Research Paper

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Initial Study of Gas Separations and Esterification Using A Composite Y- Type Zeolite Membrane

Engineering

KEYWORDS : zeolite, esterification, gas transport mechanism

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INTRODUCTION

The separation of hydrocarbons from air mixtures is one of the major objectives of chemical and petrochemical industries. There are various methods that these industries employ to achieve good separation. These include adsorption, rectification, membrane technology and use of cryogenics[1]. Modern membrane technology can also be used in implementing Process intensification (PI) which is an innovative design method that is aimed at decreasing production cost, waste generated and size of equipment used as well as energy utilization[2]. Gas separations using membranes is a pressure driven process that has numerous industrial applications in chemical and petro-chemical industries including petroleum refineries[3]. In recent years there has been an increase in demand for light hydrocarbons for use as petrochemical feedstock and for fuel. This has been met to a large extent by the recovery of these components from petroleum gases and natural gas by the use of a depropanizer[4]. The use of membranes for gas separations is growing at a slow but steady rate[5]. Baker in 2002 made an estimate that the market scale of gas separations using membrane technology by the year 2020 will be five times that of year 2000[5]. There are many opportunities for membrane gas separations as many efforts have been made in the last couple of years to develop an effective method for the separation and subsequent removal of impurities from natural gas. There are ongoing researches on the use of nano-composite membranes to separate gaseous mixtures hence making it one of the emerging technologies that is growing fast. The membrane to be used for crude oil and natural gas processes have to be selective for hydrocarbon vapours and be chemically and thermally stable[6].

The use of inorganic membranes can also be incorporated in the petrochemical industries to selectively eliminate water from the reaction product during esterification of lactic acid to form ethyl lactate[7]. Ethyl Lactate (EL) is an important organic solvent produced from biomass and considered to be biodegradable. It can be used as food additives (can be found in soy products, wine and beer), agricultural processes (used in cadmium and copper removal from the contaminated soil), flavor chemicals and perfumery[8]. The US Food and Drug Administration (FDA) have approved the use of EL in food products due to its low toxicity[9]. Recently, the production of EL from the esterification process of lactic acid with the respective alcohol in the presence of a catalyst suffers the major drawback of purity and low conversion due to chemical equilibrium[10]. Generally, esterification reactions are usually limited by equilibrium and therefore do not reach completion. Although the traditional method of solving equilibrium problems in esterification reactions involve the addition of an excess amount of alcohol to the reaction system[8], using a membrane can result in higher conversion by shifting the chemical equilibrium towards the formation of the product by in-situ removal of water from the reaction mixture[11].

Microporous inorganic membranes having pore sizes of less than 2 nm have been studied extensively for gas separation applications because of their good resistance to harsh chemicals, good thermal and mechanical stability as well as stability under high pressure when compared to polymeric membranes[21]. Today much of the research work is being directed towards the investigation of new membrane material and the development of new membrane structures that exhibit both higher selectivity and permeability of the target gases[15]. Zeolite crystals have been seen from literature to act as separation membrane as they have regular and well defined pore size and structure.

A membrane's permeance and selectivity has an influence on the economics of a gas separation process[15]. Permeance is the rate at which a substance permeates through a membrane and is dependent on several factors like the pore size and material of the membrane. The selectivity of a membrane is the fundamental parameter to achieving high product purity as well as high recoveries; hence for the potential growth of membrane gas separation process, the production of highly permeable and selective membranes for the desired gas is essential. The development of inorganic membranes like silica and zeolite has increased the potential of membrane gas separation applications as they can withstand aggressive chemicals as well as high temperatures. However, the drawbacks on the use of such membranes, includes their high cost, modest reproducibility, brittleness, low membrane area and low permeability in the case highly selective dense membranes[3].

