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Preparation and Characterization of Inorganic Membranes for Hydrogen Separation

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ABSTRACT

A tubular commercially available alumina support was coated using the dip coating technique. The objective is to prepare silica and Pt impregnated membranes. Scanning electron microscopy (SEM), energy diffraction X-ray analysis (EDXA), nitrogen adsorption-desorption at 77 K and gas permeation measurements were employed for membrane characterization. The permeation of H_2, He and N_2 revealed that the membranes are crack-free. H_2/N_2 selectivity for the silica membrane obtained the highest value of 2.93 at 0.9 barg and 25 ^{0}C. On the other hand, H_2/He selectivity of 1.96 at 1.6 barg and 300 ^{0}C for the Pt membrane was obtained and found to be higher than the theoretical Knudsen selectivity. While the silica membrane realised on the thin film coating to enhance the selectivity to hydrogen, the Pt impregnated membrane on the other hand enhance hydrogen transport through an activated surface diffusion in addition to Knudsen flow.

Keywords: Tubular alumina support; silica membrane; Pt membrane; hydrogen selectivity

Introduction

Hydrogen is currently mainly used in the chemical industry for the chemical production of methanol and ammonia, and for cleaner transportation fuels [1]. Hydrogen is anticipated to replace fossil fuels in the near future, and thus significantly contribute to the atmospheric air quality [1]. The increasing demand for cleaner energy has resulted in the global need to adopt the projected hydrogen economy as the key possible long-term solution to the growing energy crises [2]. In recent years, the use of conventional fossil fuel sources has increased as a transitional measure towards hydrogen economy where coal gasification is considered as dominating the process in delivering hydrogen due to its enormous reserves which is speculated to last for at least 50 decades [3].

Literature shows that hydrogen can actually be separated with inorganic membranes [4-8]. Inorganic membranes derived from silica, ceramics and metal alloys are candidates for high temperature gas separation. Palladium (Pd) [4, 9], platinum (Pt) [9] and their alloys are the ideal membranes applied for high purity hydrogen production from mixed gas streams even though these metals are expensive [4, 9, 10]. Pd-based membranes are attractive for membrane reactor applications because dense Pd is highly permeable to hydrogen and if properly configured can offer better thermal stability and selectivity than polymer and microporous membranes [9]. Transport of hydrogen through dense Pd membranes follows the solution diffusion mechanism where only hydrogen is transported resulting in high purity (99.9999%), but have been limited in commercialization due to issues which include support quality, surface poisoning due to carbon species, hydride formation, and irreversible damage caused by bulk sulfide formation [9, 11, 12].

Sol-gel method has been proposed by many researchers as the ideal technique for membrane preparation [8]. This technique has many merits for preparing pore separation layer on the support [8]. Silica membranes are among the candidates for low-cost hydrogen separation and purification [2, 3]. In fact, these membranes can accommodate the separations of hydrogen, nitrogen, carbon dioxide, helium and oxygen. The main characteristics of inorganic membranes are permeance and selectivity or separation factor [13]. Permeance is a measure of the gas flow rate per unit area per unit pressure difference. Permeance is a more practical unit than permeability because the thickness of the membrane in most cases is not known very accurately [13]. Permeance of gas is therefore defined as;

$$F = q/A\ \Delta P \qquad (1)$$

where F is the Permeance (mol/m^{-2} s^{-1} Pa^{-1}), q is the molar flow (mol/sec), A is the surface area of the membrane (m^2), ΔP is the pressure difference across the membrane (Pa).

Permeability of gas is defined as the permeance multiplied by the thickness of the membrane and is written as;

$$P_e = L \text{ x } F \qquad (2)$$

where P_e is the Permeability (mol-m/m^{-2} s^{-1} Pa^{-1}) and L the thickness of the membrane (m).

The selectivity is defined as the ratio of the pure component permeabilities (P_y and P_z) for single gases. It can be written as;

$$\alpha_{y,z} = P_y/P_z \qquad (3)$$

where P_y is the permeability of y component (mol-m/m^{-2} s^{-1} Pa^{-1}), and P_z is the permeability of z component (mol-m/m^{-2} s^{-1} Pa^{-1}).

The transport of gases through membranes behaves differently as the pore diameter is reduced. Gas transport can be affected by pressure and temperature. A change in temperature can also affect the flow regime differently even at the same pore diameter. Hence, it is critically important to be able to follow the changes in the transport mechanisms of different gases during pore diameter reduction to help determine the extent to which pores have been reduced [13].

The main gas transport mechanisms through porous membranes are influenced by viscous flow, Knudsen diffusion, surface flow and solution-diffusion. Viscous flow also known as poiseuille flow, it occurs if the mean free path (average distance travelled by a gas molecule from one collision to the other) is smaller than the pore diameter. The flow characteristics are determined primarily by collisions among the molecules and no separation is obtained between the different gaseous components. In gas membrane separation processes, viscous flow mechanism is an insignificant transport mode because it is non-selective. Transport of gases through Knudsen diffusion occurs if the mean free path is effectively larger than the pore diameter. If the collisions among the permeating molecules and the pore wall of the membrane are more frequent than intermolecular collisions, the separation is based on molecular weight difference. Therefore, Knudsen permeance states that the permeation flux is proportional to the inverse square root of the product of the molecular weights and temperature of the gases. Knudsen diffusion plays a significant role in gas transport through alumina (Al_2O_3) membrane and it normally occurs on mesoporous membrane [8]. Surface diffusion mechanism occurs if the diffusing molecules exhibit strong affinity with the pore walls of the membrane and migrates along the pore surface and desorbs on the permeate site of the membrane. In surface diffusion, the main driving force is the chemical potential. Solution-diffusion separation relies on the physical-chemical interaction of gases and the dense membrane that determine the amount of gas which accumulates in the membrane matrix [14].

