2 nm. As a result, molecular sieving effect is highly predominant. Mesopore with pore diameter between 2 nm and 50 nm are governed by Knudsen/multilayer diffusion. Macropores have large pores greater than 50nm and viscous flow, in this case results in no separation. Furthermore, Capillary condensation and surface multi-layer diffusion mechanisms are well known for high selectivity characteristics in mixed gas separations at relatively low temperature especially where the smaller pore or mesopores are designed.

Knudsen separation factor α for two single gases carbon dioxide and nitrogen can be calculated using Equation (1).

$$\alpha_{CO_2, N_2} = \sqrt{\frac{M_{N_2}}{M_{CO_2}}} \tag{1}$$

where M_{CO_2} and M_{N_2} are the molecular weights of CO_2 and N_2 respectively.

Knudsen separation factor α for binary gases CO_2, N_2 can be calculated using Equation (2) [1].

$$\alpha_{CO_2, N_2} = \frac{\left(C_{CO_2} / C_{N_2}\right)_{permeate}}{\left(C_{CO_2} / C_{N_2}\right)_{feed}} \tag{2}$$

where C_{CO_2} and C_{N_2} are the percentage concentrations of CO_2 and N_2.

The separation system is however established on the different permeability of the different chemical gaseous compounds through the membrane and is achieved by the application at varying pressures.

3. Experimental

The objective of this experiment is to develop a high molecular dual-layer silica alumina membrane through a dip coating, thereby determining the intrinsic selectivity of the 6000 nm ceramic support selected for the fabrication purpose. This will further demonstrate the ability of the membrane to separate CO_2 from flue gas mixtures. The expectation is that the modification will favour CO_2 even though it has a higher molecular weight than N_2. A fresh support is shown in **Figure 1** which is then immersed in the silica solution as shown in **Figure 2**. The membrane substrate is immersed in the silica solution repeatedly and the gas transport measured after each dip.

Figure 3 depicts a picture of the gas transport test permeation system. The multi-layer silica ceramic membrane was held in a stainless steel reactor. At each end, graphite seals were held tight on the tube side. The gases used were carbon dioxide and nitrogen (with a purity of at least 99.9%) and a mixture of 14% carbon dioxide with the balance of nitrogen, all delivered by BOC (UK).
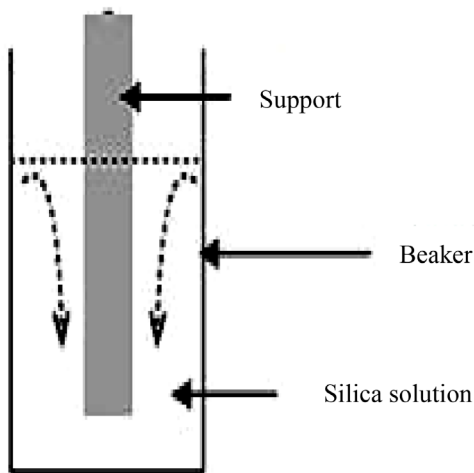
Figure 1. Fresh support.

Figure 2. Sequential dip-coating of the membrane support gas transport test.
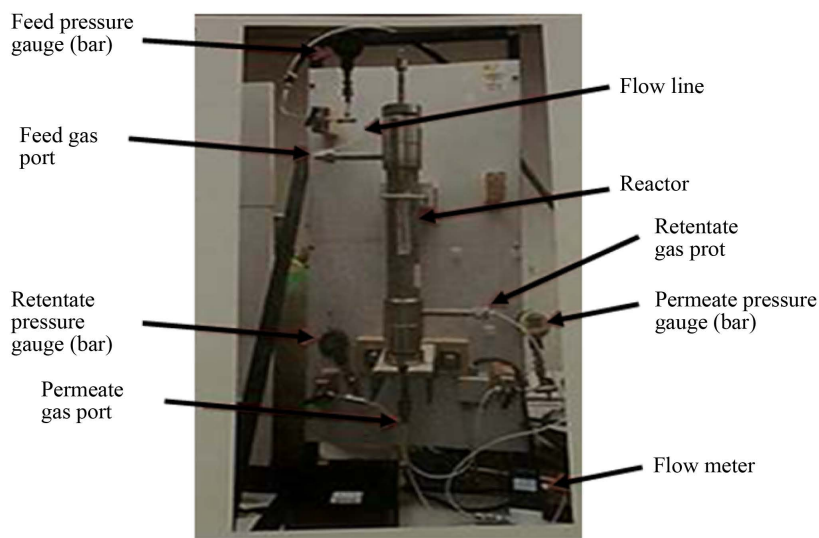

Figure 3. Apparatus set up.

