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Synthesis of Gas Transport through Nano Composite Ceramic Membrane for Esterification and Volatile Organic Compound Separations

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Abstract: The transport behaviour of carrier gases with inorganic catalytic ceramic membrane used for ethyl lactate production and VOC (volatile organic compound) recovery in the gauge pressure range of 0.10-1.00 bar and temperature range of 333 K was investigated. The gases include Ar (argon), N₂ (nitrogen) and CO₂ (carbon dioxide). The gas kinetic diameter with respect to permeance was found to occur in the order of Ar > CO₂ > N₂, which was not in agreement with molecular sieving mechanism of transport after the first dip-coating of the support. However, gas flow rate was found to increase with gauge pressure in the order of Ar > CO₂ > N₂, indicating Knudsen mechanism of transport. The porous ceramic support showed a higher flux indicating Knudsen transport. The surface image of the dip-coated porous ceramic membrane was characterised using SEM (scanning electron microscopy) to determine the surface morphology of the porous support at 333 K.

Key words: Inorganic ceramic membrane, permeance, gas flow rate and kinetic diameter.

1. Introduction

VOCs (volatile organic compounds) are a large group of organic compounds that have high vapour pressure which means they can easily evaporate into the atmosphere. Light hydrocarbons such as methane, ethane, propane and butane are considered as a part of this group [1].

In this context, VOC refers to the mixture of hydrocarbon gasses ranging from methane to butane. The main component is methane which is considered a greenhouse gas with a GWP (global warming potential) of 21, while CO₂ has GWP of 1; hence the effect of 1 unit of methane emitted is equivalent to the effect of 21 units of CO₂ emitted. The other components of VOC which mainly consists of propane and butane are commonly referred to NMVOC (non-methane volatile

organic compound) and they react chemically with nitrous oxides that result in the formation of ground level ozone [2], which has detrimental effects to the environment and to human health as well. Emission of VOC to the atmosphere from shuttle tankers worldwide has not been systematically measured and observed. The emission has great impacts on the environment as well as on causing great monetary loss.

There are various measures in place for the control of VOCs emitted from shuttle tankers. However, the main problem in the recovery of VOCs from tankers is that the evaporated hydrocarbons are diluted in vast amounts of inert gasses when the gas mixture is displaced by the inflow of oil during loading of the cargo tanks [3]. Storage, production and transportation of crude oil and gasoline results in the emission of VOC, mainly from the loading and offloading operations [1].

The global increase in the development of remote oil

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fields has increased the need for the use of shuttle tankers as a means for transporting crude oil as well as motivated research into the use of membrane technology as a viable option for the recovery of hydrocarbons from crude oil during shuttle tanker loading and offloading operations. In the last few years, the potentialities of membrane operations had been widely recognized. In some preliminary investigations, polymeric membranes such as silicone rubber have been used [4]. The membranes that are more permeable to lighter hydrocarbons are the polyacetylene polymers, the micro porous absorbent carbon and the silicon rubber [4]. Though they have high selectivity, they cannot withstand harsh chemical environments as well as high temperatures, while ceramic membranes have adequate thermal and chemical durability [2].

The factors considered for the selection of membranes for a given application are strongly related to several factors like the separation efficiency, productivity, durability and mechanical integrity [5]. Different aspects need to be investigated in-depth in order to maintain good separation process including [6]:

- structure and material of the membrane;
- membrane transport properties which include permeability, permeance and selectivity;
- module and process design.

Gas separation membranes are used for numerous applications. Table 1 shows the various applications of membranes.

