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Comparison of hydrogen transport in dense and porous ceramic membrane systems.

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Comparison Of Hydrogen Transport In Dense And Porous Ceramic Membrane Systems

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ABSTRACT

In this study, hydrogen permeation behaviour was investigated for both dense and porous ceramic composite membranes. Selected porous supports were tested and highly active metallic species was impregnated into the porous structure using the repeated dip coating technique. Thin palladium films deposited onto a 15 nm pore size porous ceramic alumina support using both conventional and modified electroless plating methods were also studied. The hydrogen transport behaviours of the membranes were investigated, including the effect of high-temperature treatment including on the hydrogen transport. The value of the permeance in both the dense and porous systems were compared and the exponential factor n depicting the rate limiting step to hydrogen permeation in the dense membranes was also investigated. Deviations from Sievert's Law were observed from the palladium membranes when compared to the porous systems investigated in this work.

KEYWORDS: Hydrogen, Permeation, Membrane, Porous and Dense alumina

INTRODUCTION

Oil and gas resources are depleting rapidly and are envisaged to run out in a few decades which mean the world is faced with a scary but realistic future without oil [1]. A world without oil and gas will create an energy vacuum if other energy sources are not economically available before oil runs out. Already some wells are drying out in Saudi Arabia, the country with the largest oil reserves and even where new oil wells are discovered, it is becoming increasingly difficult to hit oil because oil production is getting economically unviable [2]. Oil companies are finding it increasingly difficult to achieve economies of scale thereby leading to downsizing and mergers and in some cases, outright closures. Oil is said to deplete finally in 30-40 years from now and this calls for renewed commitment to identifying alternative and renewable sources of energy including hydrogen [2]. The challenges associated with oil are more compounded with fluctuating oil prices which always cast a shadow of uncertainty over the global economy thereby limiting free trade amongst nations. Oil is also said to be the major cause of the current global armed conflicts, insurgencies and mistrust amongst nations [3]. The focus now is on energy sources that are environmentally friendly and inexhaustible so as to combat climate change and ensure energy security. Membrane separation is one of the enabling technologies in hydrogen production.

Among the various membranes, Palladium membranes have received an ever-increasing attention in the separation of hydrogen mainly due to their ability to exclusively separate hydrogen from other gases and as a result of its high mobility in palladium lattice, and application over a wide range of temperatures [4]. Palladium membranes are the preferred choice in hydrogen separation and purification due to their infinite selectivity to hydrogen when defect free [5]. The adoption of hydrogen as the global energy carrier is faced with challenges including hydrogen storage, scaling up to full commercial levels and the need for public awareness and sensitisation about the hydrogen energy system.

The use of inorganic membranes for hydrogen processes is also facing challenges such as cost, how to achieve uniform intensification, examination and treatment of defects during the deposition of the metallic layer and poisoning by impurities such as carbonaceous compounds which impeded hydrogen permeation [6]. Electroless plating method for deposition of palladium layer over porous supports also has several challenges such as the threat of impurities during surface modification for Al_2O_3 supports, the long duration which makes it prone to errors and contamination. The need arises to fabricate thin defect free composite palladium membranes with high hydrogen flux and selectivity for hydrogen separation and purification especially for use in fuel cell processes and petroleum refining applications [7]. All these challenges to the hydrogen energy system have made it imperative that sustained research is encouraged in palladium and other inorganic membranes for hydrogen production, separation and purification.

Hydrogen can be produced in several ways such as through electrolysis of water, steam methane reforming, gasification of coal and partial oxidation of natural gas [1]. The raw gas contains several gaseous impurities which must be removed to make the hydrogen in its pure form. The methods for hydrogen separation are: pressure swing adsorption (PSA), cryogenic distillation, solvent adsorption and membrane separation. Membrane separation has been identified as one of the most promising technology due to several attributes such as its low cost, low energy consumption and simple equipment [1]. Steam reforming of methane is the most widely used method for hydrogen production. However, despite its significance in hydrogen production processes, the steam methane reforming poses several challenges prominent amongst which is the restriction caused by the thermodynamic equilibrium [2]. Steam reforming also produces carbon dioxide which is an environmental pollutant. The steam methane reforming process is performed in fixed bed reactors. Due to the endothermic reaction high temperatures (>8000 C) are required which results in enormous drastic operating conditions [2]. Membrane reactors provide promising options in overcoming these challenges including high temperature and high pressure.

