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Gas Permeation Behavior of Single and Mixed Gas Components Using an Asymmetric Ceramic Membrane

Ngozi Nwogu, Edward Gobina

Abstract—A dip-coating process has been used to form an asymmetric silica membrane with improved membrane performance and reproducibility. First, we deposited repeatedly silica on top of a commercial alumina membrane support to improve its structural make up. The membrane is further processed under clean room conditions to avoid dust impurity and subsequent drying in an oven for high thermal, chemical and physical stability. The resulting asymmetric membrane exhibits a gradual change in the membrane layer thickness. Compared to the support, the dual-layer process improves the gas flow rates. For the scientific applications for natural gas purification, CO₂, CH₄ and H₂ gas flow rates were. In addition, the membrane selectively separated hydrogen.

Keywords—Gas permeation, Silica membrane, separation factor, membrane layer thickness.

I. INTRODUCTION

GROWING interest in inorganic membranes have become overwhelming due to its application at various industrial and operational process levels [1]. This applies in gas separation, treatment of waste water, purification and ultra-filtration processes. Inorganic membranes can be classified as porous or non-porous. While non-porous inorganic membrane is made up by dense metals and oxides resulting in very good selectivity and minimal permeance, porous inorganic membranes have lower selectivity and high permeance with pore sizes of up to 10nm [2]. Of importance are membranes with asymmetric structure consisting of a large pore support and a separation layer made of a different material, for instance silica, zirconia and gamma-alumina that controls the rate at which gases permeate through the membrane network [3]. According to [4], a high permeability is attained with an asymmetric design consisting of a thick macroporous support structure and a thin membrane. In their study, De Vos and Verweij used successive dipping to combine a sol-gel derived microporous silica membrane placed on the surface of gamma-alumina support [5]. The outcome of this process was the fabrication of a crack-free membrane. Standards for selecting membrane materials for a given separation are

intricate. Usually, robustness, mechanical integrity at the operational conditions, output and effectiveness in separation are important stipulations. Among these, selectivity and permeation rate are of great importance. High selectivity and permeability provides the opportunity to accomplish the desired separations in collaboration with the partial pressure producing the driving force with the membrane surface area for effective results [6], [7]. McCool et al. [1] developed cubic-shaped mesoporous membranes by hydrothermal synthesis and dip-coating on the surface and/or within the pores of alumina support disks. Gas permeation through both types of membranes were compared by the authors and in their findings established that, while Knudsen permeation dominated both membranes, the permeation through the hydrothermally prepared membranes was lower as a result of a higher membrane thickness, accordingly this was due to fractional pore blockage leading to high resistance for gas transport. In a previous work carried out in our laboratory [8] we reported on the preparation and characterization of silica modified membrane on tubular supports, which were considered as more adequate for industrial processes on account of their ease of scale-up. It was shown that these membranes were able to separate with good selectivity. The dip coating technique performed also had a significant effect toward achieving defect free membrane.

The objective of this paper is to establish techniques of dip-coating to fabricate thin defect-free asymmetric silica membrane layers and to compare and contrast permeation behaviour of H₂, CH₄ and CO₂ single gases and CO₂/N₂, CO₂/CH₄ mixed gases of known compositions. We also intend to show that highly porous micro meter layers of measurement can be successfully deposited on macroporous alumina supports.

II. BASIC CONCEPTS

Under IUPAC recommendations and classifications, gas transport and pore diameter of porous ceramic membranes are closely interconnected [9]. Notably, micro-porous membranes have pore diameter less than 2 nm. As a result, molecular sieving effect is highly predominant. Meso pore with pore diameter between 2 nm and 50 nm are governed by Knudsen/multilayer diffusion while macropores have large pores greater than 50nm. Viscous flow, in this case chances are that no separation will occur. Additionally, Capillary condensation and surface multi-layer diffusion mechanisms are well known for high selectivity characteristics in mixed

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gas separations at relatively low temperature especially where the smaller pore or mesopores are designed.

Knudsen separation factor α_{XY} for two gases can be calculated using (1):

$$\alpha_{x/y} = \sqrt{\frac{M_y}{M_x}} \quad (1)$$

where M_Y and M_X are the molecular weights of the two gases X and Y . Consequently, Knudsen number Kn can be expressed as the ratio of the mean-free path (λ) to the membrane pore radius (r), mathematically represented thus:

$$Kn = \frac{\lambda}{r} \quad (2)$$

Knudsen number is convenient in the determination and possible estimation of whether Knudsen diffusion is dominant in a permeation experiment.