Membranes used for gas separations can be generally classified into organic polymeric membranes and inorganic membranes. The organic polymeric membranes that are used for gas separations are hollow asymmetric and nonporous. An important feature in the preparation of polymer membrane for gas separations is the process of spinning them into hollow fiber membranes, which due to its large area is suitable for large scale industrial applications [8]. The major drawback for the use of these polymeric membranes is that they can not stand high temperatures and harsh chemical conditions. In petrochemical plants, natural gas treatment of plants and refineries, feed gas streams of heavy hydrocarbons can be a problem as the polymer membranes can be plasticised or become swollen [9]. The development of inorganic membranes is riveting as they can stand high temperatures and harsh chemical conditions. The major drawback for these membranes is their high cost, brittleness, low membrane area and low permeability in the case of highly selective dense membranes [9]. Inorganic membranes based on alumina, zeolites, carbon and silica have been used for the capture of CO₂ at elevated temperatures [10]. For the separation of hydrocarbons, zeolite membranes have shown interesting separation characteristics, although their separation efficiency is depended on the operating conditions like temperature, composition and total pressure [11]. In a membrane separation unit, the temperature and pressure are

Table 1 Applications of gas separation membranes (adapted from Abedini and Nezhadmoghadam) [7].

No.	Common gas separation	Applications
1	O ₂ /N ₂	Oxygen enrichment and inert gas generation
2	H ₂ /Hydrocarbons	Refinery hydrogen recovery
3	H ₂ /N ₂	Ammonia purge gas
4	H ₂ /CO	Syngas ratio adjustment
5	CO ₂ /Hydrocarbons	Acid gas treatment and landfill gas upgrading
6	H ₂ O/Hydrocarbons	Sour gas treatment
7	He/Hydrocarbons	Helium separation
	He/N ₂	Helium recovery
	Hydrocarbons/Air	Pollution control and recovery of hydrocarbons
	H ₂ O/Air	Air humidification

usually kept constant; hence a study of the separation features of the membrane is needed to get the optimal separation conditions [9].

For cylindrical membranes, the gas flow in membranes governed by Knudsen flow is given in Eq. (1):

$$j = \frac{4r_p \varepsilon}{3} \cdot \sqrt{\frac{p_o - p_l}{lRT} \left(\frac{2RT}{\pi M} \right)} \quad (1)$$

where, ε is the porosity of the membrane, M is the molecular mass of the gas, j is the flux, r_p is the pore radius and l is the pore length and p_o and p_l are the absolute pressures of the gas specie at the beginning of the pore and at length l .

The above equation is for single gas permeation. In the case of gas mixtures, there are other factors that have to be considered when determining the separation of the gases. The gases in the mixture will have different molecular masses as well as move at different speeds. For separation by Knudsen diffusion for a binary mixture of gases having molecular masses M_1 and M_2 , the ratio of their flux J_1 and J_2 is given in Eq. (2) [12]:

$$\frac{J_1}{J_2} = \sqrt{\frac{M_2}{M_1}} \quad (2)$$

To predict the selectivity of a gas over another gas in the case of binary mixtures of gases, the Knudsen selectivity is calculated as:

$$\alpha_{k,1,2} = \frac{1}{\sqrt{\frac{M_1}{M_2}}} \quad (3)$$

For membrane separations, this indicates a limitation of Knudsen flow mechanism [13]. For most separations of CO_2 and H_2 , the ratio of their flux is in the range of only 4.69, which means that in practice separation must be in multiple stages [12].

Ceramic membranes can also be incorporated into chemical reactors and thus serve as a catalyst by shifting the reaction equilibrium to the product [13]. The interest in lactate esters is increasing because of its importance as eco-friendly solvents obtained from biomass. Lactate esters such as ethyl lactate are low in toxicity with excellent solvent properties which can

replace numerous halogenated chemicals such as carcinogenic methylene chloride, toxic ethylene glycol ethers, chloroform and ozone-depleting such as CFCs (chlorofluorocarbons). Ethyl lactates solvent can dissolve a lot of petrochemical solvents [14]. The different application of ethyl lactate solvent obtained from biomass of lactic acid and ethanol is shown in Fig. 1 [15].

