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Multi-layer silica ceramic membrane for flue gas and natural gas separations

N. C Nwogu, I.R Orakwe and E. Gobina

***Abstract*— The overall goal of this paper is to foster the development of new membrane technologies to improve manufacturing efficiency and reduce CO_2 emissions. Hence, a multi-layered silica ceramic membrane with extremely low defect concentrations has been prepared through three successive dip-coating steps using a silica solution. An asymmetric structure is obtained by the deposition of silica layer on top of a combination titanium and α-Al_2O_3 support. The morphology of the three step homogenous silica layer is analysed by scanning electron microscope. The transport property of the membranes was carried out at room temperature and at pressure differences ranging from 1 to 2 bar. The fabricated membrane has reproducible high permeance for CO_2. Interestingly, an almost equal flow rate was observed for CH_4 and N_2 at a pressure of 2 bar. Separation factors obtained from CO_2/CH_4 and CO_2/N_2 are comparatively higher than Knudsen separation values.**

Key words— Carbon dioxide, flue gas, natural gas, silica membrane & separation factor

I. INTRODUCTION

SEPARATION processes involving CO_2 are currently well-recognized especially with the growing concern about global warming placing greater demands on improving energy efficiency and reducing CO_2 emissions. Hence, energy sustainable CO_2 separation technologies with value-added economics are needed for industrial processing and for future to recover CO_2 from natural gas, fossil-fuel combustion, energy generation through power supply and effluents from industrial processes. Accordingly, some literature have reported that membrane-based separations are excellent substitute to traditional methods due to their energy efficacy and durability therefore offering excellent separation with inherent features which are favourable in gas separation [1] [2]. Their usefulness and application as stated are in natural gas purification, separations involving flue gases and volatile organic compounds and hydrogen separation from industrial feed stock [2] [3] [4].

Some methods already exist for separating CO_2 from flue gas mixture namely cryogenic distillation, absorption and adsorption. In particular absorption of carbon dioxide through amine based solvent remains the leading process in large scale industrial processes but well known to be costly. The cryogenic separation of CO_2 is energy intensive due to heating and refrigerating [5]. Nevertheless, membrane has become an emerging technology and holds great potentials for bulk gas separations [6]. Generally, alumina supports are macroporous in nature with large pore sizes greater than 50nm and provides mechanical strength to the overlying asymmetric layers. Several techniques have been developed to process these supports. They include sol–gel synthesis, leaching [7] [8] [9] and chemical vapour deposition [10]. Amongst all, sol–gel processing attracts most attention due to its excellent processing steps, simplicity and its potential for pore size and pore structure control [11]. Several approaches have been suggested by Brinker et al [11] for the fundamental physical and chemical phenomena involved in the deposition of colloidal ceramic dispersions (sols) on porous supports for precise pore size and porosity control. Moreover, by choosing and manipulating the textural properties of the porous support, it is conceivable to control the size and shape of the resulting multi-layered structure to improve the flow rate and the separation factor of permeating gas molecule.

In the present study, the problem of CO_2 separation from nitrogen and methane have been addressed through the design of a novel multi-layer silica alumina ceramic membrane separation tool to improve the ideal separation factor and diffusion characteristics at room temperature and relatively low pressure.

II. EXPERIMENTAL PROCEDURE

A. Solution preparation

A silica sol is prepared by carefully adding a curing agent to a corresponding amount of the mixture of iso-pentane and silicone elastomer. After the addition is completed, the reaction mixture is kept under room temperature with constant stirring for homogeneity purposes. The reaction mixture had a Iso-pentane/silicone elastomer/ curing agent ratio of 900/100/10 (mls) in agreement with the customary formula of silica sol preparation [12][13].

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B. Multi-layer silica ceramic membrane fabrication

The tubular shaped commercial support used was supplied by Ceramiques Techniques et Industrielles (CTI SA) France and comprises of (77% α-alumina + 23% TiO2) with an average pore diameter of 6000 nm. The support has 20 mm and 25 mm internal and outer diameter respectively and a permeable length of 319 mm. The multi-layer silica ceramic membranes are prepared by dip coating the alumina support in the silica-based solution followed by spin-drying and heating. A complete dipping process involves repeated dipping to mend any cracking which may have occurred during support manufacture and most importantly to reduce the pore size of the porous alumina to achieve desired results. After 30mins three step successive dipping, the membrane was spin-dried at room temperature for another one hour before final heating in an oven for 3hours at 65^0C [12][13]. The coating through the deposition of the solution on the surface of the alumina led to the formation of a multi-layered silica membrane.

