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Preparation and Characterization of Inorganic Membranes for Hydrocarbon Separation from N₂ for Environmental Applications

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Abstract

This paper reports the preparation and characterization of a tubular alumina and silica membrane for propylene (C₃H₆) and nitrogen (N₂) separation. Dip-coating technique was employed to prepare silica membrane. Nitrogen adsorption measurements reveal that this membrane possesses mesostructure with pore diameter of 3.940 nm and BET surface of 0.484 m²/g. Scanning electron microscopy (SEM) studies show that the layers are defect free and energy diffraction X-ray analysis (EDXA) confirms the compositional element of silica. Propylene and nitrogen permeation tests also confirmed that the membrane is defect free with C₃H₆/N₂ selectivity of 1.79 higher than ideal Knudsen selectivity.

Keywords: mesoporous membranes, silica membranes, nitrogen adsorption, pore size analysis, hydrocarbon separation

1. Introduction

Hydrocarbons are among the most common air pollutants expelled from many industrial processes e.g. chemical (Khan & Ghoshal, 2000), metal cleaning (Huang & Lin, 1997) among others. The venting of these hydrocarbons to the atmosphere is an enormous contribution to poor air quality. From an environmental point of view, it is imperative to separate these hydrocarbons from waste gas stream. Different countries in the world have regulations in place that tightly regulate these emissions. The United States Environmental Protection Agency proposed the air quality standards of a maximum 3 hour concentration of hydrocarbon content not to exceed $1.6 \times 10^{-4} \text{ kgm}^{-3}$ (0.24 ppm) (Ghoshal & Manjare, 2002). The European community has set a limit not to exceed 35 g of total organic compounds (TOC) per cubic meter gasoline loaded (Ghoshal & Manjare, 2002). In addition, the Gothenburg Protocol that was adopted by the EU in 1999 to abate acidification, eutrophication and ground level ozone sets emission levels for sulphur, nitrous oxide, VOCs and ammonia hence, when fully implemented it is expected that European VOC emission will be cut down by 40% when compared to 1990 levels (Derwent, *et al.* 2010). In many countries emissions of VOCs and non methane volatile organic compounds (NMVOCs) are not subject to control, hence loss of hydrocarbons into the atmosphere can cause severe environmental pollution and great monetary loss. A number of emerging techniques are being developed as a substitute to more established processes such as absorption, adsorption and condensation and membrane processes (Khan & Ghoshal, 2000; Huang & Lin, 1997).

Membrane processes has recently emerged as the state-of-the-art technology for such application. This technique was earlier applied in the last five decades for desalination purposes (Khan & Ghoshal, 2000), volatile organic compounds (VOC) removal (Khan & Ghoshal, 2000; Huang & Lin, 1997; Tahir & Koh, 1999; Saracco & Specchia, 2000; Pina, *et al.*, 1996; Pina, *et al.*, 1997; Benard, *et al.*, 2009; Benard, *et al.*, 2010) and natural gas processing (Kajama, *et al.*, 2014). Polymeric membranes such as hollow fibre composite membrane of silicone rubber have been used. Polymeric membranes have very low permeabilities for solvents but their selectivities are quite high (Huang & Lin, 1997). Indeed, polymeric membranes cannot resist harsh chemical environments and cannot withstand high temperatures. Therefore, ceramic membranes can substitute polymeric membranes since these are chemically resistant and thermally stable. The driving force (partial or total pressure) is the pressure difference across the membrane (Vercauteren *et al.*, 1998). Gas transport mechanisms through porous membrane

include: surface diffusion, Knudsen diffusion, capillary condensation, Poiseuille or viscous flow, and molecular sieving mechanisms (Coronas & Santamaria, 1999; Lee & Oyama, 2002; Sidhu & Cussler, 2001). In Knudsen diffusion mechanism, gas molecules diffuse through the pores of the membrane and then get transported by colliding more frequently with the pore walls (Lee & Oyama, 2002; Phattaranawik, *et al.*, 2003), Knudsen mechanism also occurs if the mean free path (λ) of the permeating gas molecule is greater than pore diameter (d). This indicates that the Knudsen number (K) is greater than 1, i.e. $K = \lambda/d > 1$ (Sidhu & Cussler, 2001). Viscous flow mechanism takes place if the pore radius of the membrane is greater than the mean free path of the permeating gas molecule (Lee, *et al.* 2005; Benito, *et al.* 2005). Gas separation by molecular sieving mechanism takes place when the pore dimensions of the inorganic ceramic membrane approach those of the permeating gas molecules (Li, 2007; and Lee, *et al.* 2005). In capillary condensation mechanism, separation can take place in the pores of the membrane with mesoporous layer in the presence of condensable gas species. Surface diffusion mechanism occurs when the adsorption of the permeating gas molecule occurs on the pore surface of the membrane material thereby increasing the gas transport performance (Lee, *et al.* 2005; Javaid, *et al.* 2005).