As a solvent, ethyl lactate can be employed in the removal of silicon oil, greases and adhesives in cleaning several metals surfaces for coating and fabrication applications. However, this solvent can also be found in soy products, wine and beer, and had been recommended for use in the food industries for many years [14]. Although ethyl lactate has shown a lot of advantages, the production volume of this solvent in the industry have also decreased. New technology has emerged in order to improve ethyl lactate separation through the esterification of lactic acid and ethanol using pervaporation membrane process and reactive distillation [14]. The worldwide demand of ethyl lactates solvent is estimated roughly to be 1,300,000 to 150,000 tons per annum. However, the global consumption of this solvent is expected to increase rapidly in the nearest future [16]. Lactic acid esterification reaction is a reversible reaction in nature hence; the conversion of lactic acid is limited by equilibrium [17]. In order to obtain high yields of the ester, different methods have been introduced

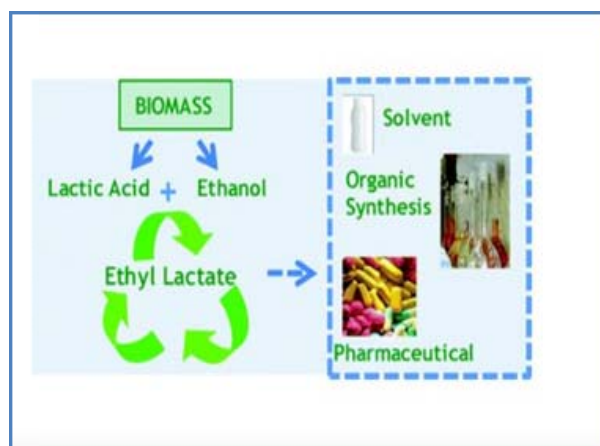


Fig. 1 Different application of ethyl lactate [16].

including the addition of alcohol to the reaction and increasing the temperature. Also, employing a ceramic membrane as catalyst can help to shift the equilibrium to the more product side by selective removal of water. Compared to other membranes, ceramic membrane can withstand the effect of thermal, mechanical and chemical stability. The ceramic membranes are recently used to possess an asymmetric structure which consists of a support layer such as α -alumina and zirconia with fine pores which controls the permeation flux [18]. This membrane can be categorised into different types depending on the pore size including microporous with the pore size \square 2nm, mesoporous 2-50nm, macroporous \square 50nm and dense ceramic membrane [19]. Materials including SiO_2 , Al_2O_3 , ZrO_2 and TiO_2 are the most frequently used materials for ceramic membrane. Basically, the macroporous layer provides the mechanical support, while the mesoporous layer which is the middle layer links the pore size differences between macroporous (support layer) and the microporous (top layer) where the actual separation occurs [20]. Inorganic membrane can be prepared using different separation methods including sol-gel, sintering, chemical deposition and dip-coating methods [21]. The dip-coating has been widely employed to fabricate ceramic membrane with macroporous to microporous level based on the porous support and is also a convenient membrane preparation technology. Generally, the conventional dip-coating process involves two major steps: support dipping and support withdrawal [22]. The suitability of a ceramic membrane depends on the membrane selectivity and permeability [23]. However, gas transport through porous ceramic membrane can be explained using different mechanism of transport including surface diffusion, viscous flow, molecular sieving and Knudsen diffusion [24]. Viscous flow occurs if the pore radius of the membrane is larger than the mean free path of the permeating gas molecule, in this case, more collision will take place between the pore wall of the membrane than that between the permeating gas

molecule. Knudsen diffusion is likely to be mechanism controlling the rate of transport if the mean free path of the permeating gas molecule is greater than the pore size of the membrane [25]. Molecular sieve occurs when the diameter of the gas molecule is roughly the same as the pores of the membrane. Surface diffusion mechanism enables permeation rate relative to Knudsen diffusion in such a way that the gas is strongly adsorbed on the pores of the membrane [25].

2. Experiment

The carrier gas permeation test through a porous inorganic ceramic membrane was carried out using four different gases namely He (helium), N_2 (nitrogen), Ar (argon) and CO_2 (carbon dioxide). The membrane pore size was 15 nm, the length of the membrane was 36.6 cm, while the inner and outer radii of the membrane were 7 mm and 10 mm, respectively. The gas flow rate was determined using the digital flow meter (L/min). The gas pressure was measured between pressure range of 0.10-1.00 bar and temperature range of 333-433 K. Fig. 2 shows the schematic diagram of the gas permeation temperature setup. The gases were purchased from BOC, Aberdeen, UK. The commercial porous ceramic membrane was supplied by CTI, France.