The application of alumina membranes for gas separation has several merits of which they are chemically inert, high mechanical strength and are resistant to high temperature up to 2050 K [8]. A separation layer of < 4 nm pore diameter can successfully be produced with alumina membranes, and some studies disclosed that a membrane with pore diameter < 1 nm can actually be produced [8]. From an economical point of view, alumina membrane dominates with more than 50% of the global market for technical ceramic membrane [8].

The objective of this study was to employ an alumina support to prepare silica and platinum membranes in order to form a separation layer. The behaviour of permeation of pure gas H_2, He and N_2 on the tubular alumina support, silica membrane and Pt-alumina membrane was examined. Their corresponding selectivities at different pressures and temperatures were also evaluated and compared with the theoretical Knudsen selectivity.

Experimental

Support

A commercial tubular alumina support was employed in this study. The support was mesoporous (2-50nm) consisting of 7 and 10 mm internal and outer diameter respectively. The support possesses a permeable length of 348 mm and a porosity of 45%. The permeation area was 0.0062 m^2. Table 1 shows the detailed description of the membranes.

Silica Membrane

Silica membrane was prepared based on the work of [15, 16]. The dip-coating solution was prepared by mixing 50 ml of silicon elastomer and nine parts of isopentane contained in a glass tube to obtain a clear and colourless solution. A curing agent equivalent to one-tenth of the elastomer was added and the resulting solution was mixed at room temperature. The solution was then allowed to age for 30 minutes after which the ceramic support was immersed for 30 minutes. The membrane was then oven dried at 65 ^{0}C for 24 hours to form an ultra-thin layer on the support. The same procedure was repeated for subsequent coatings. Up to three dip-coated membranes were prepared and evaluated for these experiments.

Table 1: Characteristics of ceramic membranes

Membrane	Operating temperature (K)	Pore diameter (nm)	Internal diameter (mm)	Outer diameter (mm)	Porosity (%)	Length (mm)	Area (m^2)	Wall thickness (μm)
Alumina Support	298-573	4.17	7	10	45	348	0.0062	-
Silica membrane	298-573	3.94	7	10	-	348	0.0062	-
Platinum membrane	298-573	3.70	7	10	45	348	0.0062	10.97-12.55

Platinum Membrane

The Pt-impregnated membrane was prepared using the following procedure. A solution of hexachloroplatinic acid (H_2PtCl_6) was used as platinum precursor. The deposition method used was based on the evaporation-crystallisation procedure proposed by Uzio et al. [17]. The tubular alumina support was first dried at 65 ^{0}C. The tube was then dipped for 2 hours in pure water (in our case we used deionised water). Following this the tube was dipped for 10 hours in a 10g/l of H_2PtCl_6 solution. The sample was then dried at ambient temperature to favour evaporation from the inner surface and deposition on the top layer. Metallic platinum was obtained after thermal treatment of the sample under flowing H_2 at 400 ^{0}C for at least 10 min followed by N_2 flow for 10 min at 400 ^{0}C.

The experimental set-up consisted of a membrane reactor, gas delivery system for pure gases, a permeate and retentate exit, a flow meter and a K-type thermocouples fixed on the reactor (Fig. 1). However, prior to permeation experiments the reactor and all connections were tested for leaks by means of a soap solution. The permeation tests involved passing the gas into the shell-side and directed to permeate through the coated membrane surface at different pressures and temperatures. The permeate was connected to the flowmeter to measure the flow rates.

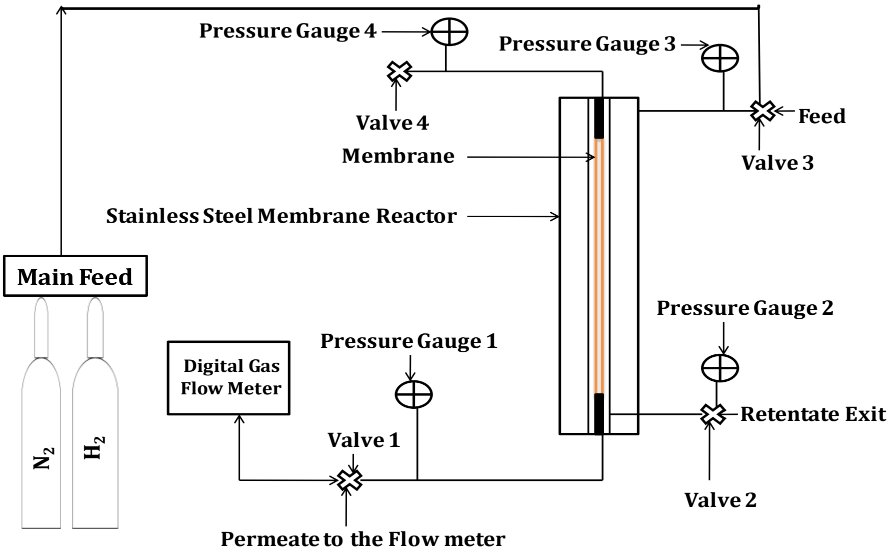

Fig. 1. Schematic diagram of the experimental setup.