Uhlhorn, *et al.* (1990; 1992) used gamma alumina (γ -Al₂O₃) membranes with a pore diameter of 2.5 nm and magnesium oxide (MgO) modified membranes with a lower pore size in order to separate propene from nitrogen (C₃H₆/N₂) mixtures. The membranes recorded both permeabilities and separation factors higher than those for Knudsen diffusion.

The characterization of porous ceramic membranes is typically elaborated by the flux and the selectivity which are influenced by the pore size distribution, intrinsic membrane surface properties and porosity (Smart, *et al.* 2013). According to the International Union of Pure and Applied chemistry (IUPAC) definition, membranes pores structure are classified as mesoporous (2-50nm), microporous (< 2nm) and macroporous (> 50nm) layers. Porous metallic membranes with the pore size greater than 0.3nm are normally used as sieves for larger molecules and particles (Li, 2007; Guizard & Princivalle, 2009; Ismail & David, 2011).

Scanning electron microscopy (SEM) is a technique used to analyse the morphological surface of the membrane and their cross-sections. It can also be employed for high magnification of the membrane separation layer. Energy diffraction x-ray analysis (EDXA) is used to analyze the elemental compositions of the membrane. N₂ adsorption-desorption isotherm (77 K) is a standard technique employed to characterize the pore structure and network of a material. It is perhaps simple and the most widely used method to determine the specific surface area, pore size and pore size distribution for meso and micro porous adsorbents (Smart, *et al.* 2013; Choma, *et al.* 2003). The gas adsorption isotherm is divided into six categories (Smart, *et al.* 2013; Choma, *et al.* 2003; Weidenthaler, 2011). Five of the six categories are mentioned in the IUPAC recommendations (Choma, *et al.* 2003).

Type I isotherm is governed by adsorption in micropores sample (with < 2nm pore size) at low relative pressure, while Type II isotherm is regarded as a non-porous or macroporous (with > 50nm pore size) adsorbents formation of multilayers of adsorbate on surfaces of adsorbent. Type III isotherm is also a non-porous or macroporous adsorbents with weak adsorbent-adsorbate interactions. Type IV isotherm is a typical mesoporous adsorbents with initial monolayer-multilayer coverage on external and mesopore surface and is followed by capillary condensation in mesopores with different types of hysteresis loops which are observed depending on the shape of pores. Type V isotherm is also a mesoporous adsorbents with weak adsorbent-adsorbate interactions. An example of this uncommon isotherm is observed for water adsorption on activated carbon (Weidenthaler, 2011). Type VI isotherm is a highly uniform surface which shows a layer-by-layer adsorption (Smart *et al.* 2013; Choma *et al.* 2003; Weidenthaler, 2011).

In this study, the permeation of propylene and nitrogen through silica membrane were carried out at various pressures as the driving force and ambient temperature. N₂ sorption at 77 K, SEM and EDXA were employed for membrane characterization.

2. Experimental

2.1 Membrane Support

Commercially available porous alumina supports of tubular configuration supplied by CTI (France) consisted of 77% alumina + 23% TiO₂ were employed for this experiment. The tubular alumina support used for this experiment is depicted in Figure 1. The alumina support had an internal and outer diameter of 7 and 10 mm respectively with a permeable length of 348 mm and a porosity of 45%.



Figure 1. Commercial tubular ceramic support

Pressures of 0.05 to 0.45 barg and temperatures of 22 °C (295 K) were applied. Crushed samples of the unmodified and modified membranes (Figure 2 a and b) were used for characterization (nitrogen adsorption and scanning electron microscopy respectively).