Membrane Characterization

The morphology of the membrane before and after coating was studied with the scanning electron microscopy (SEM) measurement as shown in **Figure 4** and **Figure 5**. The adsorption and desorption isotherms of N_2 at 77 K were measured using a Gas Sorption Analyser. Before measurements, the membranes were crushed into fine particles and degassed at a high temperature of about 300˚C. Brunauer-Emmet-Teller, the pore volumes were measured at a relative pressure of $P/P_0 = 1$, assuming all accessible pores to be filled with condensed nitrogen.
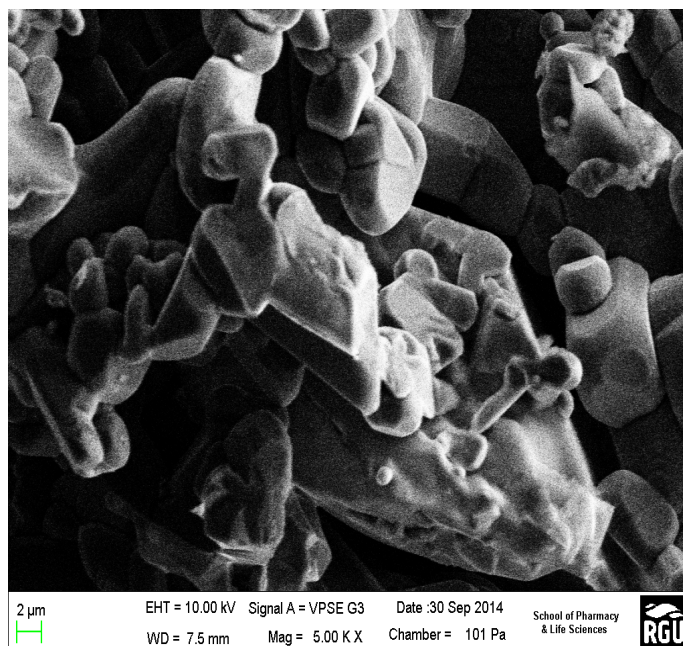
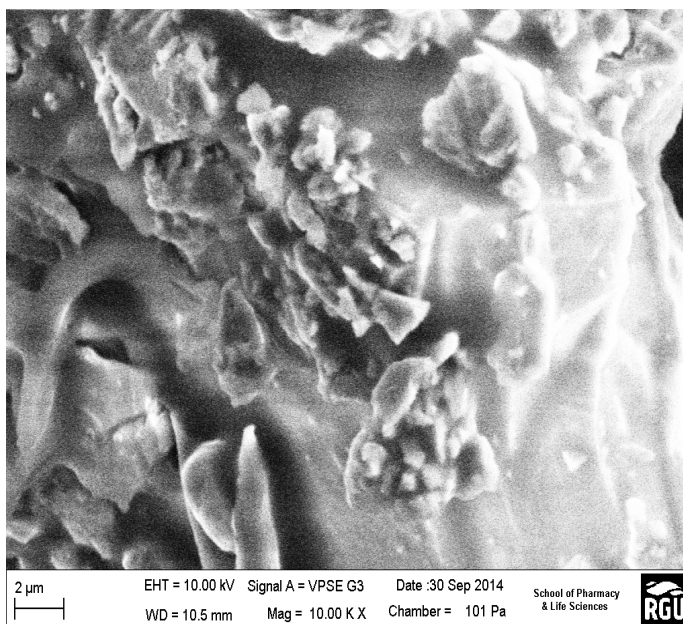**Figure 4.** SEM Image of support before modification.

Figure 5. SEM Image of the dual-layer membrane.

The surface areas were also obtained accordingly. A pictorial view of the Gas Sorption Analyser used is shown in **Figure 6**.

