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Characterisation of Inorganic Composite Ceramic Membrane for Lactic Acid Esterification Processes

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Abstract. The use of inorganic composite membranes in chemical industries has received a lot of attention more recently due to a number of exceptional advantages including thermal stability and robustness. Inorganic membranes can selectively remove water from the reaction mixture during esterification reactions in order to enhance product formation. The characterisation of inorganic composite membranes used in this work including the determination of the pore diameter and specific surface area was performed using Liquid Nitrogen adsorption at 77 K. The membrane was modified once. The permeation test for the single gases including carbon dioxide (CO_2), helium (He), nitrogen (N_2) and argon (Ar) through the inorganic composite ceramic membrane was carried out at the gauge pressure range of 0.10 – 1.00 bar and at the temperature of 393 K. The order of the gas molecular weight was He < N_2 < CO_2 < Ar. The BET surface area of the dip-coated silica membrane showed a type IV isotherm characteristic of mesoporous structure with hysteresis. The BJH curve of the silica-membrane was in accordance with mesoporous classification.

Introduction

Lactate ester is obtained from bio-based feedstock in which its separation is achieved from the esterification of ethanol and lactic acid generated from biomass raw materials. This solvent can replace the use of environmentally-damaging toxic and halogenated solvents such as chloroform and carcinogenic methylene chloride [1]. The use of inorganic ceramic membrane to selectively eliminate water from the reaction product during esterification of lactic acid is another important application that has attracted a lot of attention [2]. Inorganic membranes have found significant potential applications in high temperature and high pressure separation, filtration and catalytic membrane reactor due to its unique structure, chemical and thermal stabilities [3]. The ability of a membrane to allow the separation of mixtures is based on two parameters including selectivity and permeability of the membrane material. Selectivity is defined as the ability of a membrane to separate two different species, while permeability relates to the flux through the membrane with respect to the thickness and driving force of the membrane [4]. The reduction of pore diameter of the inorganic membranes can be achieved using different methods such as sol-gel, chemical deposition and sintering methods [3]. The gas transports through inorganic membranes are classified into five different classes namely: capillary condensation, Knudsen diffusion, surface diffusion, viscous flow and molecular sieving mechanisms. However, these mechanisms also depend on the chemical interaction between the permeating gas molecules, the membrane material and also pore size distribution of the membrane [5]. In Knudsen flow mechanism, gas separation depends on the inverse square root of the gas molecular weight. Viscous flow mechanism occurs when there is a defect or a crack on the structure of the membrane and as such, the gas molecule can move across the membrane without any separation taking place. Molecular sieving mechanism usually occurs in microporous or submicroporous systems whereby separation occurs by the diffusion of smaller molecules. Surface diffusion depends on both the mobility and adsorption of the membrane. In solution diffusion, the gas molecule dissolves into the membrane material and diffuses to the permeate side [4].

Experimental

Permeation Tests

The permeation tests of single gases (helium, nitrogen, carbon dioxide, and argon) were carried out at 120 ºC to determine the gas transport mechanism based on the procedure developed by Gobina (2006) [6]. The schematic diagram of the permeation test setup is shown in figure 1.

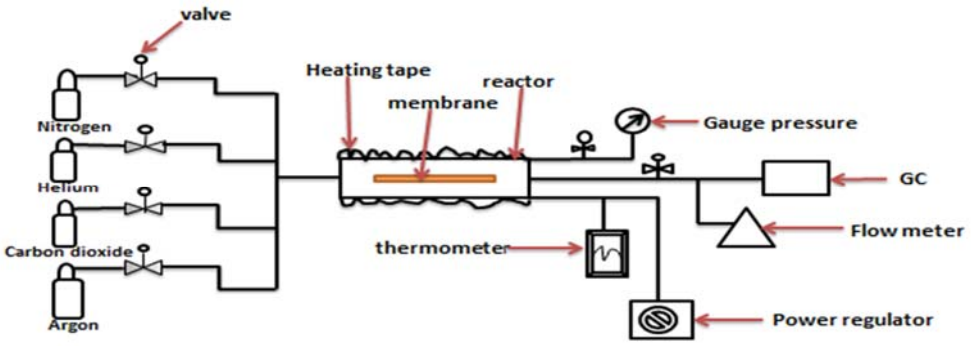

Fig 1. Schematic diagram of gas permeation setup [7].