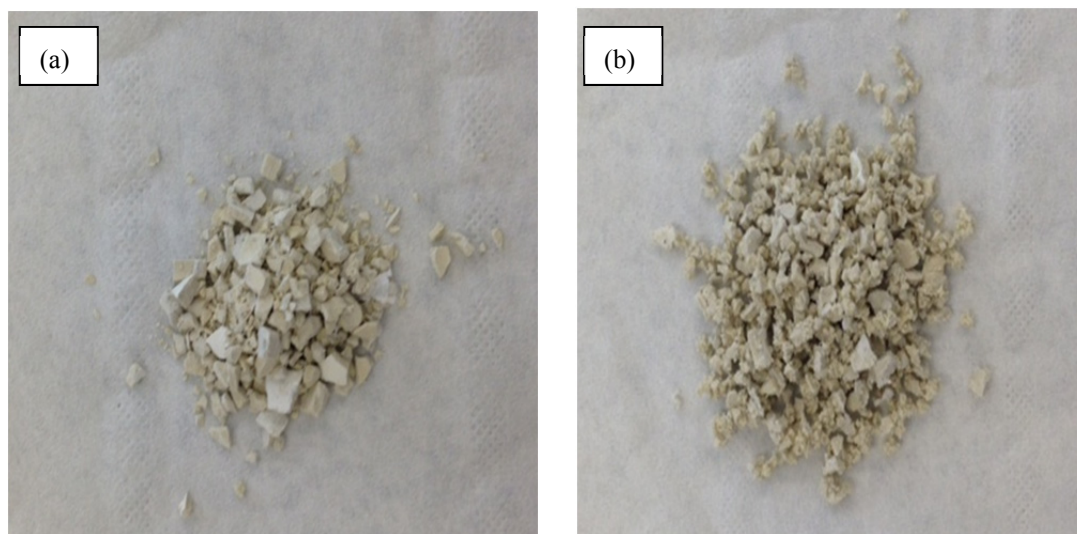


Figure 2 (a). Crushed sample of the support (unmodified), (b). Crushed sample of silica membrane (modified)

2.2 Membrane Preparation

The solution use for membrane preparation was prepared by mixing 50 ml of silicone elastomer (Sylgard[®]) and nine parts of isopentane contained in a glass tube to obtain a clear and colourless solution. A curing agent (Sylgard[®]) 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 °C for 24 hours (Gobina, 2006; Nwogu, et al. 2013) to form an ultra-thin layer on the support. The same procedure was repeated for subsequent coatings.

2.3 Membrane Characterization

The Brunauer-Emmett-Teller (BET) method for surface area, Barrett-Joyner-Helanda (BJH) method for pore size distribution, and the adsorption-desorption isotherm of unmodified support and silica modified membrane were obtained from N_2 sorption isotherm (Quantachrome instrument version 3.0). Prior to N_2 sorption analysis, weighted crushed samples were degassed for 180 min at $300\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C}/\text{min}$. The inner, outer and cross-sectional surface morphologies of the support and membrane were analyzed by SEM (Zeiss EVO LS10). The support was found to be defect free. EDXA was also employed to analyze the elemental compositions of the material before and after modification.

2.4 Gas Permeation Measurements

Permeation behaviour of pure gases nitrogen (N_2) and propylene (C_3H_6) were measured at different feed pressures ranging from 0.05 to 0.45 bar. Permeate readings were recorded as l/min at ambient temperature.

3. Results and Discussion

3.1 Structure of Unmodified and Modified Membranes

Figure 3(a and b) depicts the SEM images of the inner and outer surface of the unmodified membrane. The images exhibit a defect free support. Figure 4(a and b) depicts the inner and outer surface of the silica modified membranes. It can be seen in Figure 4(b) that ultra-thin layer was formed on the outer surface of the membrane and the silica layer is clearly visible from the micrograph. From this image, one can see a good bonding to the support without any pinholes on the layer.