4. Results and Discussion

An analysis of the adsorption and desorption curves for membrane pore size distribution were estimated using the method given by Barrett *et al.* [12] and shows the nitrogen adsorption isotherms in **Figure 7**, **Table 1**, **Figure 8** and **Table 2** respectively. The isotherms measured for the membranes are classified as Type IV isotherms according to the IUPAC classification [12] [13].
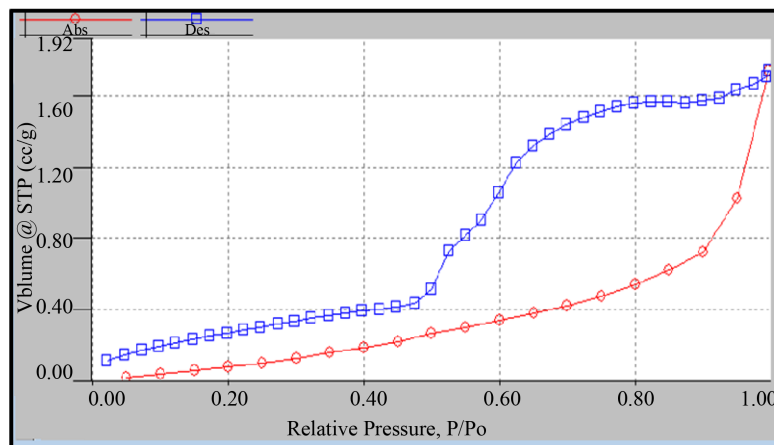
Figure 6. Gas sorption analyser.

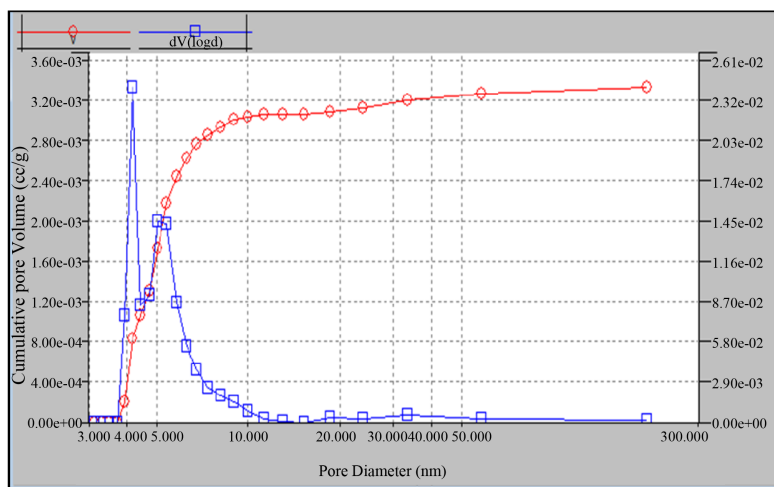**Figure 7.** Graph of linear isotherm of gas adsorption and desorption for multi-layer membrane.

Figure 8. BJH method of desorption summary for pore diameter determination of the multi-layer membrane.

A plot of CO_2 and N_2 single gases permeance across the dual-layer silica ceramic membrane as function of gauge pressure is shown in **Figure 9**. As can be observed, the gas permeance increased with pressure. CO_2 permeance was higher than that of nitrogen. **Figure 10** depicts single gas permselectivity compared to ideal Knudsen. Here, the experimental separation factor was higher than that of the ideal Knudsen, an indication of a very promising result which can be applied at industrial scale. Further investigations on binary gases were made as shown in **Figure 11**. Results obtained also gave good CO_2 recovery. An overall comparison of single and binary gases as demonstrated in **Figure 12** and confirms a membrane giving a higher CO_2 selectivity for binary mixture in comparison to single gases.

Table 1. BET summary.

Slope	782.459
Intercept	2.477e+03
Correlation coefficient, r	1.000000
C constant	1.316
Surface Area	1.068 m^2/g

Table 2. BJH summary.