The membrane preparation was carried out by dipping as shown in Fig. 3. A certain amount of isopentane was measured into a 1,000 mL glass cylinder and a known amount of silicon elastomer was added to the solution together with a known amount of sylgard. The mixture was allowed to stir for 30 min. After 30 min, the support was immersed into the solution and allowed in the solution. After 30 min, the support was taken out from the bulk of solution (sol-solution) and air dried for 30 min. The support was transferred to the oven and allowed in the oven for 2 h at a programmed temperature of 65 °C before the analysis with the different gases at different temperatures [26]. Fig. 3 shows the schematic setup of the membrane dip-coating process. The membrane was

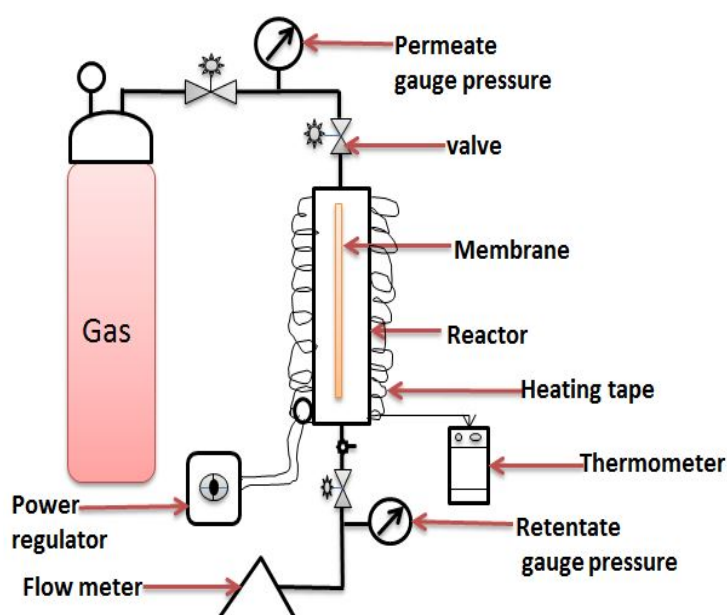


Fig. 2 Gas permeation temperature setup.

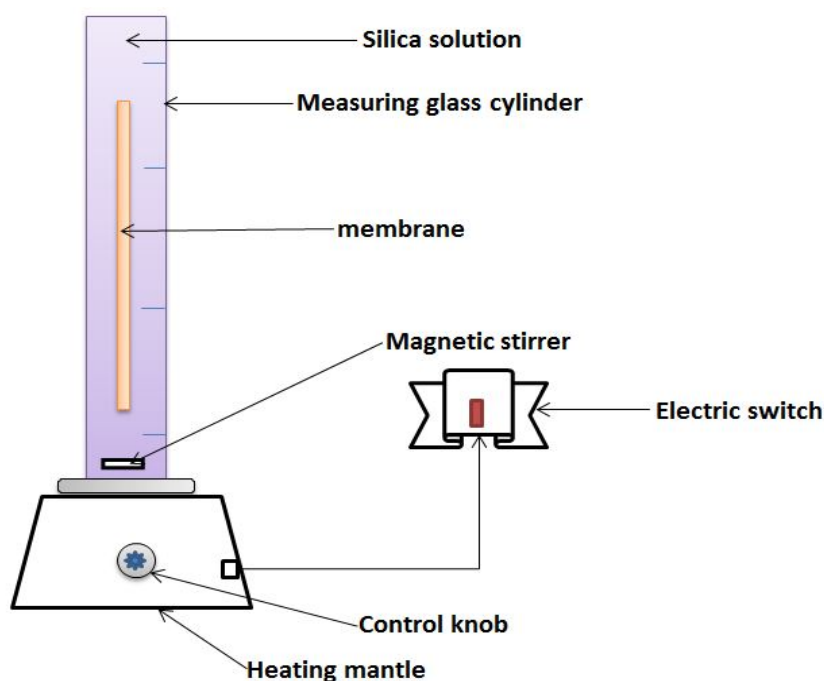


Fig. 3 Schematic setup for membrane preparation process.

coated once to determine the effect of the membrane coating with temperature. The membrane preparation process was carried out in a clean room environment to obtain a defect-free ceramic support.