In common with most modern technology fields, the development of inorganic membranes is currently witnessing exponential growth. Inorganic membrane technology offers great opportunities to those companies and individuals who can find innovative ways of utilizing new materials, and new preparation technologies to create the designer membranes of the future.

Because of their size, the mobility of the gaseous materials is strongly affected by molecular collisions. Each molecule of gas then has random component to its motion as well as macroscopic motion of the gas stream. This makes it much more likely for the gas molecule to collide with the membrane surface even when the macroscopic flow is parallel to that surface. Gas separation in inorganic membranes typically can occur by surface adsorption on the membrane material. The gas molecules can stay on the surface, but it is also possible for them to be adsorbed into the membrane material or be displaced back into the gas stream if other gaseous molecules come along that have a greater affinity to that surface binding site.

The gases in the incoming flow can have a range of properties, so no single membrane can possess optimal separation efficiency. It has been shown that overall membrane effectiveness including cost can be enhanced by combining membrane materials with different proprieties in a multi-layered configuration [1, 2]. In this configuration, the membrane forms a thin separating layer on the surface of a coarser support. The proprieties of the two parts complement each other, the thin layer provide the permselectivity while the coarse support provides the mechanical stability. This can be extended to using many layers to achieve a composite multi-layered membrane whose physical and chemical characteristics change continuously along the direction of the flow. This type of multi-layered membrane can have high separation efficiency since it can be designed so as is to match the proprieties of the incoming fluid stream. This type of effect is now being built into inorganic membranes so that different separation mechanism can occur and matched to the remaining material that need to be removed from incoming flow-stream.

An example would be the use of membrane in which the density changes with depth. The low-density pores of the coarser support are quite effective in maintaining strength. Since more selective membranes invariably cost more, it is important to compare the economics, maintenance needs and efficiencies of using a single, noncomplex material as opposed to separate multiple components that have individual maintenance and efficiency cycles. The material that can be used to make inorganic membranes are also including a new dimension to separation design. Manufacturing capabilities have improved to allow membrane preparation from these new materials, or combining them with conventional materials, to provide multi-layered membranes with enhanced proprieties.

THEORETICAL CONSIDERATIONS

The permeance of a gas through the hybrid inorganic membrane is the gas flux, (i.e., the gas flowrate divided by the membrane area, A) divided by the pressure drop, P_1-P_2 across the membrane. In the simplest approximation the flux is the sum of a viscous and Knudsen contribution and can be described by equation 1:

$$F_0 = F_{Knudsen} + F_{Viscous}\left(\frac{mol}{m^2 s}\right) \tag{1}$$

where $F_{Knudsen}$ and $F_{Viscous}$ are the Knudsen and viscous contributions respectively and are defined by:

$$F_{Knudsen} = \frac{8r_p(P_1 - P_2)}{3\delta(2\pi MRT)^{\frac{1}{2}}}\left(\frac{mol}{m^2 s}\right) \tag{2}$$

$$F_{Viscous} = \frac{r_p{}^2(P_1^2 - P_2{}^2)}{16\delta\mu RT}\left(\frac{mol}{m^2 s}\right) \tag{3}$$

Substituting equations (2) and (3) into equation (1) gives equation 4:

$$F_0 = \frac{8r_p(P_1 - P_2)}{3\delta(2\pi MRT)^{1/2}} + \frac{r_p{}^2(P_1^2 - P_2{}^2)}{16\delta\mu RT} \tag{4}$$

Equation (4) can be normalized to take into consideration the separating layer thickness. This is achieved by re-arranging and then multiplying both the L.H.S. and R.H.S. of equation 4 by $\frac{\delta}{(P_1 - P_2)}$ to give equation (5):

$$\frac{F_0\delta}{(P_1 - P_2)} = F_T = \frac{8r_p}{3(2\pi MRT)^{1/2}} + \frac{r_p{}^2(P_1 + P_2)}{16\mu RT}\left(\frac{molm}{m^2 sPa}\right) \tag{5}$$

where F_T is the normalized permeance or permeability of the multi-layered membrane.
Equation (5) can also be written in the more convenient form of equation 6:

$$F_T = \frac{8r_p}{3(2\pi MRT)^{1/2}} + \frac{r_p{}^2}{8\mu RT}\left(\frac{(P_1 + P_2)}{2}\right)\left(\frac{molm}{m^2 sPa}\right) \tag{6}$$