Nitrogen Adsorption

Figure 2 shows the schematic diagram of the Liquid Nitrogen adsorption instrument. The sample was weighed before and after the analysis. Prior to the analysis, the sample was degased with helium and nitrogen gases in order to remove impurities before the analysis and also for measuring the total volume of the sample. The degassing temperature was set at 65 ºC for 2 hrs prior to the sample analysis. The liquid nitrogen temperature was 77 K. The surface areas of both the internal and external pores of the membrane support were determined using the Brunauer-Emmett-Teller (BET) isotherm while the pore size distribution of the sample was obtained using the Barrette-Joyner-Halenda (BJH) curve. A similar procedure to that of Vospernik et al. (2004) [8] was employed in the analysis with some modification in the temperature. The sample cell was 27.7g while the membrane + sample cell was 34.8g. The sample was analysed at 350 ºC for 6 hrs after the degassing process.

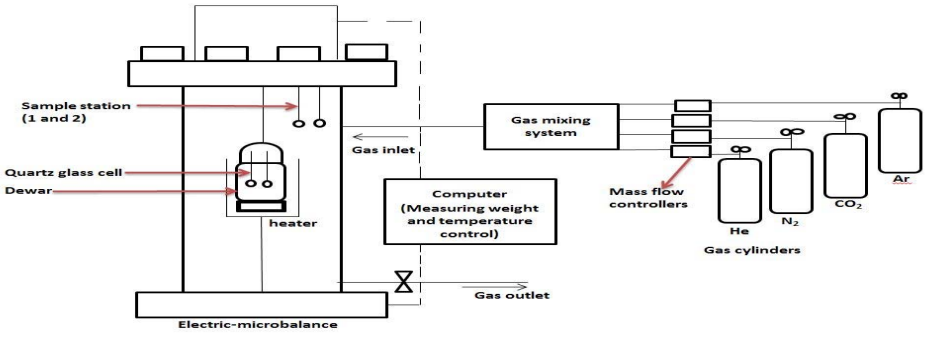

Fig. 2 Schematic diagram of the liquid nitrogen adsorption.

Results and discussion

Figure 3 shows the plot of the gas permeance ($molm^{-2}s^{-1}Pa^{-1}$) against the inverse square root of the gas molecular weight (mol/g) at 393 K.

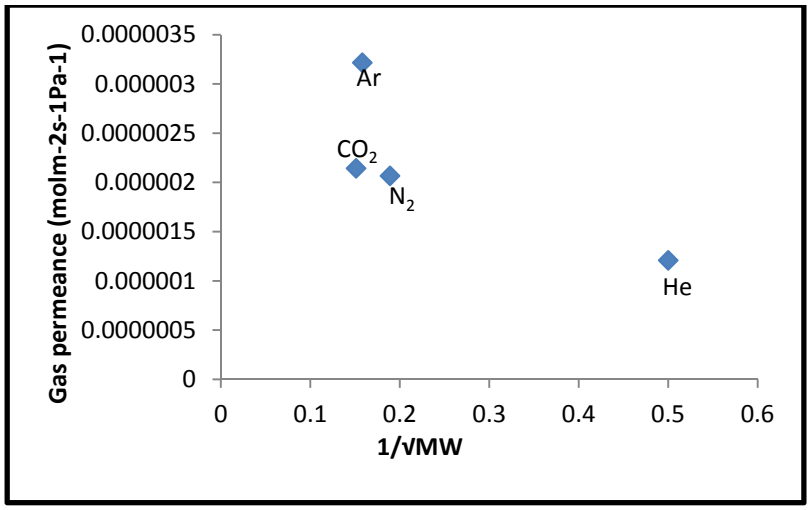

Fig. 3 Gas permenace ($molm^{-2}s^{-1}Pa^{-1}$) against inverse square root of the gas molecular weight (mol/g) at 393 K.

From figure 3 it was found that Ar with the molecular weight of 40g/mol showed a higher permeance in contrast to CO_2 with the molecular weight of 44g/mol. For the gas flow to be described by Knudsen mechanism of transport, it was expected that the result in figure 3 could have been a straight line graph starting from the origin with CO_2 (44g/mol), Ar (40g/mol), N_2 (g/mol) and He (4g/mol) point passing through the best fit line. However, it was suggested that Knudsen flow mechanism was responsible for CO_2 and N_2 gas flow, whereas He and Ar were controlled by another flow mechanism at 393K. The decreasing order of the gas molecular weight is given as $He < N_2 < Ar < CO_2$.