The support was weighed before and after modification to determine the amount of deposited

membrane. The membrane thickness was then calculated using Eq. (4).

$$L = \frac{W_2 - W_1}{A\rho(1 - \varepsilon)} \quad (4)$$

where, L = membrane thickness (m), W_2 is total weight of the support and membrane (g), W_1 is weight of the

alumina support (g), A is membrane area (m), ρ is theoretical density of alumina (kg/m^3) and ε is porosity of the membrane (%) [23]. The actual weight before and after deposition was measured to be 48.3 g and 49.0 g, respectively.

3. Results and Discussion

The gas flow rate (mol/s) was plotted against gauge pressure to determine the flow mechanism between the gases and the pore walls of the membrane. The results obtained in Fig. 4, show that the gas flow rate increase with increase in trans membrane pressure for all the gases were not in accordance with the gas molecular weight (CO_2 (44), Ar (40) and N_2 (28)). The gas flow rate was found to be in the order of $\text{Ar} > \text{CO}_2 > \text{N}_2$. CO_2 has a higher molecular in contrast to Ar and N_2 , but Ar was found to show a higher flow rate. This could have been as a result of the effect of higher temperature and pressure on the ceramic support thereby causing a higher adsorption of Ar as it interacts with the pore walls of the membrane. Although the gas flow rate was not exactly based on the order of their molecular weight, Ar and CO_2 with higher molecular weight showed a higher flow which was in good agreement with Knudsen diffusion mechanism which relates to gas molecular weight [27].

The plot of the gas flow rate (mol/s) against the inverse of the square root of the gas molecular weight (kg) was investigated at the gauge pressure of 0.10 bar and a temperature of 333 K to determine the gas transport mechanism that is operational. From Fig. 5, it can be seen that the Ar with a low molecular weight of 40 showed a higher flow rate than CO_2 with a higher molecular weight of 44. The relationship between the gas flow and the inverse of the square root of the gas molecular weight was expected to give a straight line for three gases, which could have indicated Knudsen mechanism, but the reverse was the case which shows that there could be another mechanism of transport that could be responsible for the gas flow through the pore of the ceramic support which could have resulted from

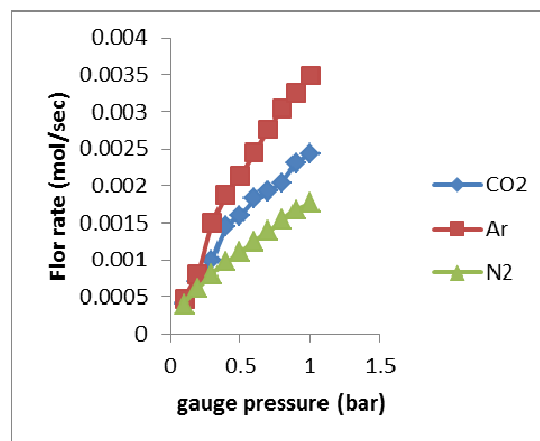


Fig. 4 Gas flow rate (mol/s) against gauge pressure (bar).

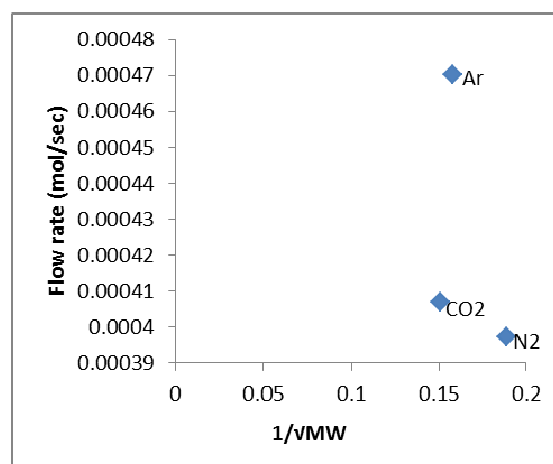


Fig. 5 Gas flow rate (mol/s) against the inverse of the square of the gas molecular weight at 0.10 bar and 333 K.

the silica solution that was used in coating the membrane surface.