III. EXPERIMENTAL

The objective of this experiment is to carry out a dip coating techniques on an alumina support using a silica based solution as the coating. In so doing the intrinsic selectivity of the 6000nm ceramic support selected will be determined. This will further demonstrate the ability of the membrane to separate CO_2 from natural gas mixtures. The expectation is that the modification will favour CO_2 even though it has a higher molecular weight when compared to the other gases (CH_4 and H_2).

The dip coating procedure is displayed in Fig. 1. As can be observed, the membrane substrate is immersed in the silica solution for the coating to take place on the support surface. To achieve this, the top and bottom of the tube inner bore was blocked off to avoid deposition of the solution on the inside surface.

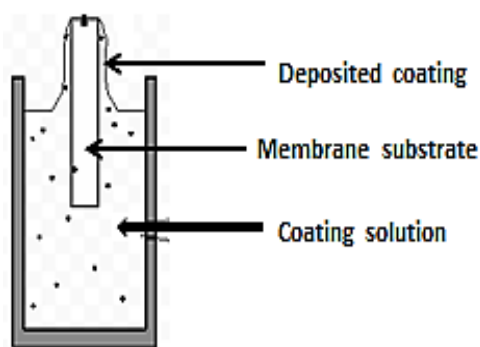


Fig. 1 Successive dip-coating of the membrane support

IV. GAS TRANSPORT TEST

Fig. 2 depicts a schematic diagram of the gas transport test system. The asymmetric membrane was held in a stainless steel tubular housing. At each end, graphite seals were held tight on the tube side to ensure that good fastening is accomplished. The gases used were carbon dioxide, methane

and hydrogen (with a purity of at least 99.9%) and a mixture of 60% carbon dioxide with the balance of nitrogen –and 30% CO_2 with balance of CH_4 , all delivered by BOC (UK).

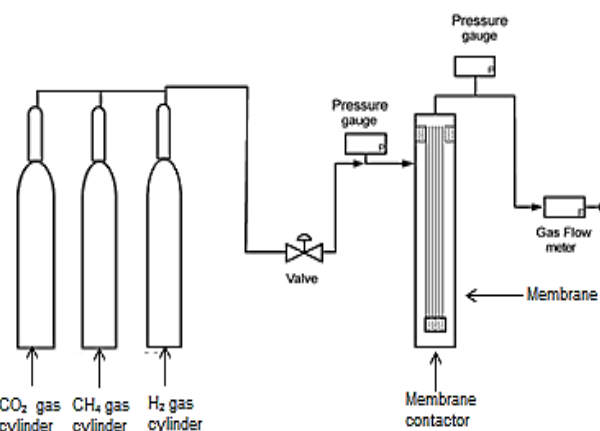


Fig. 2 Gas transport through an asymmetric ceramic membrane at room temperature

V. MEMBRANE CHARACTERIZATION

The morphology of the membrane before and after coating was studied with the scanning electron microscopy measurement (model). The adsorption and desorption isotherms of N_2 at 77K were measured using a Gas Sorption Analyser (model). 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. The surface areas were also obtained accordingly. An analysis of the adsorption and desorption curves for membrane pore size distribution were estimated using the method given by [10]. This is shown in Fig. 9 and Table III respectively.

VI. RESULT AND DISCUSSIONS

Fig. 7 shows the obtained nitrogen adsorption isotherms. The surface areas are given in Tables I and II. The isotherms measured for the membranes classified as Type IV isotherms according to the IUPAC classification [10], [11]. A plot of H_2 , CO_2 , and CH_4 single gas flow across the support in relation to the feed pressure is shown in Fig. 3. As can be seen, H_2 flow rate in comparison to CO_2 and CH_4 was very high by more than 5times whereas CO_2 has the least permeation. It can be suggested that CO_2 selectivity was not favored for the 6000nm alumina support used. Hence, a dip-coating alteration of the support was carried out in an effort to boost CO_2 transport and enhance CO_2 selectivity of the membrane.

