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Hydrogen Separation Using Silica-Based Composite Membranes

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Abstract

Silica sol-gel membranes have been developed for moderate temperature (300 °C) separation of hydrogen (H₂) from nitrogen (N₂), methane (CH₄) and argon (Ar) gas molecules. Tubular ceramic support with 15 nm nominal pore diameter and 45% porosity was modified by dip-coating method. Gas permeation characteristics were evaluated. Defect free silica layer over the substrate for hydrogen gas separation was obtained. Hydrogen gas permeate flux of 4.82×10^{-1} mol/sec m² at 1.0 barg feed pressure was obtained. Selectivities of H₂ over N₂, CH₄ and Ar of 3.07, 2.23 and 3.75 at 300 °C, 200 °C and 300 °C and 0.9 barg were obtained with the silica membranes. The gas permeation and the selectivity performance of the membrane were evaluated.

Introduction

Hydrogen separation was initiated by Permea (which is now a section of Air Products) in the past three decades through the application of Prism membrane [1]. From that time, a considerable increment worth about US\$ 150 million annually was injected into membrane-based gas separation [1]. Research into the application of membrane-based gas separation as well as catalytic processes play a vital role in the petrochemical industry particularly for the state-of-the-art membrane science and technology. The state-of-the-art membrane technology can effectively compete with the conventional ones in the areas of energy-saving, using simple and non-harmful materials, recovery of minor but valuable compounds from the main stream, easy to operate, low maintenance process [2] to mention a few examples.

As the widely accepted clean energy carrier, for instance in the utilization of fuel cell systems hydrogen could help to address the problems linked to energy security which includes air pollution and global climate change. The need for hydrogen is growing and will increase potentially in the near future due to its higher demand [3]. Hydrogen can be produced from many sources, in fact its main source is natural gas which account for about 90% hydrogen [4]. Other sources include; water, coal, oil, biomasses, industrial waste among others [3-5].

Porous ceramic membranes have been used for light gas molecules separation e.g. hydrogen and helium from gas mixtures [5, 6]. Microporous and dense membranes are suitable for high temperature gas separation [3]. Microporous membranes are membranes with less than 2 nm pore sizes. The system generally has a macroporous support with some ceramic intermediate layers and a highly selective top layer [3]. The top layer possesses the separating capacities. Dense inorganic membranes are made of either polycrystalline ceramic materials or metals which select specific gas species to pass through the dense material [3].

Silica based membranes have been considered in high-purity hydrogen separation [5, 6]. These can be achieved by either sol-gel or chemical vapour deposition (CVD) processes as reported in most literatures [5-7].

The objective of this paper is to modify alumina porous membrane support with silica for the selective separation of hydrogen using the proposed sol-gel technique. The tubular ceramic membrane consists of 77% alumina and 23% TiO₂ which has a nominal pore diameter of 15 nm. The membrane has a permeable length of 348 mm with I.D and O.D of 7 and 10 mm respectively. The surface morphology of the silica membrane was prepared using the repeated dip-coating method [8, 9].

Experimental

Membrane preparation and characterization

The experimental set-up used in this study is shown in Fig. 1. It consists of a stainless steel tubular membrane reactor cell. Graphite rings seals which are high temperature resistant consisting of an I.D and O.D of 10.2 and 24 mm are used as a seal to firmly hold the membrane within the stainless steel reactor. Gas flow system used were single gases (H₂, N₂, CH₄ and Ar), with a purity of $\geq 99.99\%$ supplied by BOC (UK). A digital flowmeter to measure the permeation rates across the membrane was also used.

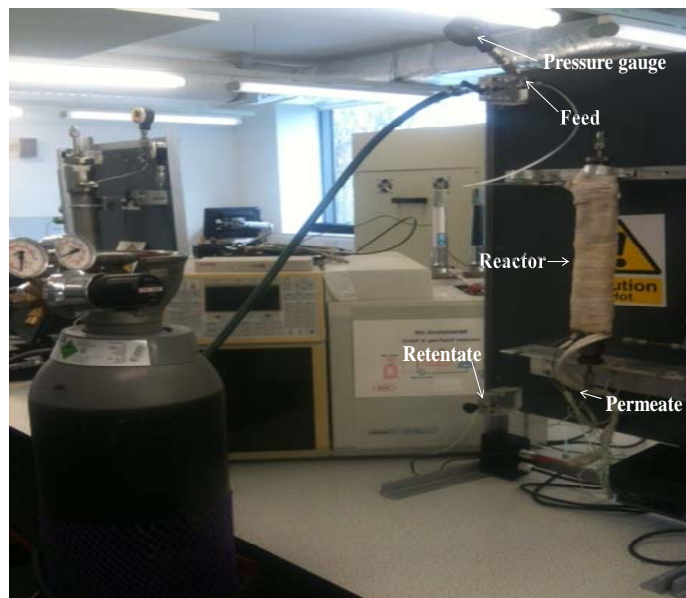


Figure 1: Experimental set-up for the tubular membrane module.