The immersion of the support in the silica solution is shown in fig. 1. The support substrate is immersed in the silica solution repeatedly and the gas transport measured after each dip.

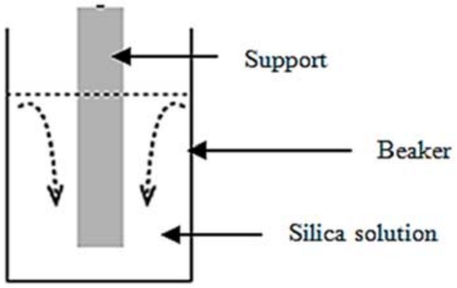

Fig 1: Successive dip-coating of the membrane support

C. Membrane characterization

The scanning electron microscope (Zeiss EVO LS10) was employed in determining the morphology of the membrane. The SEM recordings were made on the membrane toplayer section by cutting the membrane in smaller specimens.

D. Gas permeation test

Gas transport tests through the multi-layered silica membrane were carried using the permeation system and the apparatus set-up as depicted in fig. 2. The tubular-shaped membranes were placed in stainless-steel permeance cells. At each end, graphite rings were used to hold the membrane and create a seal. The pressure difference across the membrane was measured by pressure gauges. Single gases namely; CO_2, CH_4 and N_2 (with a purity of at least 99.9%) were used for testing, all delivered by BOC (UK). The pressure at the feed side was varied between 1 to 2 bar. The flow rates of all inlet and outlet streams were directly measured by digital flow meters.

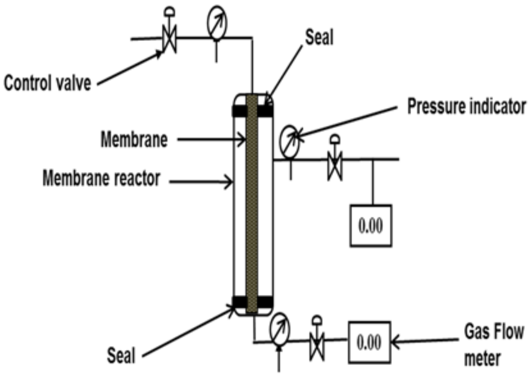

Fig 2: A simplified concept of membrane separation process.

Thus, for a single membrane tube, the ideal separation factor *α,* for pure-gas permeation can be defined by the ratio of permeances of individual pure gases. Whereas the Knudsen separation factor can be obtained using the equation below:

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

Where α is the separation factor, M_{CO2} is the molecular weight of the CO_2 and $M_{ti,}$ the molecular weight of either nitrogen or methane gas component.

III. RESULT AND DISCUSSION

A. Morphological characterization of silica membrane

The scanning electron micrographs obtained is presented in Figs 3 – 6. The three step dip-coating reveals an incremental deposition of a thin silica layer obtained after 3 times dipping. The image results indicate that the silica coating is deposited on top of the alumina support layer as a distinct layer. The colour difference between each dipping is also very distinct. The second and third dip has a lighter appearance than the first as a result of the silica. The support and the first dip are also coarse in nature while the second and third dip appears smoother in nature.