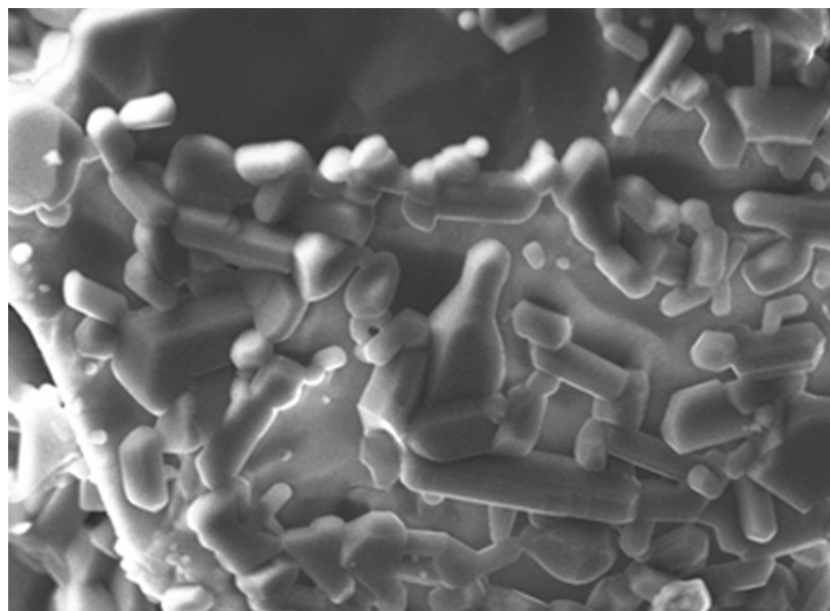


Figure 3(a). SEM image of the support (unmodified) inner surface

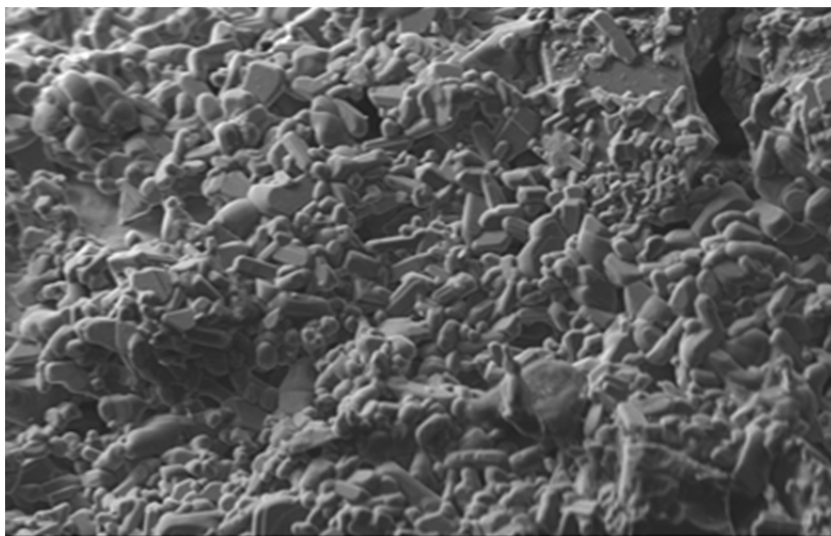


Figure 3(b). SEM image of the support (unmodified) outer surface

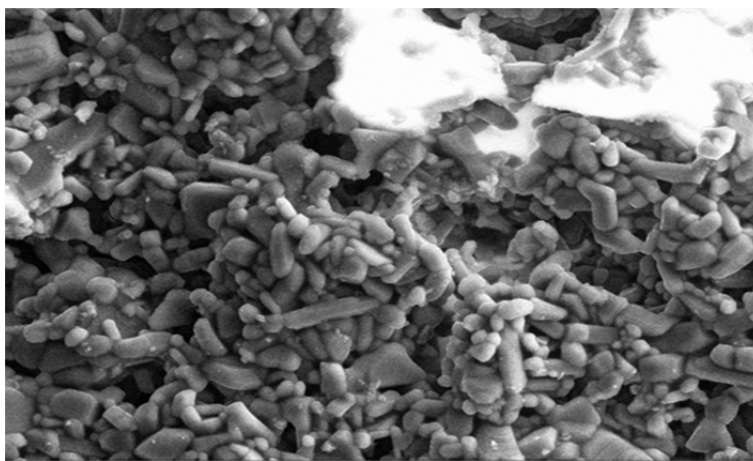


Figure 4(a). SEM image of silica membrane (modified) inner surface

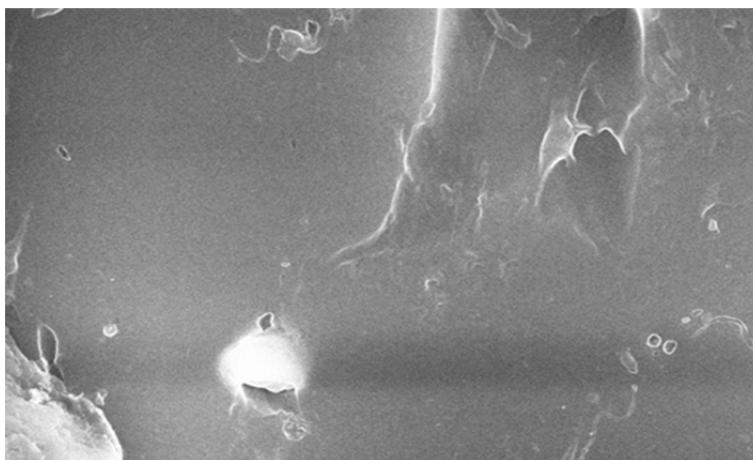


Figure 4(b). SEM image of silica membrane (modified) outer surface

Figures 5(a and b) & Figure 6(a and b) depicts the EDX analysis for unmodified and modified membrane. These Figures show the elemental compositions of the membrane before and after modification. It can be obviously seen in Figure 5(a and b) that there was no sign of silica particle before modification. However, silica particles

were observed after modification as indicated on the EDXA result in Figure 6(b).