Several polymeric membranes were characterised and their permeation properties for the separation of propylene and toluene were investigated[12,13,14,15]. An important feature in the preparation of polymer membrane for gas separations is the process of spinning them into hollow fibre membranes and due to its large area is suitable for large-scale industrial applications[2]. The major drawback for the use of these polymeric membranes is that they are unable to withstand high temperatures and harsh chemical conditions. In petrochemical plants, natural gas treatment plants and refineries this can be a problem as the feed gas streams usually contains heavy hydrocarbons and the polymer membranes can be plasticised or become swollen[3]

The separation of gases in membranes is driven by the difference in the rate of movement of the different species through the membrane. For membranes having large pore sizes of 0.1 to 10 μm, the gases permeate via convective flow and there is noseparation of the gases because flow depends on the viscosity of the gases. For mesoporous membranes, separation is based on the collision between the gas molecule and the membrane pore wall and hence the mean free path of the gas molecules is greater than the pore size. The diffusion here is governed by Knudsen mechanism and the rate of transport of any gas is inversely proportional to the square root of its molecular weight[17]. However, for a microporous membrane with pore size less than 2 nm, separation of gases is based mostly on molecular sieving. The transport mechanism in these membranes is often complex and involves surface diffusion that occurs when the permeating species exhibit a strong affinity for the membrane surface and thus adsorbed on the walls of the pores[17].

The permeation of gases through a membrane is dependent on both the diffusion and the concentration gradient of the species along the membrane. The selective transport of a gas molecule through a membrane is often associated with the pressure, temperature, electric potential and concentration gradient. The permeability and selectivity are some of the parameters that are used to determine a membrane's performance. The permeance P ($molm^{-2}s^{-1}Pa^{-1}$) represents the proportionality coefficient with the flux at steady state of a particular gas through a membrane:

$$P = \frac{Q}{A.\Delta p} \qquad [1]$$

Where Q is the molar gas flow rate through the membrane ($mols^{-1}$), A is the membrane surface area (m^2) and Δp is the pressure difference across the membrane (Pa).

For a multilayered membrane, the separation layer thickness is determined by weighing the support before and after modification and is calculated by the following equation[22]:

$$\delta = \frac{W_2 - W_1}{A\rho(1-\epsilon)} \qquad [2]$$

Where A is the membrane area (m^2), ρ is the density of the membrane (gcm^{-3}), ε is the porosity (%) and w_1 and W_2 are the initial and final weight of the membrane respectively (g).

The permeability$P_r$of the membrane is a measure of the quantity of a component that permeates through the membrane[25] and is given by the equation:

$$P_r = \frac{P}{\delta} \qquad [3]$$

The calculated gas selectivity is the ratio of the permeability coefficients of two different gases as they permeate independently through the membrane is given by:

$$\alpha_{ij} = \frac{P_i}{P_j} \qquad [4]$$

Where P_i and P_j is the permeance of the single gases through the membrane. Knudsen selectivity is used to predict the selectivity of one gas over the other, and is given by:

$$\alpha_n = \frac{1}{\sqrt{\frac{M_1}{M_2}}} \qquad [5]$$

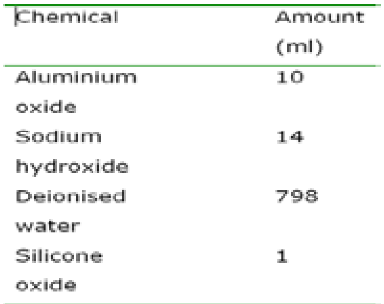
The selectivity is the measure of the ability of a membrane to separate two gases and it is used to determine the purity of the permeate gas as well as determine the quantity of product that is lost.

EXPERIMENTAL

Membrane preparation process

A solution containing Silicone oxide, aluminium oxide, sodium oxide and deionised water was prepared and homogenised at room temperature for 20 hours, the amount of each substance used is given in Table 1. Zeolite crystals were deposited on alumina support which is subsequently dipped into the solution and kept for 20 hours at 343 K. The membrane was washed with deionised water and the pH of the rinse water was monitored. When the rinse water pH was neutral the membrane was air dried for 20 minutes and thermally treated in the oven at 338 K for 2 hours prior to permeation test.