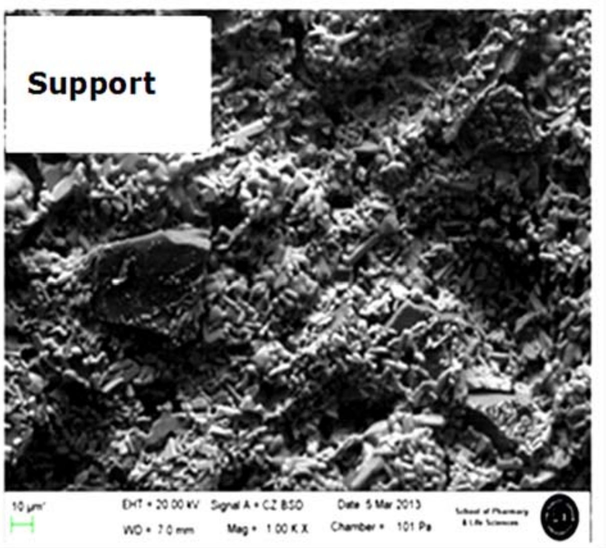

Fig 3: SEM image of the support

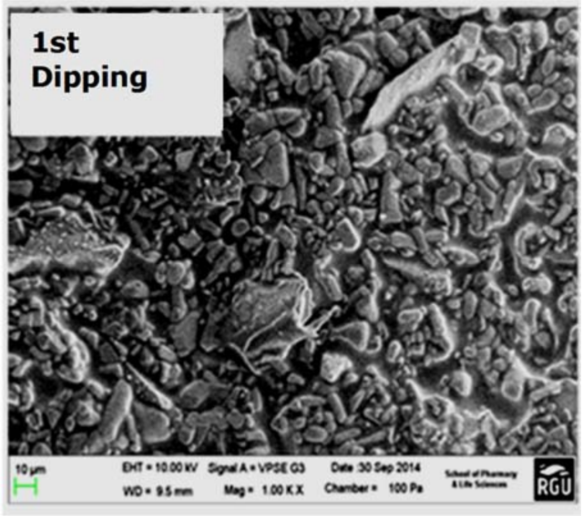

Fig 4: SEM image of 1st dip coating

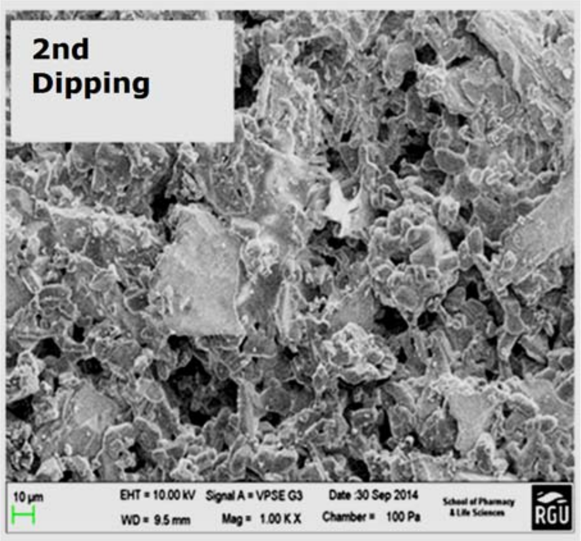

Fig 5: SEM image of 2nd dip coating

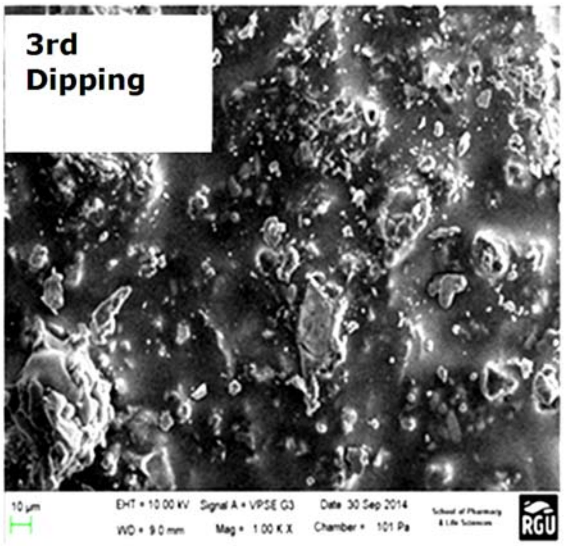

Fig 6: SEM image of 3rd dip coating

B. Gas permeation

A plot of CO_2, N_2 and CH_4 single gas flow rate under room temperature operating conditions using the support and multi-layer silica ceramic membrane as a function of feed gauge pressure is shown in Fig. 7 and Fig. 8 respectively. For the support, an exponential increase in gas flow rates can be observed with increase in feed pressure. CH_4 recorded the highest permeate flow rate followed by N_2 and then CO_2. This characteristic is typical of Knudsen mechanism since it appears to be molecular weight dependent. However for gas diffusion through the multi-layered silica membrane, we observed a clear difference in the flow rate trend. CO_2 permeated faster than CH_4 and N_2. CH_4 maintained an almost constant flow rate. Interestingly, a drastic increase in flow was observed for N_2 leading to a nearly equal flow rate to that of CH_4 at a pressure of about 2bar. A possible adsorptive type transport mechanism can be suggested on the part of CO_2. Generally, it is a well-established fact that at a relatively low temperature (room temperature), silica materials are flexible with respect to CO_2 adsorption, in which case its separation from gases like N_2 and CH_4 which are less absorbable gases