Fig. 4 shows gas transport through the modified support, it is seen that, the permeation rate for the pure gases follows $H_2 > CO_2 > CH_4$. This implies that there is a remarkable effect that has caused an increase in the selectivity of CO_2 to be higher than that of CH_4 . Although H_2 maintained high flow rate, overall, it can be recommended that the membrane be applied in CO_2 separation from even lighter gases, like CH_4 .

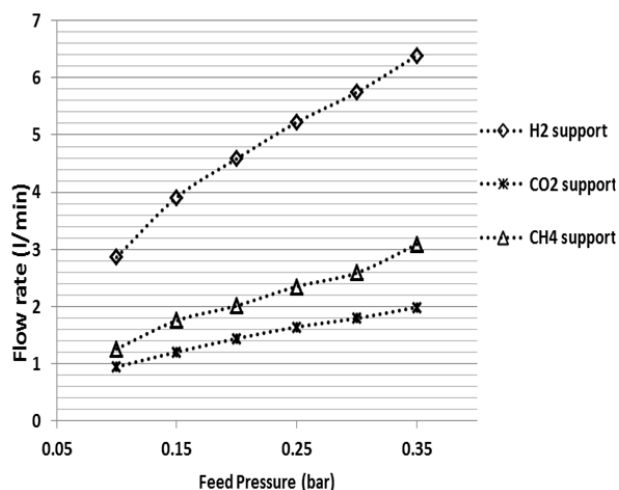


Fig. 3 Single gas flow rate measurement as a function of feed pressure for the membrane support at room temperature

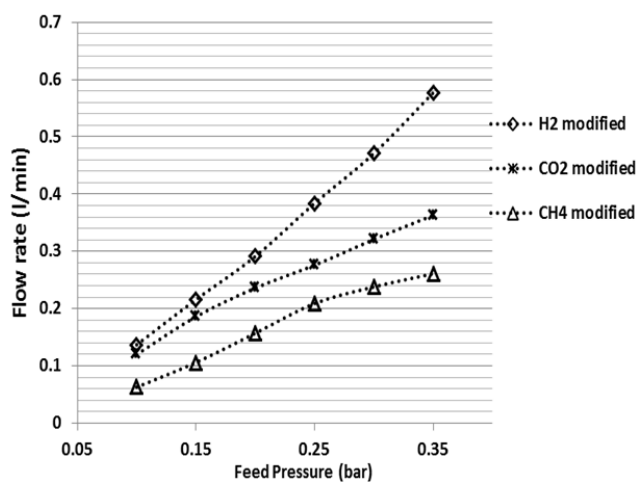


Fig. 4 Single gas flow rate measurement as a function of feed pressure for modified support at room temperature

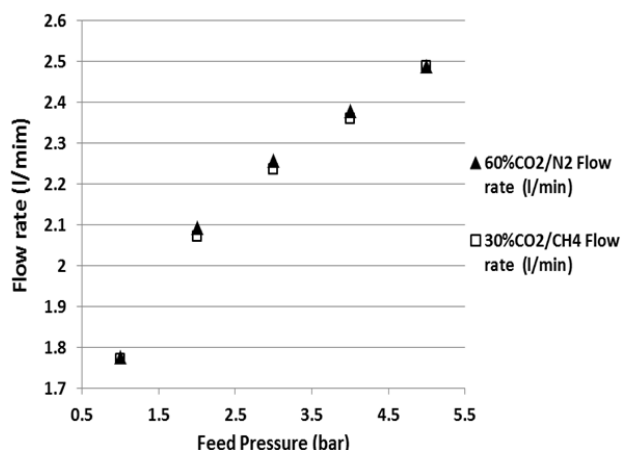


Fig. 5 Mixed gas flow rate measurement as a function of feed pressure for modified support at room temperature

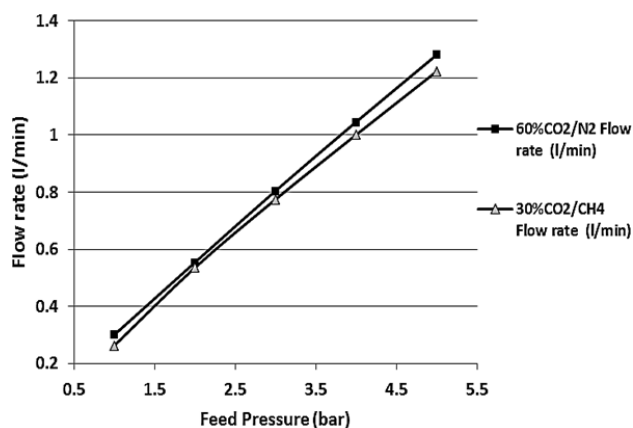


Fig. 6 Single gas flow rate measurement as a function of feed pressure for modified support at room temperature