Equation (6) can be written in a more compact form as:

$$F_T = K_0 + B_0 P_{Average} \tag{7}$$

where:

$$K_0 = \frac{8r_p}{3(2\pi MRT)^{1/2}}\left(\frac{molm}{m^2 sPa}\right),\ B_0 = \frac{r_p{}^2}{8\mu RT}\left(\frac{molm}{m^2 sPa^2}\right),\ P_{Average} = \left(\frac{(P_1 + P_2)}{2}\right)(Pa)$$

Equation (7) is straightline if F_T is plotted against $P_{Average}$ resulting in a slope equal to B_0 and an intercept on the F_T axis equal to K_0. The nature of the straightline will indicate the extent of the F_T relative contributions of Viscous and Knudsen flow.

If the graph plotted is of the form $F_T = B_0\, P_{Average}$ then the flow is characterised by viscous flow. If however, the graph plotted is of the form $F_T = B_0\, P_{Average} + K_0$, then both the Knudsen flow and viscous flow contribute to the transport characteristics. Analysis of the intercept and the slope will then yield the values of a K_0 and B_0, which upon substitution into equation (6) will enable estimation of the pore radius of the multi-layered membrane.
Examination of equations (2) and (3) shows that several possibilities exists.
(i) For Knudsen flow:

$$\frac{F_{0,A}}{F_{0,B}} = \sqrt{\frac{M_B}{M_A}} \tag{8}$$

(ii)For Viscous flow:

$$\frac{F_{0,A}}{F_{0,B}} = \frac{\mu_B}{\mu_A} \tag{9}$$

The mean free path of a gas molecule is given by equation (10):

$$\lambda = 2r_p.\text{Knudsen Coefficient (m)} \tag{10}$$

In the equation (7), both B_0 and K_0 depend on the membrane material characteristics such as thickness of the separating layer, the porosity, tortuosity, and pore radius. Temperature and type of gas also influence B_0 and K_0 as described by equation (11):

$$B_0 \sim 1/\mu T \text{ and } K_0 \sim 1/MT \tag{11}$$

where μ is the viscosity, T the temperature and M the molecular weight of the gas. Viscosities of most gases are relatively close to each other and therefore it is obvious that the gas separation will mainly depend on the difference in the molecular weight, and this will be determined by the Knudsen flow contribution of equation (6) as shown in equation (8) for a gas mixture containing components A and B.
Equation (7) is only a simple approximation where the pressure difference is the driving force for gas transport through the multi-layered membrane and does not take into account other transport mechanism such as surface flow, multilayer diffusion, capillary condensation and molecular sieving. It however gives a good indication of the performance and quality of the membrane provided that the necessary precautions are adhered to before and during gas transport measurements.

Membrane reactors could perform both the reaction and the separation process simultaneously (Process intensification) and can also shift the thermodynamic equilibrium in the water – gas shift reaction to convert carbon monoxide to hydrogen [3]. 18 High temperatures are required for the endothermic reaction as shown in equations 11 and 12 [3]:

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{12}$$

The water–gas shift reaction involves the exothermic reaction of carbon monoxide with steam [3]:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{13}$$

The selective removal of hydrogen from the reaction stream using membranes will result in a shift of the thermodynamic equilibrium to the products side. This shift will lead to high feed conversion and high purity hydrogen recovery at low temperatures [4]. Metals of groups 8-10 of the periodic table are normally used as catalysts in steam methane reforming [2]. The most important properties that make a membrane effective in separation and purification processes are permeability and selectivity [3]. Permeability is defined as 'the flux of mass through a membrane per unit of area and time at a given gradient and is a product of diffusivity and solubility [1]. Diffusivity and solubility allow the permeate to pass through the membrane and hydrogen has an extremely high diffusivity in palladium which gives it an extremely high selectivity [1]. Permeance is the total flux in terms of the membrane's ability to drive the gas through it and it describes the relationship between permeability and thickness of the membrane denoted in molar units as (mol m^{-2} s^{-1} Pa^{-1}) [4]. Higher flux denotes that a smaller membrane area is required and therefore, a lower cost of the process. In this work, a catalyst is incorporated to an alumina membrane to investigate the flow of hydrogen through the membrane at different temperatures and molar flow rates.