can preferentially result to excellent CO_2 recovery [2] [14]. The transport mechanism for N_2 and CH_4 could be suggested to be partially Knudsen but with further increase in pressure, molecular- sieving mechanism can come into play since N_2 molecule size is smaller (3.64 Å), than that of CH_4 (3.8 Å).

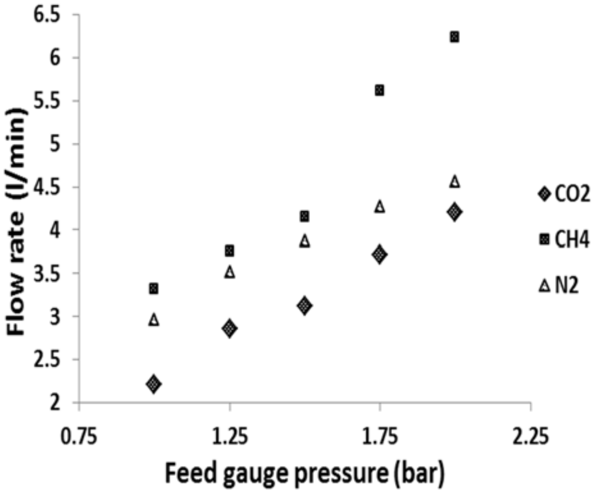

Fig 7: Single gas flow rate measurement as a function of gauge pressure across the support at room temperature

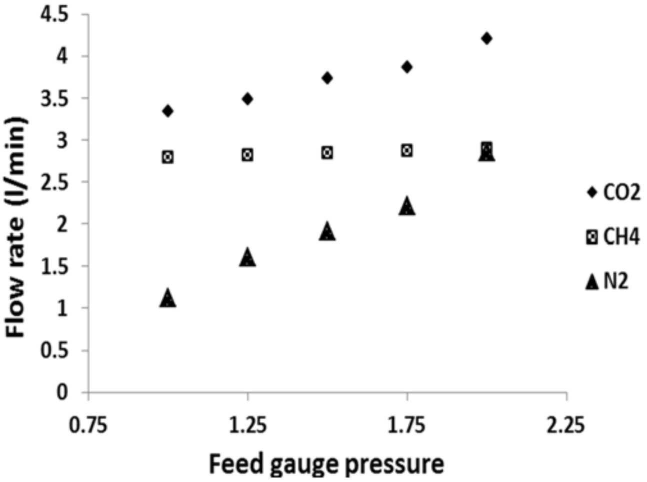

Fig 8: Single gas flow rate measurement as a function of gauge pressure across multi-layer membrane at room temperature

The ideal separation factor of the various gas pairs (CO_2/CH_4 and CO_2/N_2) for the support and the multi layer membrane were obtained for the purpose of comparison and to determine how much of CO_2 can be separated from the other gases (either N_2 or CO_2). Results obtained show a very clear distinction for both scenarios. A minimal separation was witnessed in the support whereas, a higher separation factor value was obtained for the multi-layered membrane which exceeded the Knudsen separation factor as show in Fig 9 and Fig.10. In addition the separation factor for CO_2/N_2 (2.98) was higher than that of CO_2/CH_4 (1.19) in comparison to their Knudsen values as 0.79 and 0.6 respectively. This is presented in Fig.11. Therefore, the experimental separation factor was higher than that of the ideal Knudsen, an indication of a very encouraging result which can be functionally applicable at industrial scale.