Characterization

Scanning electron microscopy (SEM) micrographs and energy diffraction X-ray analysis (EDXA) were performed on a Zeiss EVO LS10 electron microscope. Nitrogen adsorption-desorption isotherms were measured using automated gas sorption analyzer (Quantachrome instrument version 3.0) at liquid nitrogen temperature (77 K). The specific surface areas were evaluated using the Brunauer-Emmett-Teller (BET) method (Quantachrome instrument version 3.0). H_2, He and N_2 with at least 99.999 (% v/v) purity was used for the permeation tests. Permeation tests were conducted at feed pressures between 0.1 up to 1.6 barg and temperature ranging from 25 to 300 ^{0}C.

Results and discussion

Membrane characterization

The SEM images and EDXA of the outer surfaces of the alumina support, silica and Pt membranes are presented in Figs. 2, 3 and 4. As can be seen, a thin membrane was formed on the outer surface of the support after silica modification [Fig. 3]. Both silica and Pt layers on the support are clearly visible [Figs. 3 and 4]. From these images, we can observe a good bonding of the layers on the alumina support. Also, the membranes were crack-free as confirmed by gas permeation tests. From the EDXA point of view, the silica and Pt membranes obtained 32.21 and 3.52 wt. % respectively. The Pt membrane thickness ranged from 10.97 to 12.55 μm (Fig. 5).

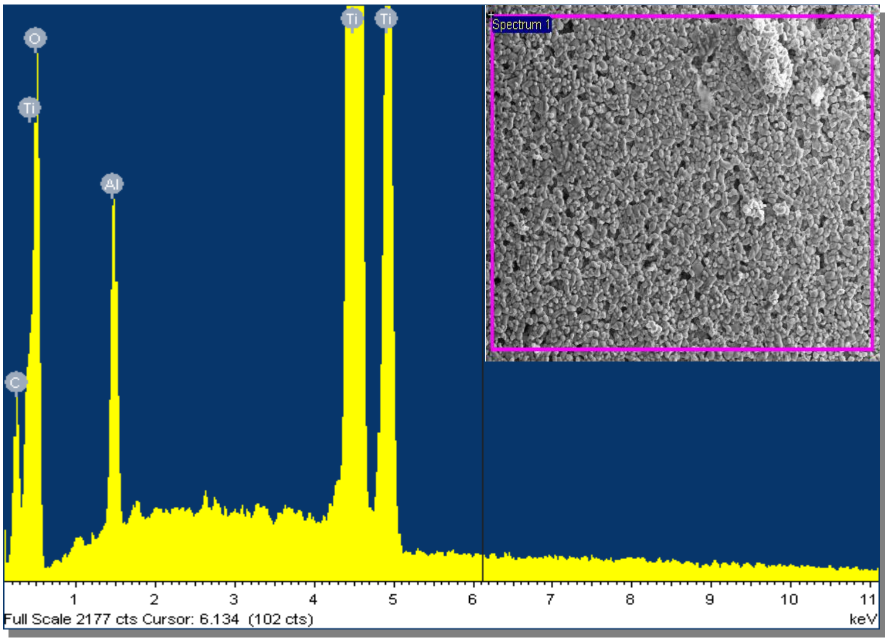

Fig. 2. SEM-EDXA image of the alumina support outer surface.

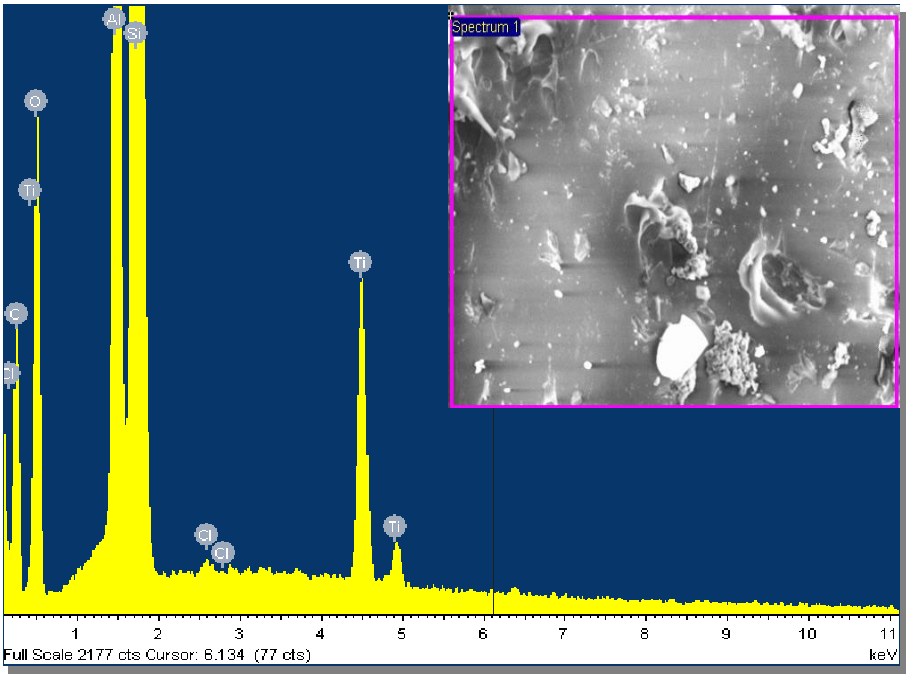

Fig. 3. SEM-EDXA image of the silica membrane outer surface.