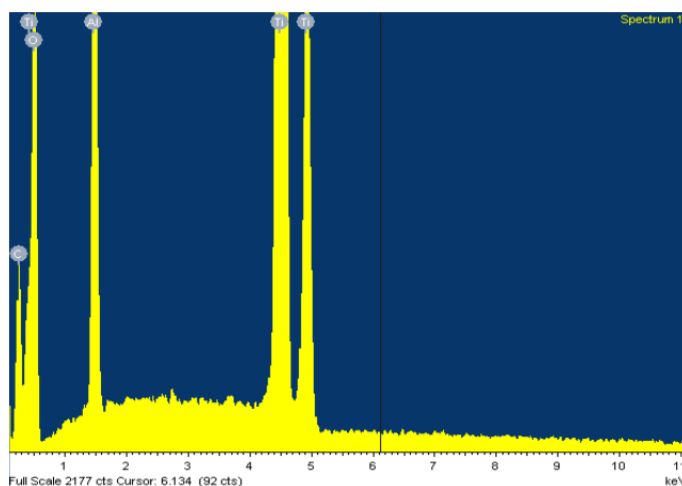


Figure 5(a). EDXA of the support (unmodified) inner surface

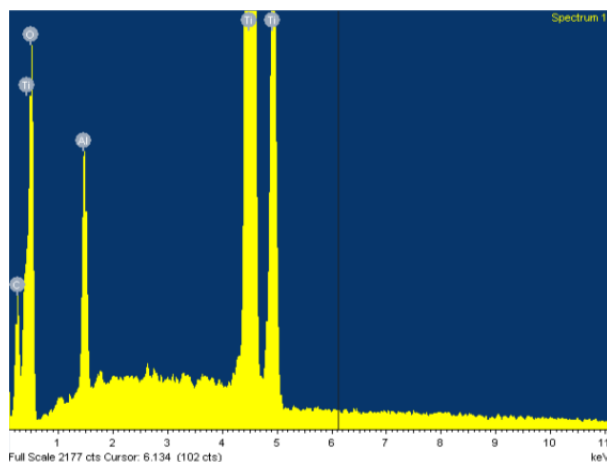


Figure 5(b). EDXA of the support (unmodified) outer surface

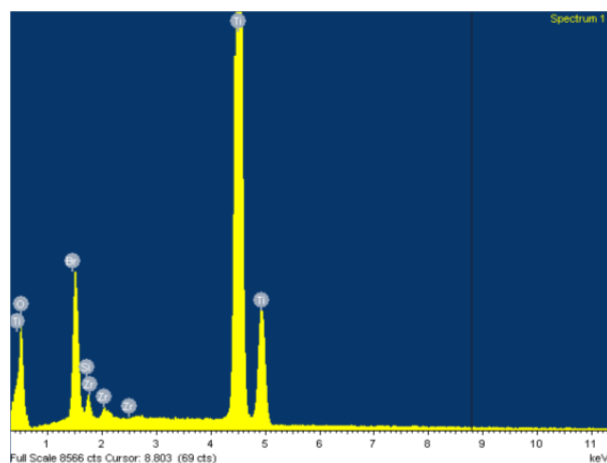


Figure 6(a). EDXA of silica membrane (modified) inner surface

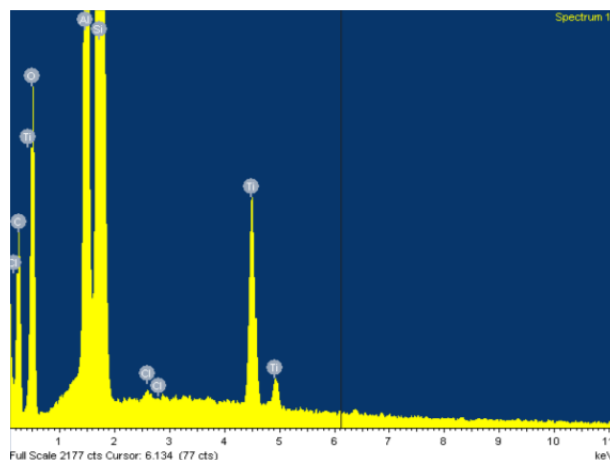


Figure 6(b). EDXA of silica membrane (modified) outer surface

Figure 7(a and b) & Figure 8(a and b) depicts the N₂ adsorption-desorption isotherms of unmodified and silica modified membranes. The adsorption-desorption isotherms exhibits a characteristics of mesopores solids (especially ceramics) resulting in type IV and V physisorption isotherm undergoing capillary condensation and hysteresis during desorption (Smart, *et al.