The effect of permeance ($\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$) with the gas kinetic diameter (\AA) was also analysed in order to determine the effect of the pore diameter on the permeating gas molecule at the gauge pressure of 0.60 bar at 333 K. The kinetic diameter of the three gases is in the order of N_2 (3.64) $>$ Ar (3.40) $>$ CO_2 (3.30). The result obtained in Fig. 6 showed that the permeance was not in complete agreement with the order of their kinetic diameter. N_2 with the higher kinetic diameter exhibited a lower permeance compared to CO_2 with the least kinetic diameter. This indicates that gas flow through the membrane was not based on molecular sieving mechanism. In the case of molecular sieving mechanism, it was suggested that the gas permeance

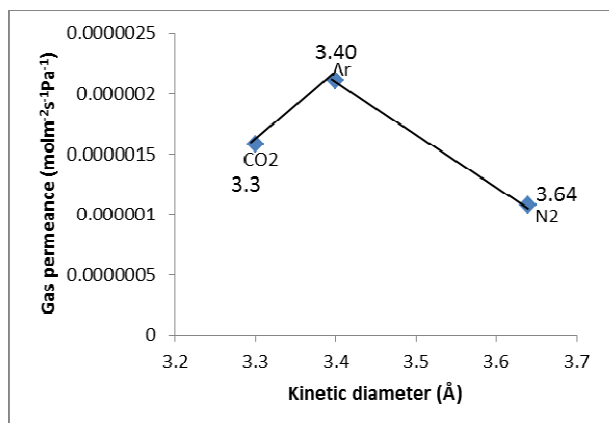


Fig. 6 Gas permeance ($\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$) against kinetic diameter (\AA) at 0.60 bar and 333 K.

could have been in the order of $\text{CO}_2 > \text{Ar} > \text{N}_2$ starting from the lowest. It was also suggested that the low permeance of CO_2 could have also be as the results of the effect of molecular size. CO_2 has a higher molecular size compared to Ar, indicating that there was no molecular sieving effect of CO_2 with the membrane, rather the mechanism of transport was suggested to be surface adsorption.

The gas flux ($\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) was further plotted at different gauge pressure (Pa) and the temperature of 333 K to analyse the effect of temperature and flow

mechanism of transport through the dip-coated membrane. According to Ref. [23], the gas flux through the inorganic ceramic membrane is usually higher with pressure. However, in mesoporous membranes, the permeation flux of the permeating gas molecule is totally dominated by Knudsen flow mechanism for gas transport at the gauge pressure below 10 bar [27]. The result obtained in Fig. 7 showed that the gas flux increases with the gauge pressure with a positive slope and regression values indicating Knudsen mechanism as the dominant transport. This

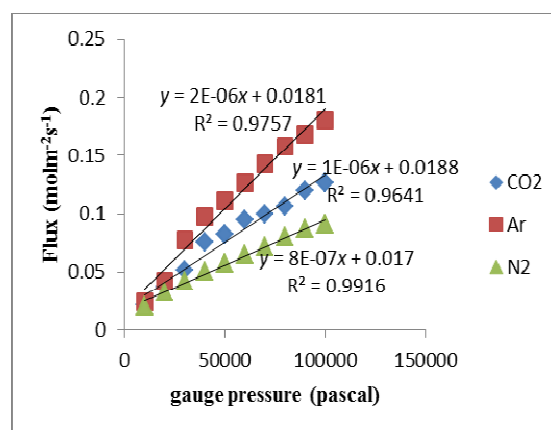


Fig. 7 Gas flux for CO_2 , Ar and N_2 at different gauge pressure (bar) and 333 K for the dip-coated support.