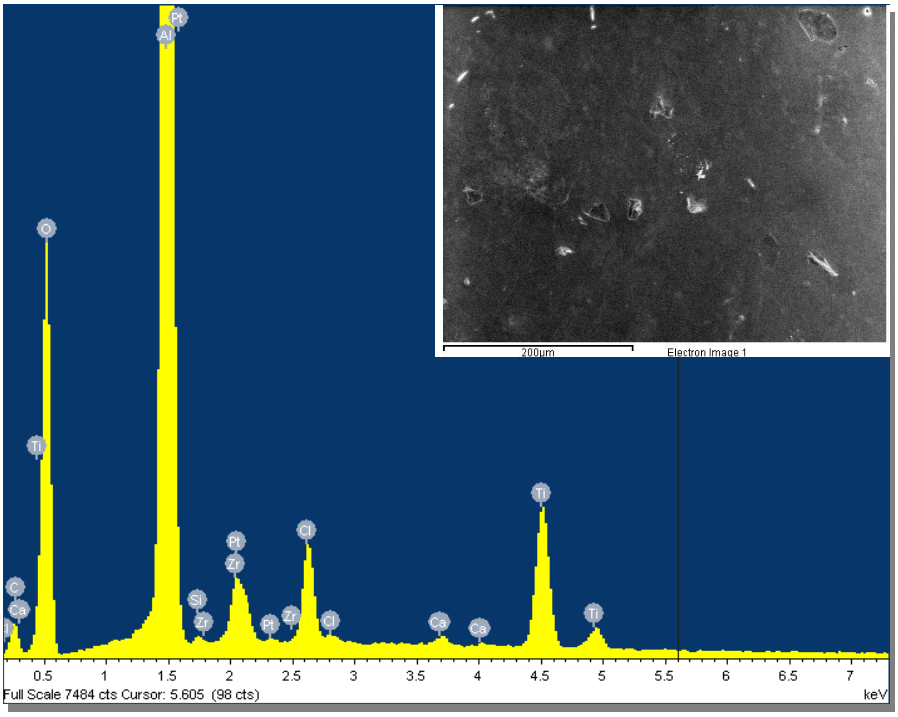

Fig. 4. SEM-EDXA image of the Pt membrane outer surface.

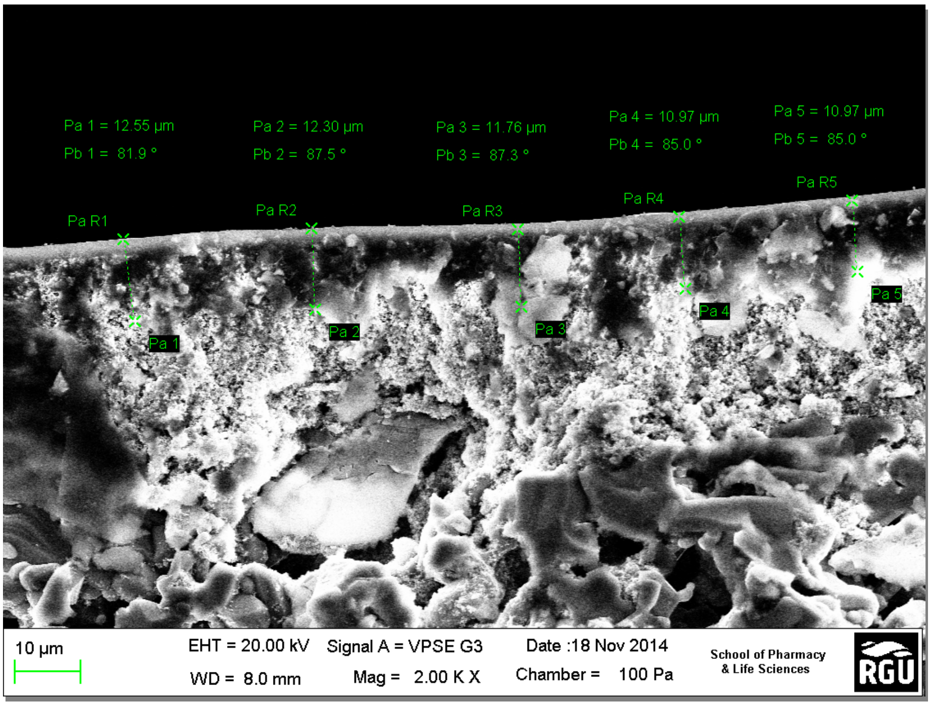

Fig. 5. SEM image of the Pt membrane edge surface.

Figs. 6, 7 and 8 shows the N_2 adsorption-desorption isotherms and the pore size distribution of the alumina support, silica and Pt membranes respectively. The isotherms on Figs. 6a and 7a exhibit a type IV adsorption characteristic of mesopores. Both isotherms possess hysteresis loops with an extremely narrow step indicating a narrow mesopore size distribution (Figs. 6b and 7b) for the alumina support, silica and Pt membranes of 4.17, 3.94 and 3.70 nm respectively (Table 2). These pore diameters were calculated by the Barret-Joyner-Halenda (BJH) model. The BET surface areas for the support, silica and Pt membranes were 0.364, 0.484 and 0.426 m^2/g respectively.

Table 2. BET surface area, average pore diameter and pore volume measurements of the alumina support, silica and Pt membranes.