* 2013). Different parameters were obtained for the Brunauer-Emmett-Teller (BET) method surface area and Barrett-Joyner-Helanda (BJH) method pore size distribution. Table 1 quantitatively shows the physical properties obtained with nitrogen adsorption for the unmodified alumina support and modified silica membrane. The BET surface area and BJH pore diameter were 0.364 m²/g and 4.171nm for the unmodified support and 0.439 m²/g and 4.179nm for the modified membrane respectively. BET surface area increased to about 0.484 m²/g after subsequent dipping. BJH pore diameter also decreased from 4.171 to 3.940nm which indicates that some amount of silica has penetrated into the support pores which shows a typical mesopore diameter in the range 2 to 50 nm. This is consistent with the above SEM and EDXA results.

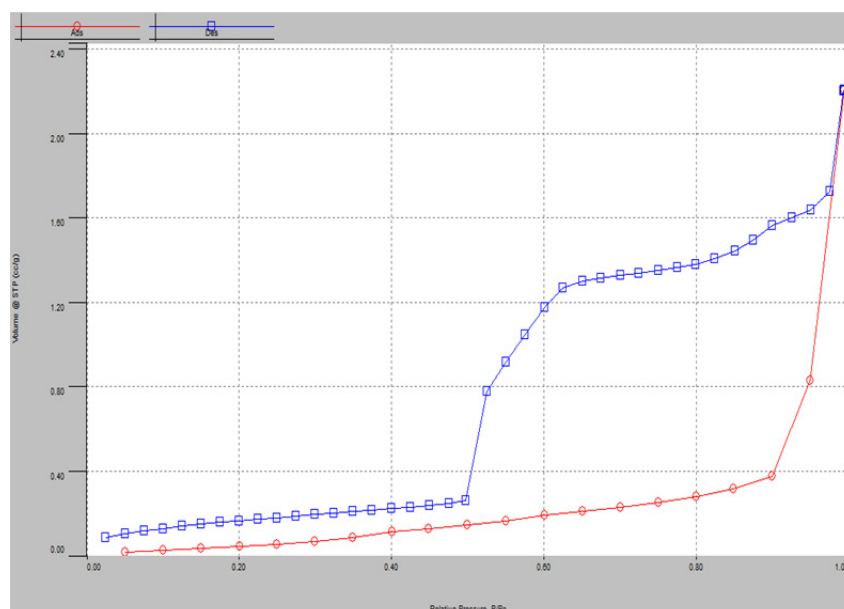


Figure 7(a). N₂ adsorption-desorption isotherm for the support (unmodified)