The graph of volume (cc/g) was plotted the relative pressure (P/P_o) to obtained the BET and BJH curves for the surface area and the pore diameter analysis of the dip-coated membrane. Figure 4 and 5 shows the BET and BJH curves for the dip-coated silica membrane.

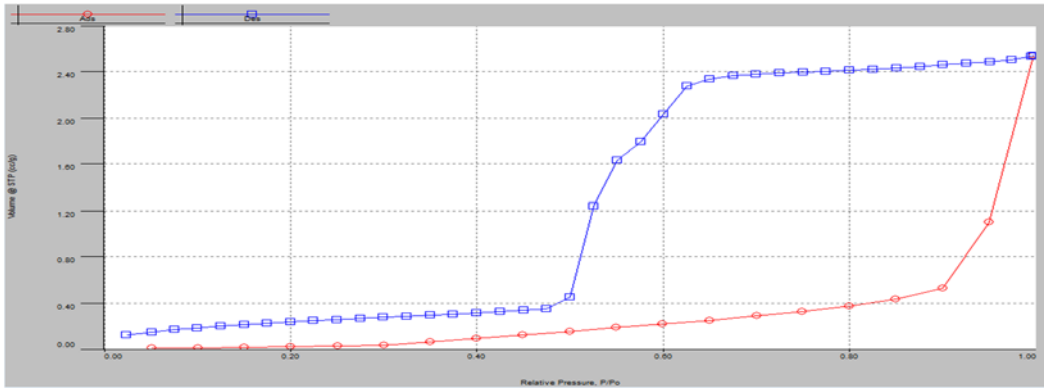

Fig. 4 Nitrogen adsorption isotherm for dip-coated silica membrane at 77 K.

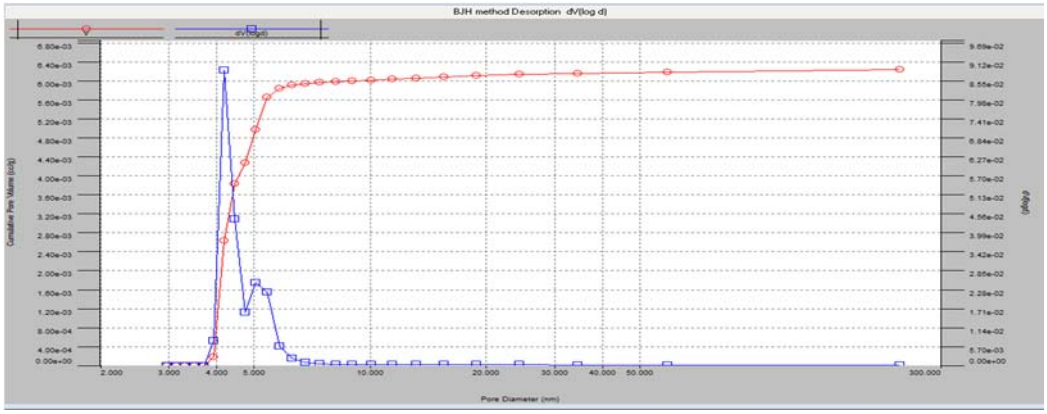

Fig. 5 BJH curve for dip-coated membrane at 77 K.

From the result obtained in Figure 4, it was observed that the silica membrane showed a type IV isotherm with hysteresis indicating a mesoporous layer which is classified in the range of 2 – 50nm. The surface area of the ceramic membrane was found to be 5.306m^2/g while the pore diameter of the membrane was 4.180nm. The result obtained from the BJH curve in Figure 5 also confirmed that the membrane pore diameter (4.180nm) was in accordance with the mesoporous classification range which will be compared in subsequent analysis.

Conclusion

The inverse square root of the gas molecular weight in relation to the gauge pressure did not show any evidence of Knudsen mechanism of gas transport. The Knudsen flow mechanism was responsible for CO_2 and N_2 gas flow which were found to be close to the best fit line, whereas He and Ar gas flow was controlled by another flow mechanism at 393K. The surface are of the dip-coated membrane possess a type IV isotherm with hysteresis indicating a mesoporous layer in the range of 2-50nm. The result for pore diameter of the silica membrane corresponded with the mesoporous membrane classification.

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