Membrane	BET surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
Alumina Support	0.364	4.17	0.005
Silica Membrane	0.484	3.94	0.005
Pt Membrane	0.426	3.70	0.005

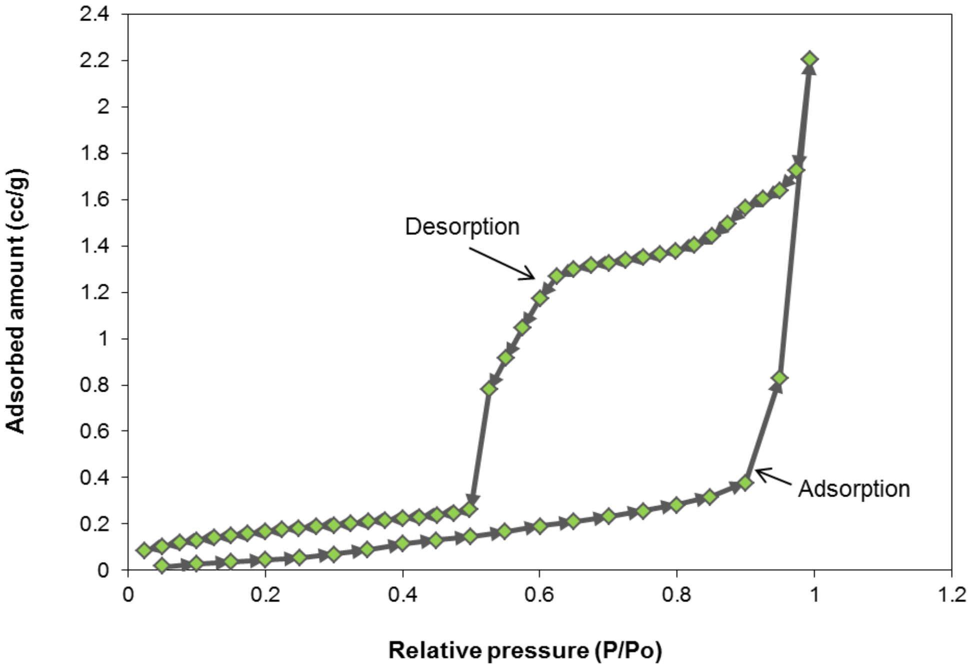

Fig. 6(a). N_2 adsorption/desorption isotherm of the alumina support.

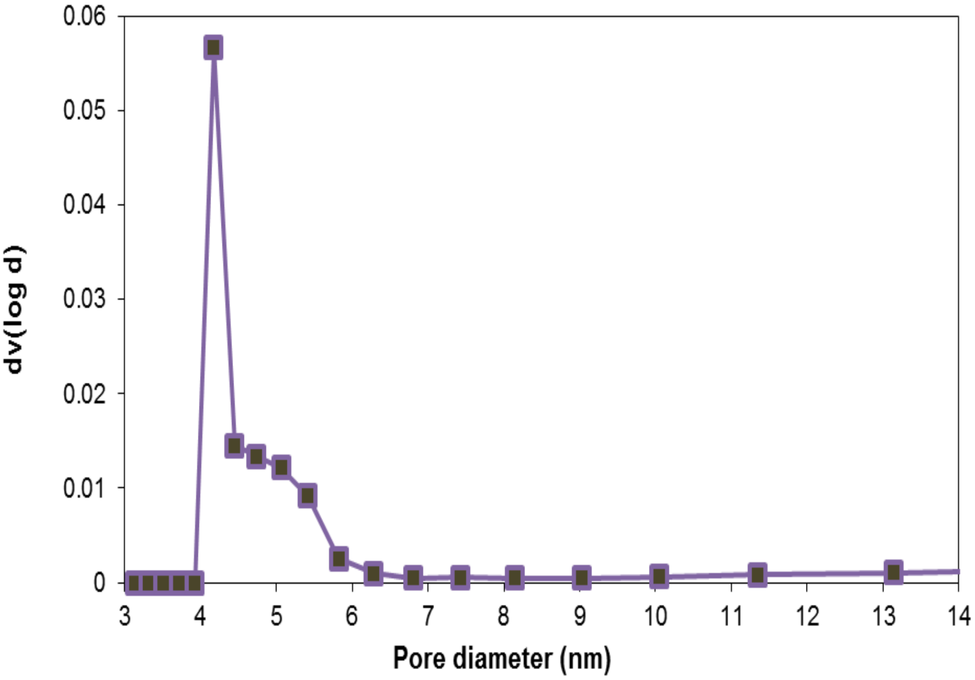

Fig. 6(b). Pore-size distribution of the alumina support measured by N_2 adsorption.

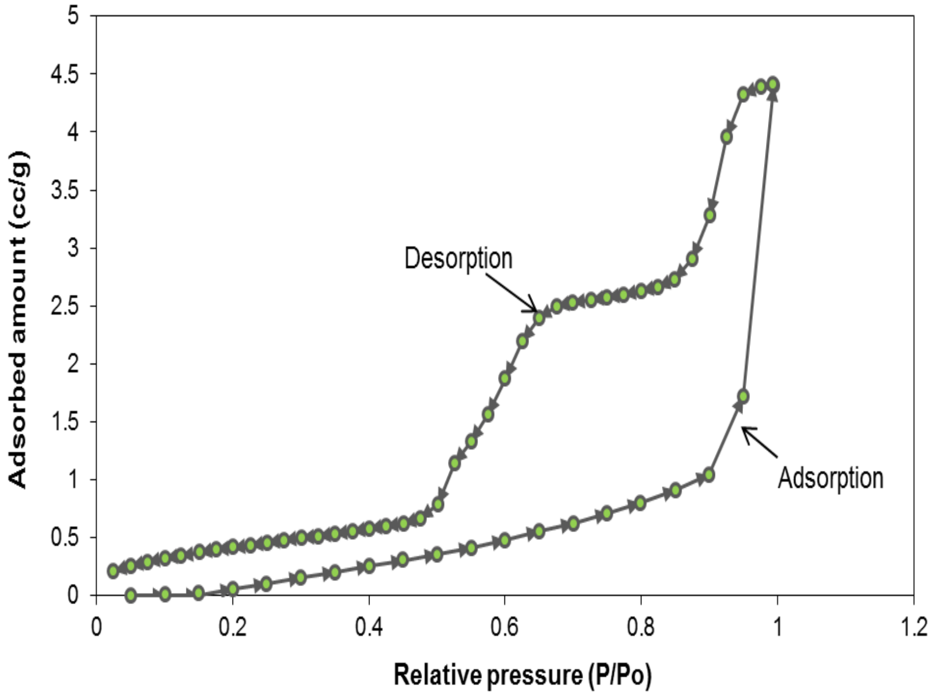

Fig. 7(a). N_2 adsorption/desorption isotherm of silica membrane.