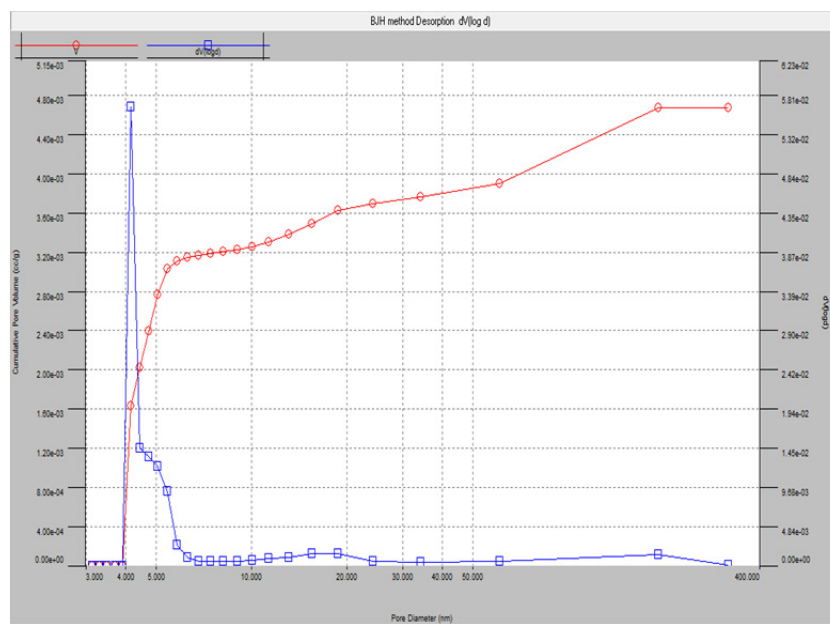


Figure 7(b). Pore size distribution for the support (unmodified)

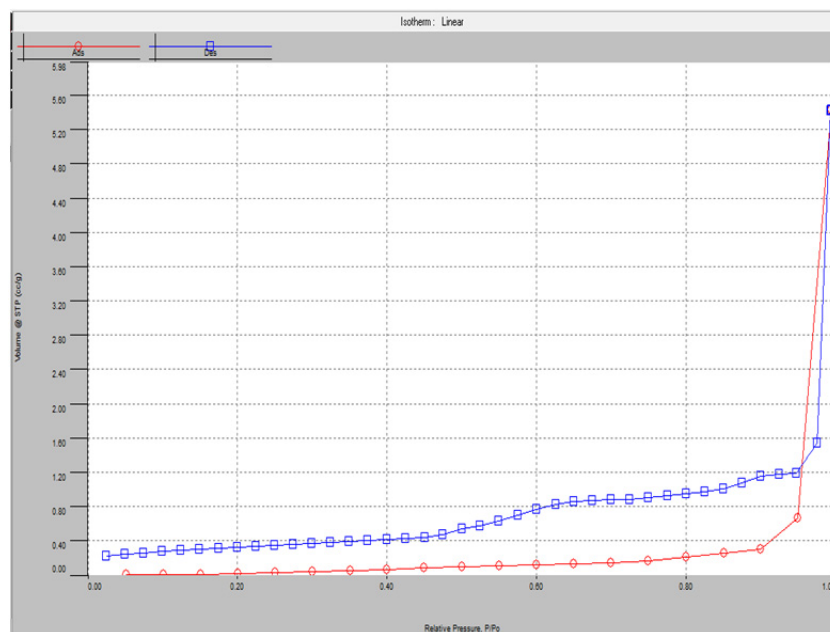


Figure 8(a). N₂ adsorption-desorption isotherm for the silica membrane (modified)

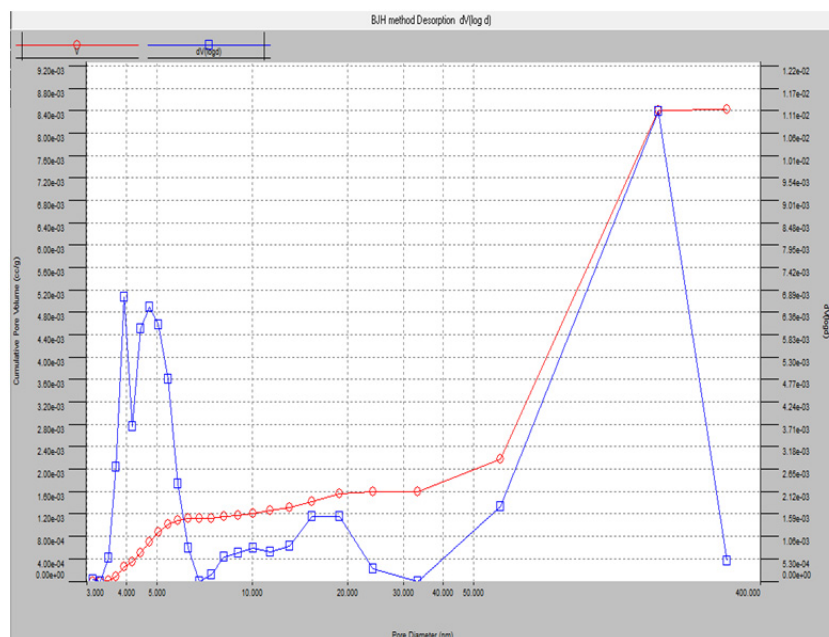


Figure 8(b). Pore size distribution for the silica membrane (modified)