The surface morphology of the silica membrane was analysed by scanning electron microscopy (SEM) (Zeiss EVO LS10) and was found to be defect free as shown in Fig. 2. Membranes thickness was measured by weighing the support before and after each coating. The thickness was then calculated using eqn. (1) [10],

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

Where L is the membrane's thickness, W_1 is the weight of the alumina support before coating, W_2 is the total weight of the support and the membrane, A is the membrane area, ρ is the density of the alumina ($3.95 \times 10^3 \text{ kg.m}^{-3}$) [11] and ϵ is the porosity of the membrane (45%).

Results and discussion

Fig. 3 shows the EDXA (Energy-Dispersive X-ray Analysis) (Oxford Instruments INCA System) of the silica membrane can be obviously seen that some amount of silica has been adsorbed by the membrane during the modification process which enhances H₂ adsorption.

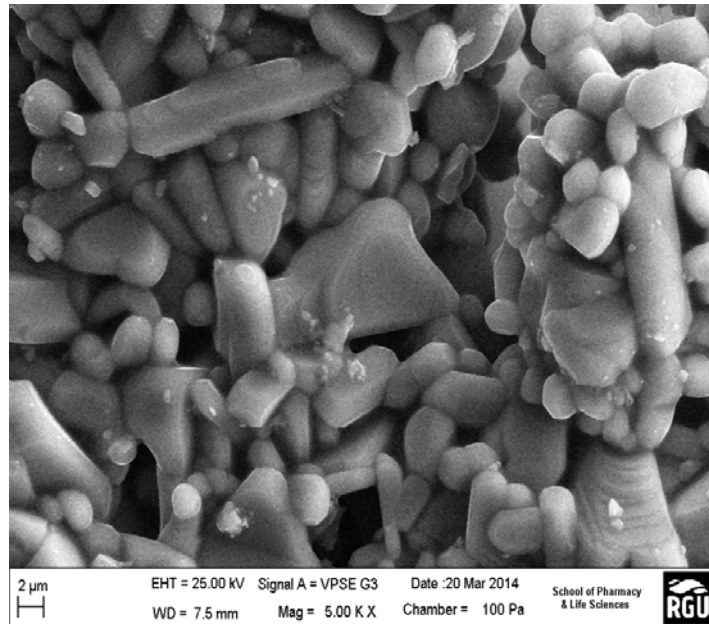


Figure 2: SEM image of the silica membrane.

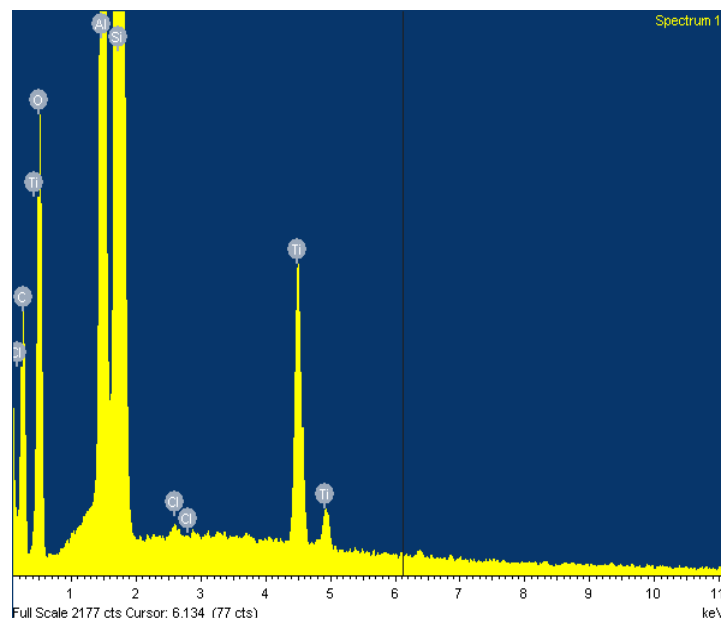


Figure 3: EDXA of the silica membrane.

Fig. 4 shows the single gas permeation results of the silica membrane at 25 °C. The permeation of molecules with the lower molecular weight recorded the higher permeate flux with increase in the order of H₂ > CH₄ > N₂ > Ar (with molecular weight 2 > 16 > 28 > 40 (g/mol) respectively). The

results indicates that hydrogen recorded permeate flux of 4.82×10^{-1} mol/sec. m^2 at 1.0 barg and nitrogen had a permeate flux of 1.62×10^{-1} mol/sec. m^2 at the same gauge pressure which resulted with almost 3 fold increment by hydrogen over nitrogen.