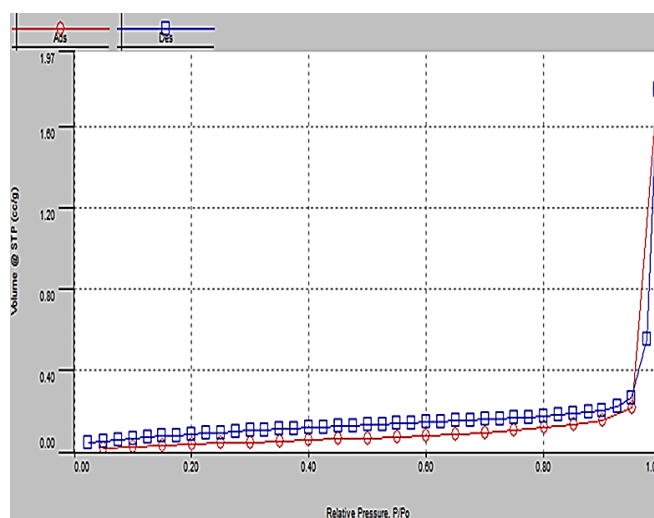


Fig. 7 Linear Isotherm of Gas Adsorption and Desorption Membrane support

TABLE I
 BET SUMMARY FOR THE MEMBRANE SUPPORT

Slope	Intercept	Correlation Coefficient, r	C, constant	Surface Area (m ² /g)
20185.340	1.433e+03	1.00000	15.082	0.161

For mixed gas transport (Figs. 5 and 6) the permeation rate of 60%CO₂ mixture with balance nitrogen had almost the same flow rate with that of 30% CO₂ mixture balance methane before modification. But after the modification, the flow rate of the mixture with a higher CO₂ composition at a relatively higher pressure of 4.5bar was only thermally higher than that of 30%CO₂ balance nitrogen. This shows that an increase in pressure does not have any effect on the permeation of CO₂ in a mixed gas stream.

In general, for both scenarios, it can be seen that viscous flow mechanism was prevalent in the membrane support while surface multi-layer diffusion mechanisms known for high selectivity characteristics in single and mixed gas separations at relatively low temperature but high pressure occurs especially with smaller pore or mesopores. A similar work

was carried out by [12]-[14] and their result are in good agreement with the present study.

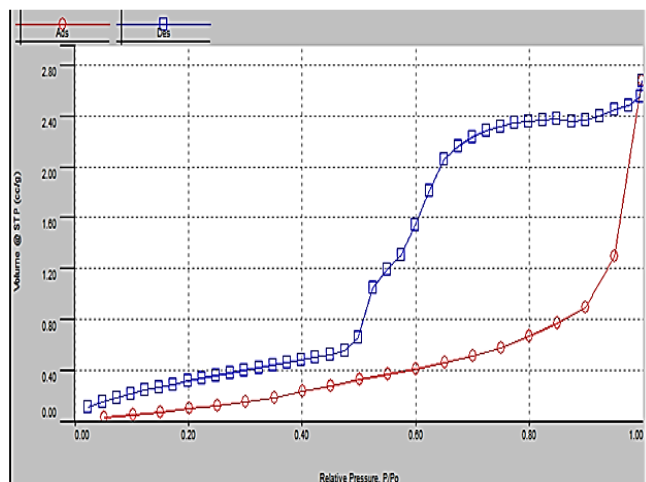


Fig. 8 Linear Isotherm of Gas Adsorption and Desorption for modified support

TABLE II
BET SUMMARY FOR THE MODIFIED SUPPORT

Slope	Intercept	Correlation Coefficient, r	C, constant	Surface Area (m ² /g)
1631.907	1.807e+03	1.00000	1.903	1.013