Table 1. Physical properties for unmodified and modified membranes

Membrane	BET surface area (m ² /g)	BJH pore diameter (nm)
Unmodified Ceramic Support	0.364	4.171
Silica Modified Membrane (5 th Dip)	0.439	4.179
Silica Modified Membrane (9 th Dip)	0.484	3.940

3.2 Nitrogen and Propylene Permeation

Figure 9 depicts gas flow rate through silica membrane as a function of the feed pressure at room temperature. Nitrogen and propylene gas flow rates increases with the feed pressure. It can be seen that propylene has the higher flow rate compared to nitrogen despite its higher molecular weight (N_2 : 28 g/mol; C_3H_6 : 42 g/mol). This result is consistent with the contribution of surface flow mechanism. Figure 10 shows the selectivity of C_3H_6 over N_2 . Highest selectivity of 1.79 at 0.05 barg was obtained. This selectivity increased by a factor of 2 compared to the ideal Knudsen selectivity (0.82) which corroborates with the literature Uhlhorn, *et al.* (1990; 1992). From the obtained gas permeation and selectivity, one can conclude that hydrocarbon could be separated from nitrogen.

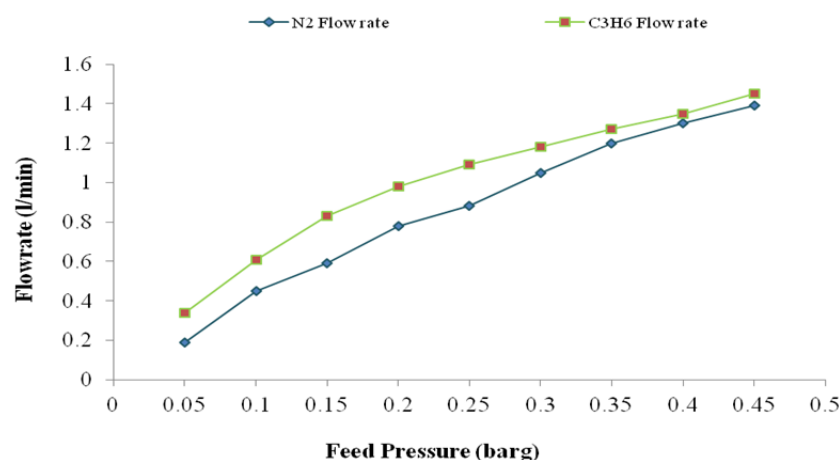


Figure 9. Gas flow rates of nitrogen and propylene as a function of feed pressure at room temperature

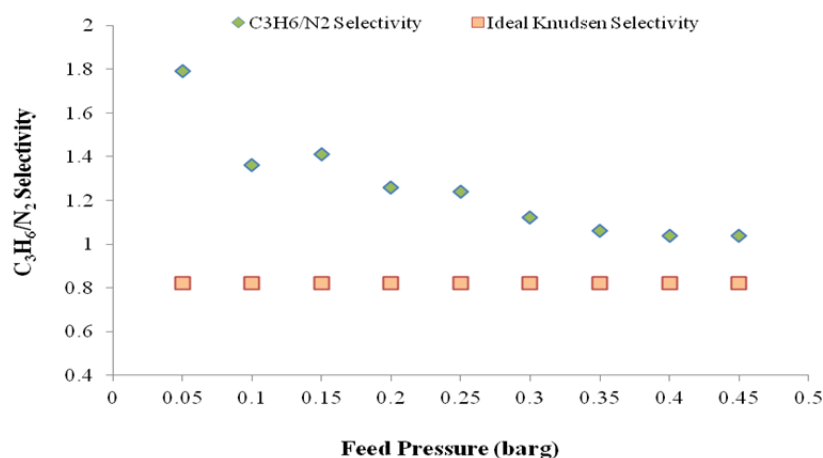


Figure 10. C₃H₆/N₂ selectivity as a function of feed pressure at room temperature

4. Conclusion

Defect-free mesoporous silica membrane has been developed on the alumina substrate by dip-coating technique. The BET surface area and BJH pore diameter of the membrane are 0.484 m²/g and 3.940 nm respectively. The prepared membrane was defect free as confirmed by the propylene and nitrogen permeation data. The high propylene selectivity obtained at low pressure drop is indicative of selective surface flow mechanism. Work is currently being carried out to compare mixed gas selectivity to pure gas selectivity.

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