EXPERIMENTAL

Materials

Materials and chemicals used in this work include:

Rhodium (III) chloride supplied by Sigma Aldrich (98% w/v)
Synthetic off-gas mixture containing 4.5% O_2, 2.5% CH_4, 12.5% CO_2, and balance nitrogen (+/- 2% uncertainty) supplied by BOC, Aberdeen Scotland.
50% CO_2 and 50 % CH_4 (+/- 2% uncertainty) supplied by BOC, Aberdeen Scotland.
Analytical grade hydrogen (98% purity) supplied by BOC, Aberdeen Scotland.
C106X/1B single stage gas regulator supplied by BOC, Aberdeen Scotland for use with non-corrosive gases.
HP 1500 series 851750 single stage gas regulator
Synthetic off-gas mixture containing 4.5% O2, 2.5% CH4, 12.5% CO2, 220 ppm SO_2 and balance nitrogen (+/- 2% uncertainty) supplied by BOC, Aberdeen Scotland.
Gas connection hose (1/4inch compression fittings)

Method

Electroless plating deposition of the Rh on 6000 nm pore size tubular ceramic cores has been achieved by dissolving 10 g of 98 % $RhCl_3$ in 500 ml of deionized water. This was left to stir for 24 h. 6000 nm γ-alumina support was subsequently soaked in water for 2 h and then dipped into the $RhCl_3$ solution and left for 20 h. Catalytic reduction of the $RhCl_3$ and activation of the rhodium metal on the membrane was carried out by passing hydrogen gas through the membrane in the membrane reactor at 573 K for 30 min.

Membrane Characterisation

SEM and EDAX

SEM uses a focused beam of high-energy electrons to generate a variety of signals at the catalyst surface. The signals (derived from electron-sample interactions) reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. Data was collected over a selected area of the sample surface and a two-dimensional image was generated. The image displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques.

Gas Permeation Test

A mixed gas permeation test has been carried out and the permeate gases were sent to the online GC (Agilent Technologies, Santa Clara, California, USA) equipped with an MS detector for analysis using an automated 6-port gas sampling valve (Agilent Technologies, Santa Clara, USA) on a 30 mm Plot H column. The experimental rig consists of a membrane reactor that was operated at high temperature using a Horst (Germany) power regulator.