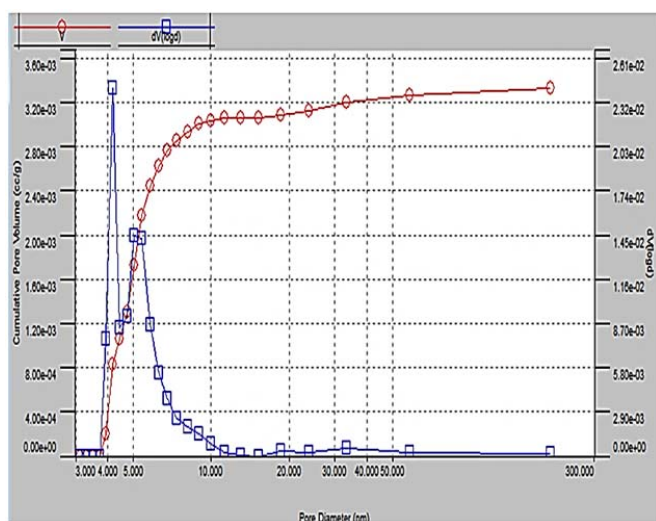


Fig. 9 BJH Method of Desorption Summary for Pore Diameter determination of the asymmetric membrane

TABLE III
BJH DESORPTION SUMMARY

Surface Area (m ² /g)	Pore Volume	Pore Diameter Dv(d) (nm)
2.434	0.003cc/g	4.182

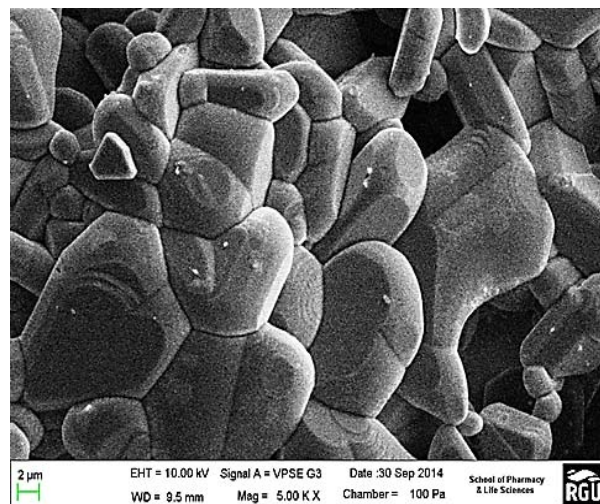


Fig. 10 SEM Image of the asymmetric membrane before modification

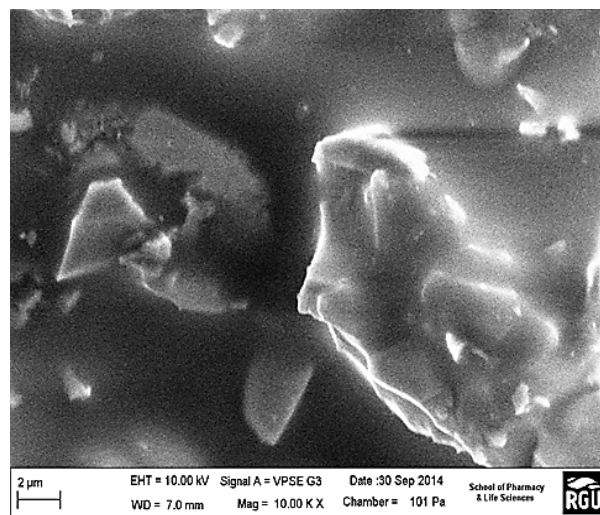


Fig. 11 SEM Image of the asymmetric membrane before modification

VII. CONCLUSION

A silica membrane was fabricated on macroporous α -alumina supports using a dip coating technique. The single and multi-gas permeation experiments indicate that the permeation characteristics of the support and membrane are governed by viscous flow diffusional mechanisms and surface multilayer with slight contribution from Knudsen flow mechanism. The higher permeation rates for CO₂ compared to CH₄ indicate a mesoporous silica layer with an interconnected pore network. This conclusion is supported further by nitrogen physisorption measurements. CO₂ adsorption had an important influence on the transport and indicates that the membrane layers possess high surface areas in the mesoporous regime. SEM images of the dip-coated membrane indicate that the layer is approximately 2 μ m thick and much more uniformly deposited directly on the surface of the alumina support. The dip-coated membranes prepared in this study favoured CO₂ gas although as suggested, it can be utilized in hydrogen gas separation and purification purposes.

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