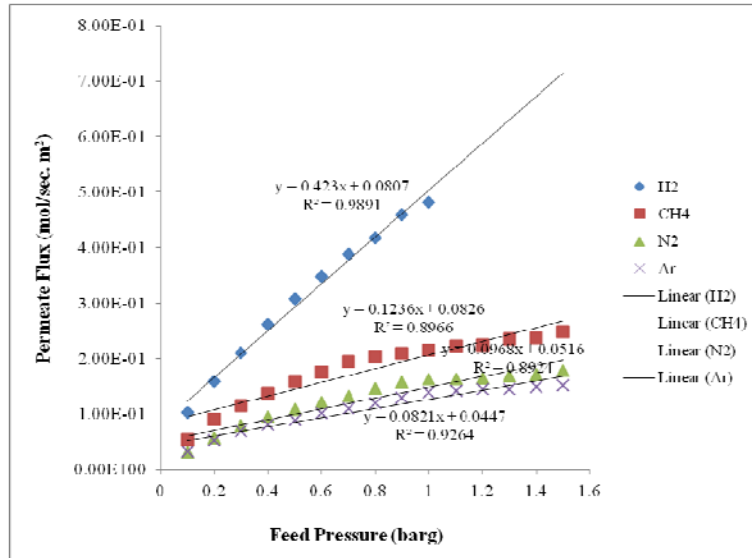


Figure 4: Feed Pressure Dependence on Permeate Flux at 25 °C.

The selectivity of hydrogen over nitrogen at 0.9 barg is shown in Fig. 5. It can be seen that higher selectivity of 3.07 was obtained at the peak temperature (300 °C) even though the selectivity diminishes to 2.72 at 50 °C and 2.89 at 200 °C. This is a good indication of possible hydrogen recovery from gas mixtures.

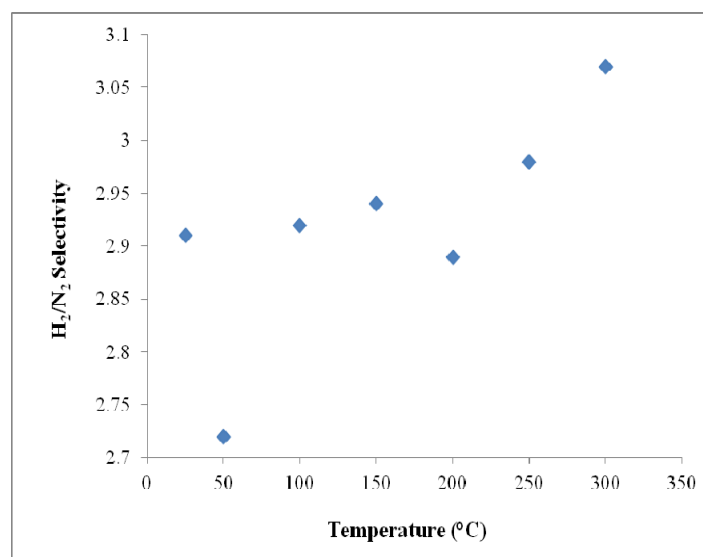


Figure 5: Temperature Dependence on H₂/N₂ Selectivity for Silica Membrane @ 0.9 barg.

Fig. 6 depicts the relationship of H₂/CH₄ selectivity at 0.9 barg against temperature. It can be observed that hydrogen selectivity over methane was 2.20 at 25 °C before diminishing to 2.16 at 50 °C. Higher hydrogen selectivity over methane was obtained at 200 °C before diminishing at the final temperature of 300 °C. From this result, one can conclude that hydrogen separation from methane could also be possible. As the temperature increases, residence time on the surface of the membrane suspected to decrease, and thus surface facilitated mechanism could dominate which results in the observed behaviour (Fig. 6).

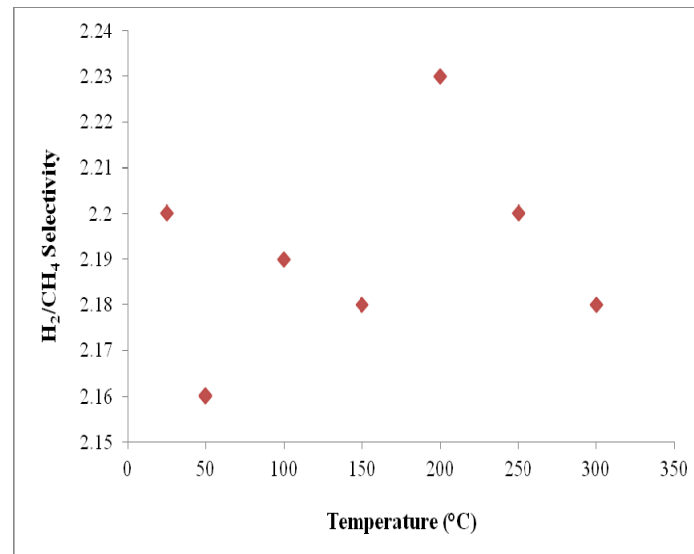


Figure 6: Temperature Dependence on H₂/CH₄ Selectivity for Silica Membrane @ 0.9 barg.