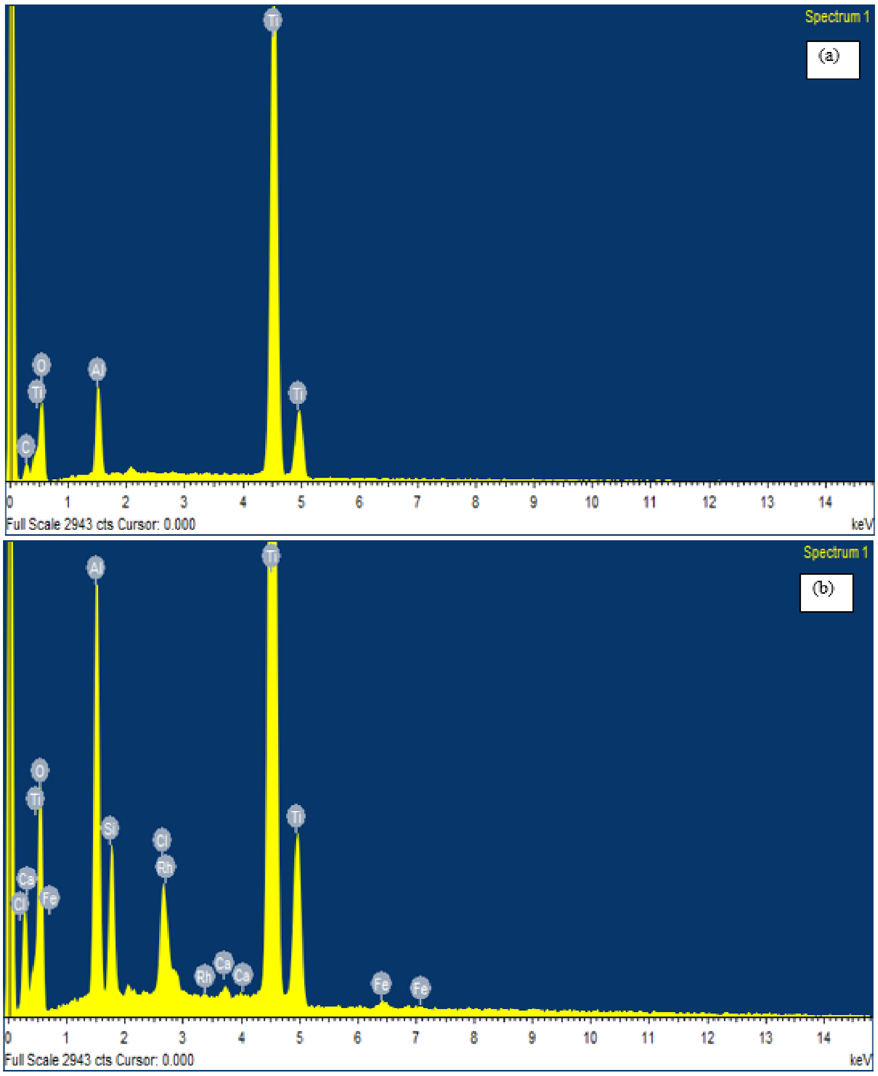

Figure 1: EDAX for (a) γ-alumina support and (b) Rh/γ-alumina membrane.

Table 1: Elemental composition of γ-alumina and Rh/γ-alumina membrane

Elements	% weight composition (γ-alumina support)	%weight composition (Rh/γ-alumina membrane)
O	7.29	20.5
Al	0.82	3.82
Si		1.43
Cl		0.97
Ca		0.14
Ti	9.68	23.63
Fe		0.23
Rh		0.94
C	0.79	

The EDAX elemental analysis showed the amount of Rh catalyst on the support to be 0.94 %. Moreover, the catalyst loading on the γ-alumina support is 0.52 %. The elemental composition is presented in table 1.

SEM images of the γ-alumina membrane and the rhodium impregnated γ-alumina membrane are presented in Figure 1.

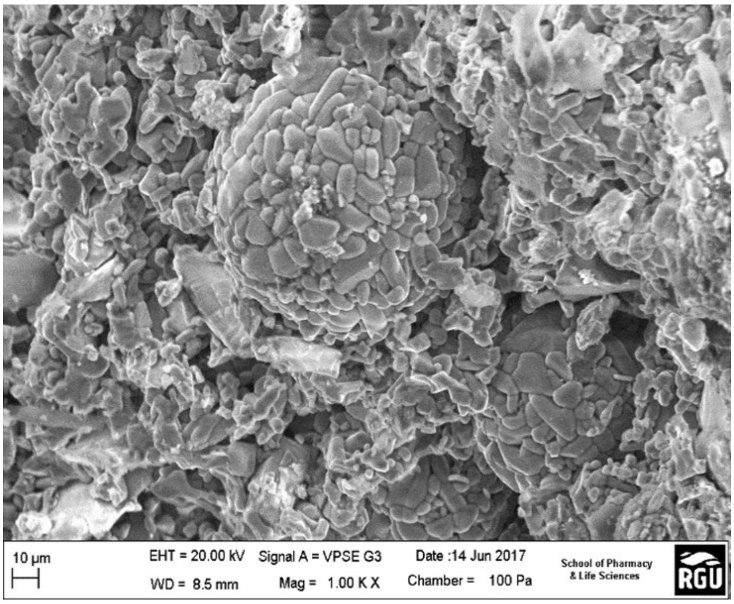

Figure 2: γ-alumina membrane.

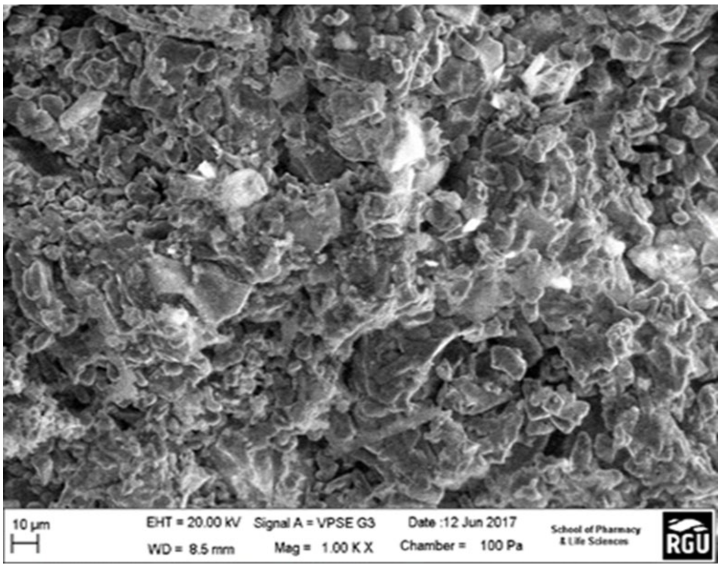

Figure 3: Rh/γ-alumina membrane.