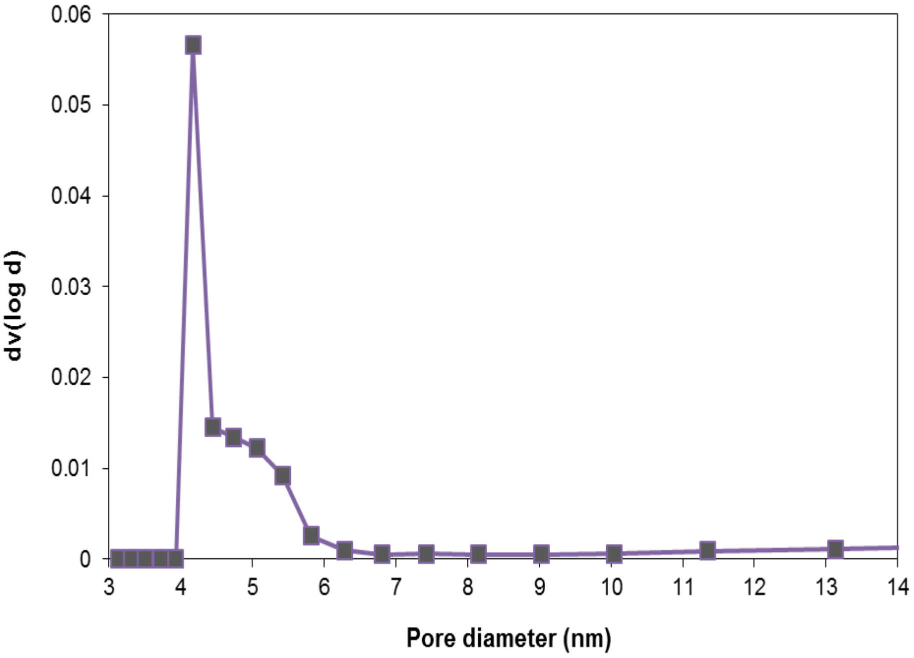

Fig. 7(b). Pore-size distribution of silica membrane measured by N_2 adsorption.

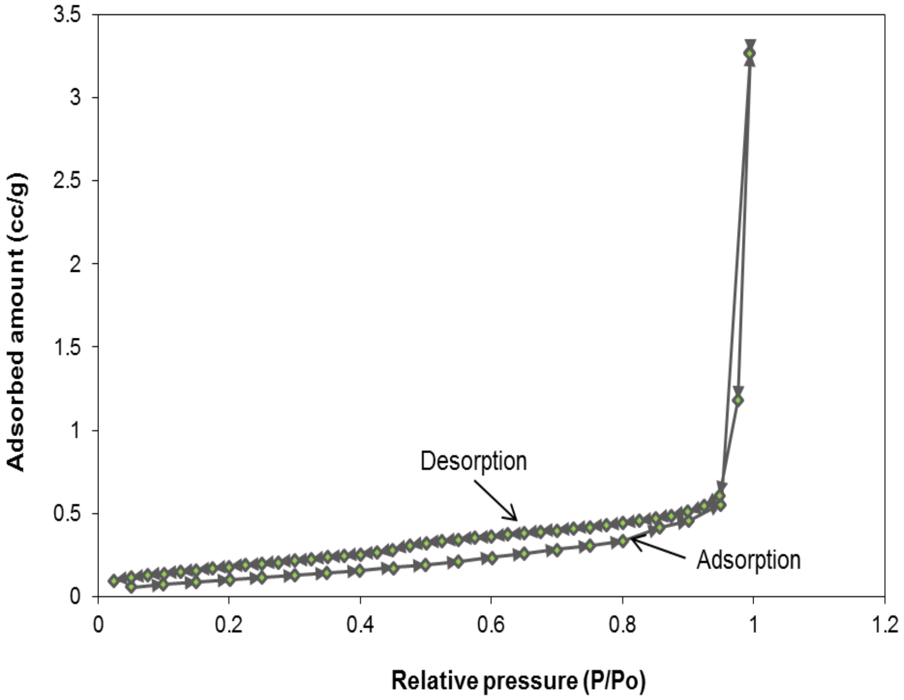

Fig. 8(a). N_2 adsorption/desorption isotherm of calcined Pt membrane.