It can be seen in Fig. 7 that hydrogen selectivity over argon was almost linear. The selectivity diminished to 3.40 at 50 °C and rose to its peak of 3.75 at the final temperature of 300 °C. Simultaneous rise in both permeate flux and selectivity for a lighter molecules indicates that a rapid transport across the membrane probably through surface diffusion transport mechanism.

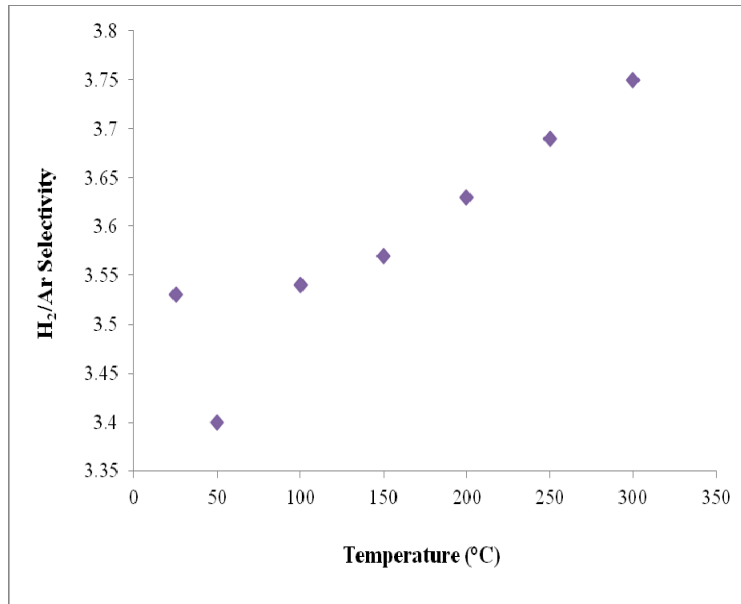


Figure 7: Temperature Dependence on H₂/Ar Selectivity for Silica Membrane @ 0.9 barg.

It can be seen in Fig. 8 that hydrogen, methane, nitrogen and argon flow rates decrease with increasing temperature at 0.5 barg feed pressure. This decrease due to increase in temperature is typical of Knudsen flow mechanism.

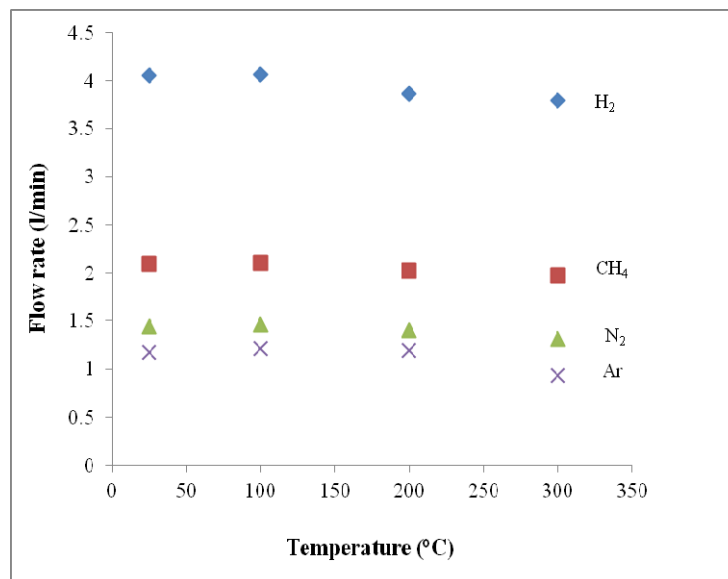


Figure 8: Temperature Dependence on Single Gas Flow rate @ 0.5 barg Feed Pressure.

Conclusion

Modification of inorganic membrane support with silica was demonstrated via dip-coating method. Permselectivities of hydrogen over nitrogen and argon increase with an increase in temperature due to the decrease in surface diffusion of nitrogen and argon. Although the separation factor is not extremely high, higher hydrogen selectivity over methane was obtained at 200 °C before diminished at the final temperature 300 °C.

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