Nitrogen Adsorption/Desorption

Physical adsorption of gases on a materials surface is one of the most important techniques for the characterisation of nanosized porous materials. This method provides details about the surface area, pore volume and pore size distribution. Several different types of physisorption isotherms (Figure 2 and 3) have been observed for both the activated and unactivated Rh modified membranes.

The specific surface area of the membranes has been determined from the adsorption of nitrogen on the external and internal surface of the membranes at 77.35 K using a quantachrome adsorption gas analyser.

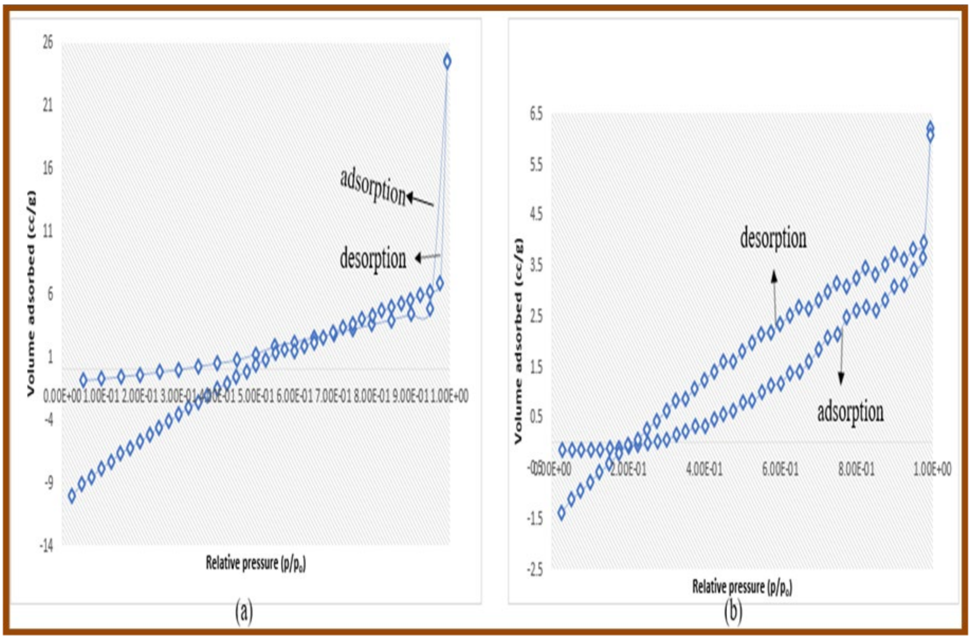

Figure 4: N_2 adsorption/desorption isotherm of (a) un-activated Rh membrane and (b) activated Rh membrane.

The difference in the hysteresis isotherms is caused by the difference in adsorbent behaviour of Rh before and after passing H_2 at a temperature of 573 K (Figure 4a and 4b). The observed loop is generally associated with materials that have mesoporic structures. The adsorption behaviour of mesoporous materials can be determined using adsorbent-adsorbate interactions.

The BJH graph (Figure 4) shows the adsorption and desorption branches, which have been used to determine the pore size of the membrane. This was determined to be 2.973 nm with a specific surface area of 17.447 m^2/g.

Single Gas Permeation Test

Single gas permeation of CH_4, CO_2 andH_2 through the γ-alumina membrane is presented in Figure 5. The permeance of H_2 was shown to increase as the pressure was increased to 1 x 10^5 Pa. This indicates that the membrane can selectively remove hydrogen at higher pressures. The order of gas permeance through the membrane was H_2 (2.00 mol/g), CH_4 (16.04 mol/g) and CO_2 (44.00 mol/g). Therefore, the flow mechanism was based on the relative molecular masses of the gases. This is indicative of Knudsen flow mechanism.