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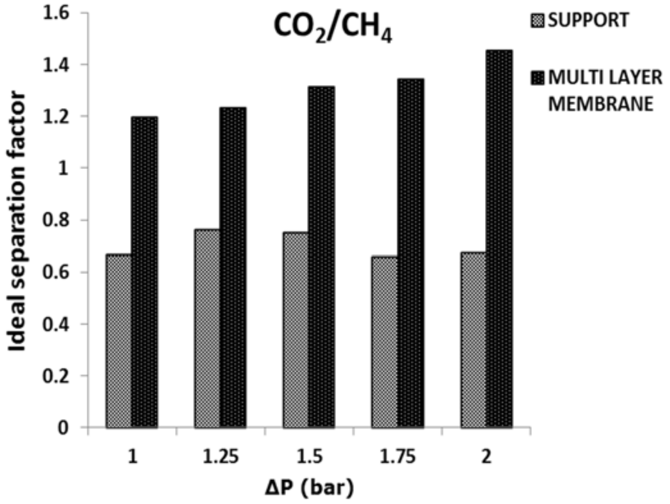

Fig 10: CO_2/CH_4 Ideal separation factor as a function of difference in pressure for both support and multi-layer membrane

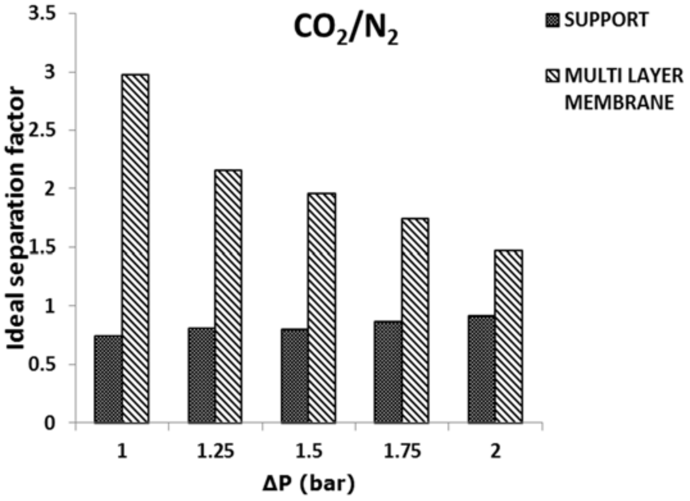

Fig 10: CO_2/CH_4 Ideal separation factor as a function of difference in pressure for both support and multi-layer membrane

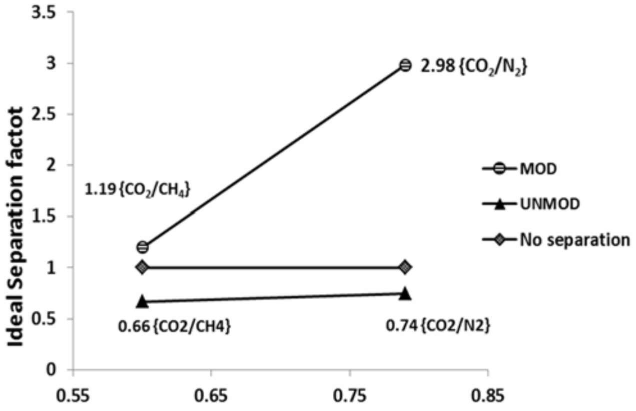

Fig 11: Relationship between ideal separation factor and Knudsen for support (unmod) and multi-layer silica membrane (mod)

IV. CONCLUSION

A multi-layered silica ceramic membrane have been designed to enhance separation, permeation and reproducibility characteristics through a dip coating process by the deposition of a silica-based solution on the surface of a porous alumina support under a neat and dust-free environment at a temperature of 65^0c for 3hrs. This was done to help reduce the large pores of the support. The membrane designed improved gas diffusion and the separation factor especially for CO_2. The membrane favoured CO_2 with very high flow rate 4.2 l/min compared to 2.89 and 2.86 (l/min) for CH_4 and N_2 respectively. In additional, the membrane selectively separated CO_2 from N_2 and CH_4 having a separation factor of 1.19 and 2.98 higher that Knudsen separation of 0.79 and 0.6 respectively and therefore can find great application in flue gas/natural gas purification and separation processes for reduction of anthropogenic CO_2 as a known greenhouse gas. Additionally, the combined approaches are proved to be effective for achieving molecular sieving in inorganic silica membranes

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