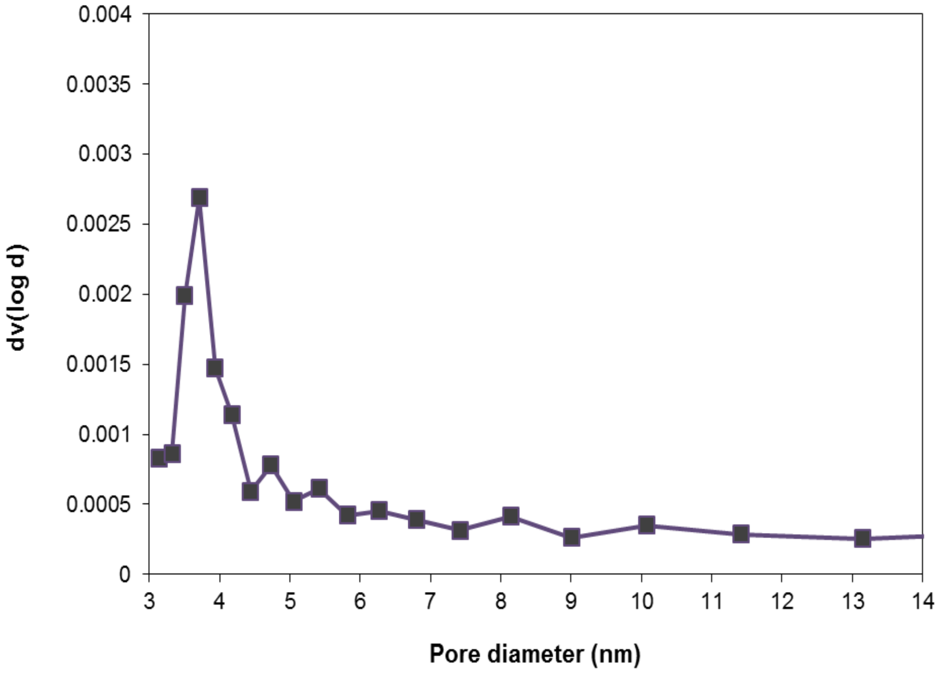

Fig. 8(b). Pore-size distribution of calcined Pt membrane measured by N_2 adsorption.

Gas permeation

Fig. 9 shows N_2 gas permeation as a function of feed pressure applied across the alumina support, silica and Pt membranes. N_2 gas permeate increases significantly as the feed pressure increases. This increase in N_2 permeate is attributed with the contribution of viscous flow through the alumina support. For the coated silica and Pt membranes, the N_2 permeate is less dependent of the feed pressure compared to that of the alumina support. This is an indication of a reduction in viscous flow with respect to the N_2 permeate on silica and Pt membranes which would occur in large pinholes if they were present [18]. These was also supported with the pore diameter values obtained (Table 1). The permeate of N_2 for the silica and Pt membranes were almost independent of feed pressure above 0.7 bar, indicating that the permeation of the gas above 0.7 bar is governed by Knudsen diffusion mechanism. This result shows that the crack-free membranes obtained was in good agreement with the SEM results.

Fig. 10 shows H_2/N_2 selectivity for the alumina support, silica and Pt membranes in relation to feed pressure at ambient temperature. It can be seen that, silica membrane obtained the highest factor of 2.93 at 0.9 barg, which is slightly lower than the expected value from the theoretical Knudsen diffusion (3.74). In this case, it is therefore possible that surface flow for N_2 at the top layer is the governing transport [18, 19]. Fig. 11 shows the selectivity of H_2/He single gas at the temperature between 25 ^{0}C up to 300 ^{0}C and 1.6 barg feed pressure on Pt membrane. H_2 selectivity of 1.96 over He was obtained at 300 ^{0}C which is 2 fold higher than the theoretical knudsen selectivity.

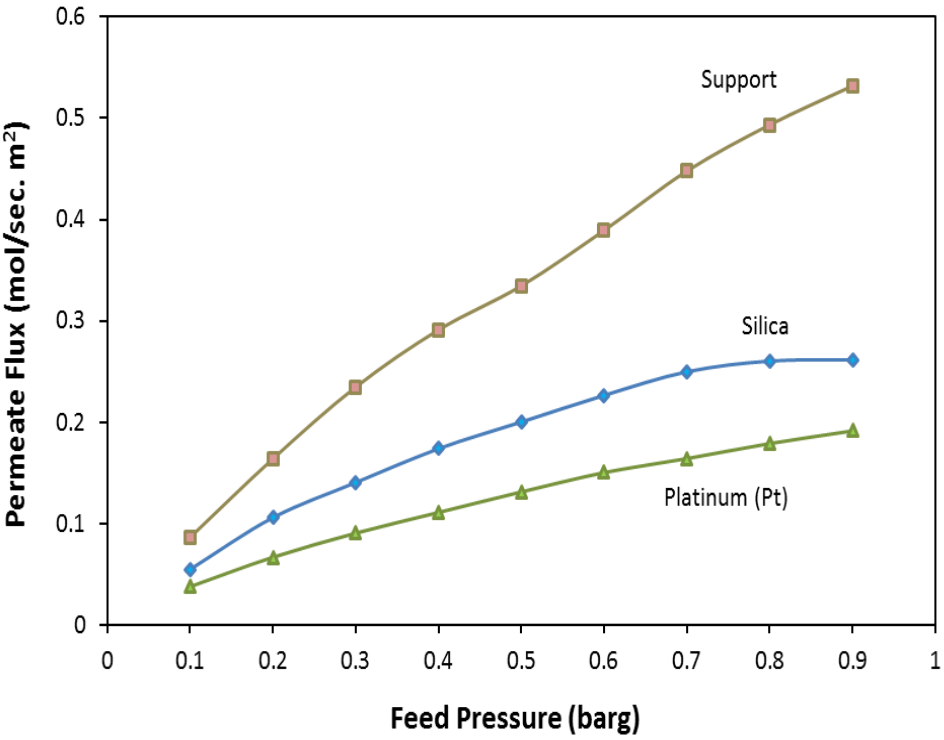

Fig. 9. N_2 permeation of the alumina support, silica and Pt membranes against feed pressure at 25 ^{0}C.