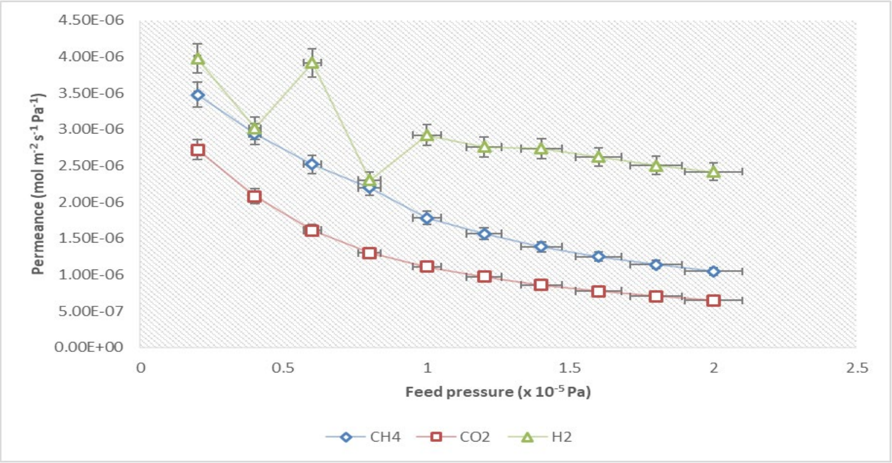

Figure 5: Gas permeance through the γ-alumina membrane at 293 K.

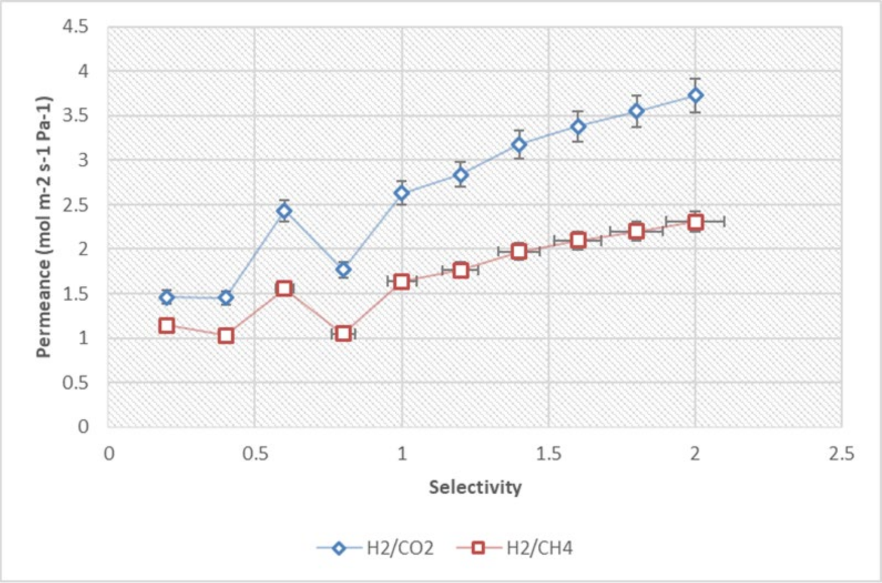

Figure 6: Selectivity of the γ-alumina membrane at 293 K to hydrogen.

Figure 6 shows hydrogen selectivity through the alpha-alumina membrane. The selectivity was found to increase with increased gas feed pressures. Consequently, continual removal of hydrogen from the gas stream will enhance the CO_2 and CH_4 conversion rates. This is one of the advantages of a membrane reactor over a packed bed reactor (PBR).

Patil et al. (8) have previously carried out methane reforming reactions with a noble metal catalyst at 823 K at Pa in a CMR. This consisted of a palladium-based membrane. Moreover, conversion enhancements of 27 – 53% were achieved. Tong and Matsumura (9) also investigated methane reforming reactions with a CMR. They used a commercial nickel catalyst at 773 and 823 K and obtained hydrogen permeances of mol m-2 s-1 Pa-1. In this work, hydrogen permeances of 2.4 – 3.9 mol m-2 s-1 Pa-1 have been achieved. These are found to be equivalent to those obtained in the literature.

CONCLUSION

A hybrid inorganic membrane has been prepared on tubular porous carbon support by dip-coating technique. The method by combining resistance is used to estimate this film thickness which shows good agreement with SEM measurements. Hydrogen permeation behaviour was investigated for the dense and porous ceramic composite membranes and it was found to have a higher permeance than carbon dioxide and methane.

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