Surface Area	0.167 m^2/g
Pore volume	0.033 cc/g
Pore diameter Dv (d)	3.136 nm
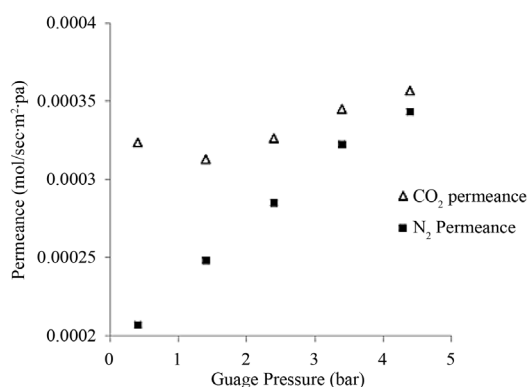
Figure 9. Single gas permeance measurement as a function of gauge pressure dual-layer membrane at room temperature.
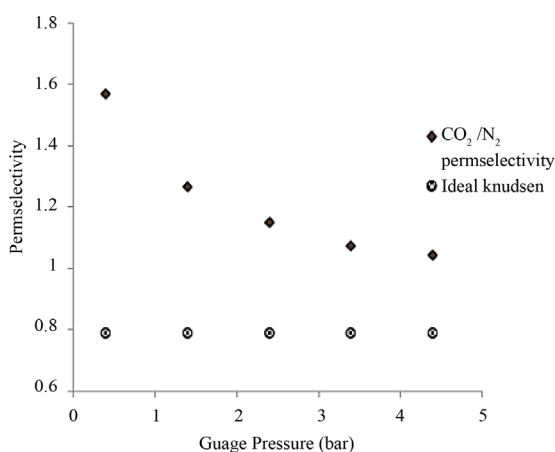
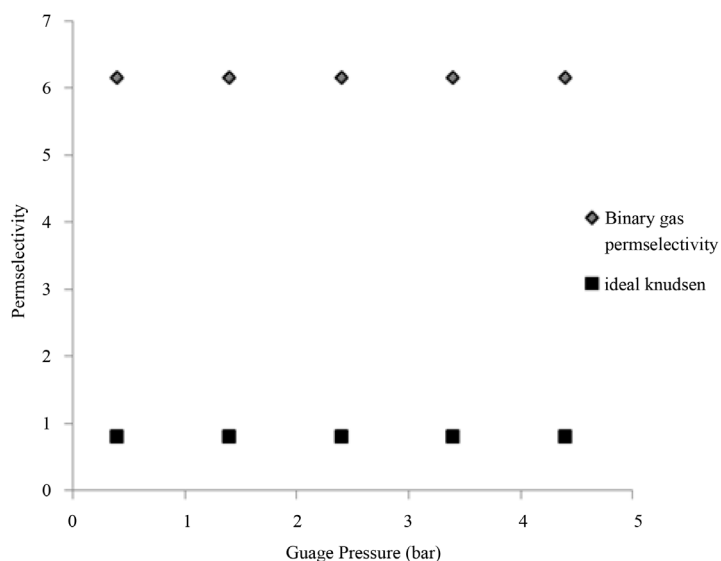**Figure 10.** Single gas perm selectivity and Ideal Knudsen relationship.

Figure 11. Binary gas perm selectivity and Ideal Knudsen relationship.
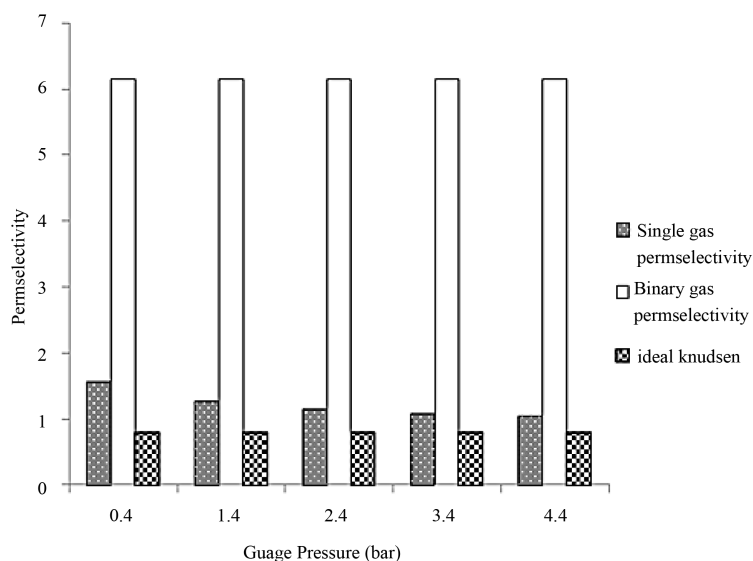

Figure 12. Combined perm selectivity measurement for both single gases and binary mixture.

In general, for both scenarios, a surface multi-layer diffusion mechanism known for high selectivity characteristics in single and mixed gas separations at relatively low temperature but high pressure occurs especially with smaller pores. A similar result obtained by some researcher [14] [15] and their result are in good agreement with the present study.

5. Conclusion

A dual-layer silica membrane was fabricated on macro porous alumina supports using a dip-coating technique. Single and mixed-gas permeation experiments indicate that the permeation characteristics of the fabricated membrane are governed by surface multilayer diffusion with small influence of Knudsen flow mechanism. The higher permeation rates for CO_2 compared to N_2 designate a mesoporous silica layer with an interconnected pore network. This conclusion is supported further by nitrogen adsorption measurements. SEM images of the dip-coated membrane indicate that the layer is approximately 2 μm thick and much more uniformly deposited di-

rectly on the surface of the alumina support. The dip-coated membranes prepared in this study favoured CO_2 gas in binary gas mixture and most importantly for flue gas separation application

Acknowledgements

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