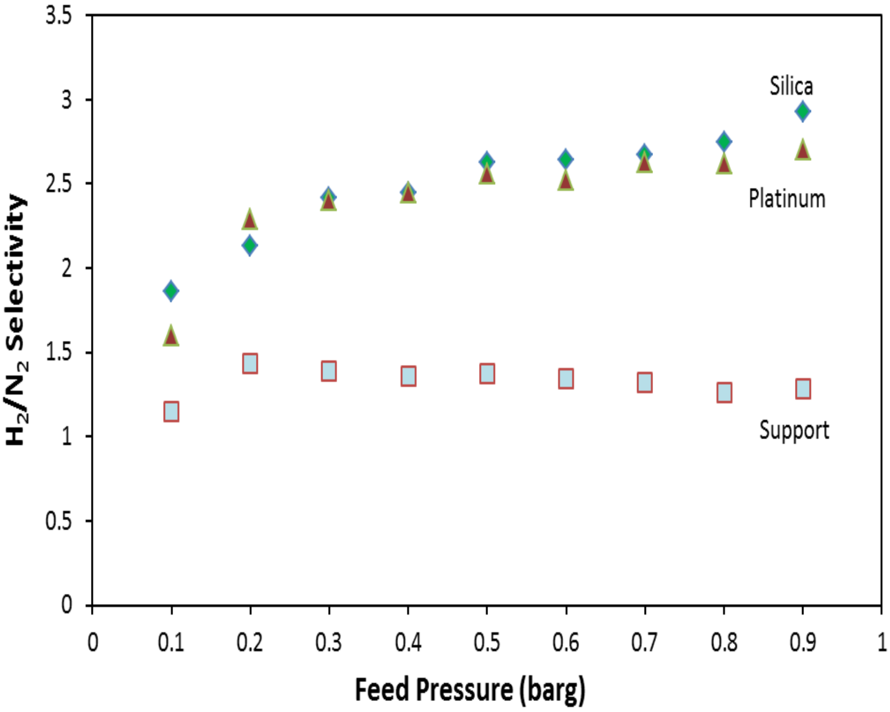

Fig. 10. H_2/N_2 Selectivity of the alumina support, silica and Pt membranes against feed pressure at 25 ^{0}C.

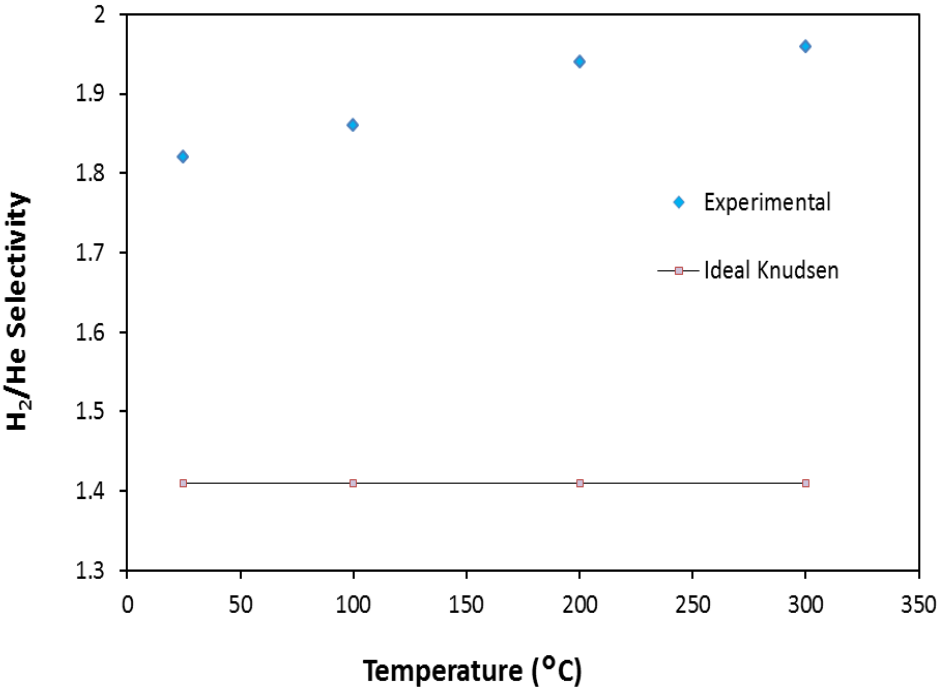

Fig. 11. H_2/He Selectivity against temperature on Pt membrane at 1.6 barg.

Conclusion

Silica and Pt membranes were prepared using a commercial tubular alumina support via the simple but effective dip-coating method. The mean pore diameters of the alumina support, silica and Pt membranes were 4.17, 3.94 and 3.70 nm respectively. The membranes were crack-free as confirmed by H_2, He and N_2 gas permeation tests. The silica membrane obtained a higher H_2/N_2 selectivity of 2.93 at 0.9 barg and ambient temperature. On the other hand, a H_2/He selectivity of 1.96 at 300 ^{0}C and 1.6 barg for the Pt membrane was also obtained and found to be higher than that of the theoretical Knudsen selectivity as a result of activated surface diffusion of hydrogen.

Nomenclature

A	surface area of the membrane	(m^2)
F	permeance	(mol/m^{-2} s^{-1} Pa^{-1})
L	thickness of the membrane	(m)
P_e	Permeability	(mol-m/m^{-2} s^{-1} Pa^{-1})
P_y	permeability of y component	(mol-m/m^{-2} s^{-1} Pa^{-1})

P_z	permeability of z component	(mol-m/m^{-2} s^{-1} Pa^{-1})
q	molar flow	(mol/sec)
ΔP	pressure difference across the membrane	(Pa)

Greek Symbols

$\alpha_{y,z}$	selectivity	-

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