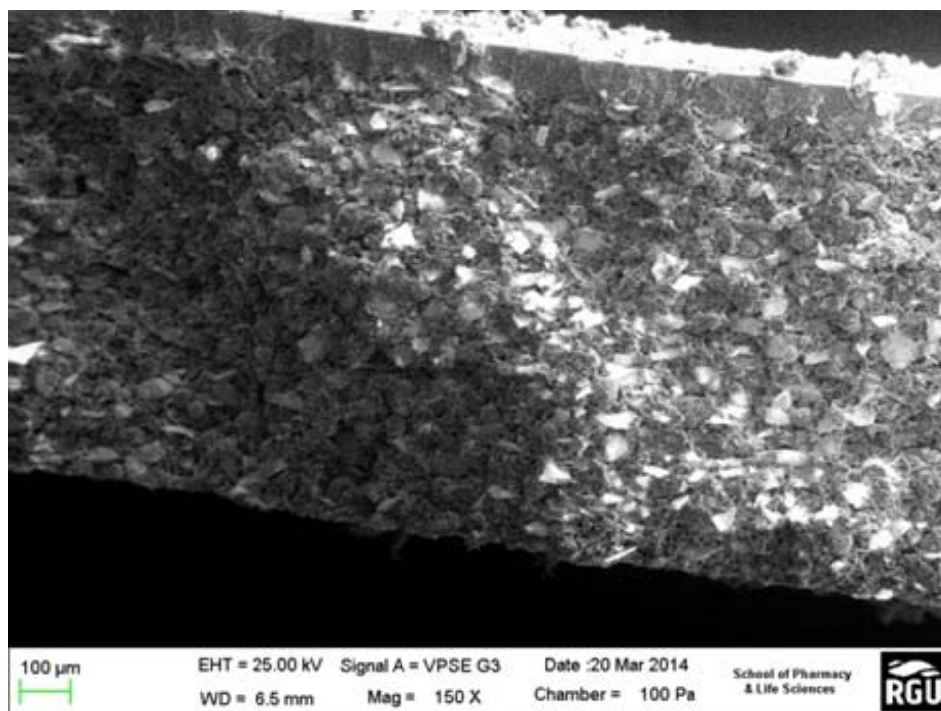


Fig. 8 SEM of the interior surface image of the dip-coated membrane.

result was in agreement with a review by Ref. [23]. The gas flux ($\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) against gauge pressure (Pa) is shown in Fig. 7.

The surface image of the porous ceramic membrane was also investigated to determine the surface morphology of the dip-coated membrane. The surface examination of the dip-coated membrane was focused at the magnification of 150 x with the scale of 100 μm . From the result obtained for the interior surface image in Fig. 8, it was observed that a shiny crystalline surface indicating the effect of the silica layer in which the membrane was coated with. Although the membrane showed a crystalline surface, there was no noticeable crack on the surface indicating that the layer was free from defect.

4. Conclusions

The carrier gas transport of ceramic membrane was achieved. Knudsen flow mechanism of transport plays a major role in the gas transport through a ceramic membrane. The membrane thickness was found to increase after the dip-coating process which was attributed to the silica solution that was used in the membrane preparation. The gas Kinetic diameter in relation to the gauge pressure did not completely support the molecular sieving mechanism of transport. The low permeance of CO_2 was attributed to the effect of its molecular size. The inverse of the square root of the gas molecular weight did not follow the trend of a straight line graph as was expected. The gas flux graph showed a good correlation value R^2 of up to 0.9916 and a large positive slope indicating dominant Knudsen flow mechanism at the temperature of 333 K. The low permeance of CO_2 indicated the effect of the gas molecular size as a result of surface adsorption mechanism. The interior surface image examination showed a whitish surface on the exterior surface which was attributed to the silica solution that was used in coating the membrane surface. There was no noticeable crack on the surface of the membrane indicating a defect-free layer supporting Knudsen diffusion as the

dominant mechanism of transport.

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