TABLE - 1
Composition of the modification solution for zeolite membrane



Chemical	Amount (ml)
Aluminium oxide	10
Sodium hydroxide	14
Deionised water	798
Silicone oxide	1

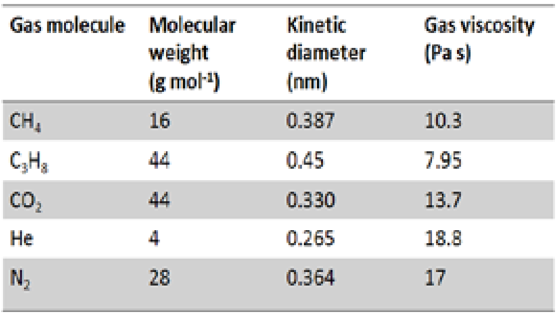
Characterisation

The membrane was characterized and the morphology was determined by the use of the Zeiss EVO LS10 scanning electron Microscope (SEM) with an Oxford Instruments INCA System dispersive X-Ray Analyzer to determine the elemental composition of the membrane.

Permeation measurements

The performance of the zeolite membrane was evaluated by measuring single gas permeances and using equation 2 to calculate the selectivity for a gas pair. Various gases with different kinetic diameters and molecular weights (CH_4, C_3H_8, He, CO_2, and N_2) were fed separately into the membrane at 298 K. The gauge pressure used was in the range of 0.1 MPa to 1 MPa. The permeance of the gases through the membrane was calculated by the use of equation 3. Table 1 gives the molecular weight and kinetic diameter of the permeated gases.

Table 2: Molecular weight and kinetic diameter of the permeated gases (adapted from 38)



Gas molecule	Molecular weight (g mol⁻¹)	Kinetic diameter (nm)	Gas viscosity (Pa s)
CH_4	16	0.387	10.3
C_3H_8	44	0.45	7.95
CO_2	44	0.330	13.7
He	4	0.265	18.8
N_2	28	0.364	17

RESULTS AND DISCUSSIONS

Permeation properties

Effect of the kinetic Diameter

The flux of the gases was expected to follow the order of the kinetic diameter of the gases as zeolites from literature[3] are expected to act as molecular sieves and separate gases based on their kinetic diameters. The order of the kinetic diameter of the molecules is He < CO_2< N_2< CH_4 < C_3H_8 (Table 1) hence the gas molecule having the smallest size is expected to have the highest flux and the heaviest is expected to have the lowest flux. Thus an inverse relation exists between the flux and the kinetic diameter.

$$J\ \alpha\ \frac{1}{kd} \qquad [6]$$

Where kd is the kinetic diameter of the gas molecules.

The graph of the flux against the inverse of the kinetic diameter is presented in Fig. 1.

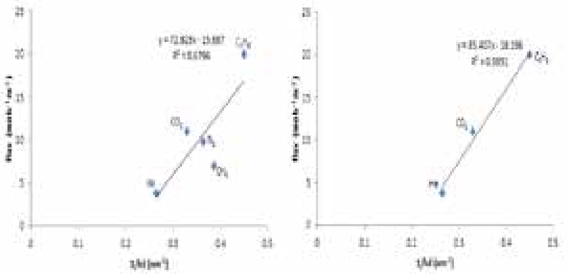


Figure 1: Effect of inverse of kinetic diameter of various gases on the flux of the gases through a zeolite membrane.

The zeolite membrane showed molecular sieving for He, CO_2 and C_3H_8 as can be seen from Fig 1 (a), N_2 and CH_4 did not follow the molecular sieving mechanism as can be seen from Fig. 2 (b). This suggests there could be another mechanism of transport for N_2 and CH_4.

Effect of Molecular Mass

The permeanceof single gases through the Y-type zeolite membrane at 298 K was determined using equation (1). The order of permeance of the gases followed the inverse of the square root of their molecular weight (Table 1), He > CH_4> N_2> C_3H_8 ≈ CO_2. The plot of the gas permeance against the inverse square root of the molecular weights of the gases showed that there is evidence of Knudsen flow mechanism in the flow of the gases through the zeolite membrane. Fig 2 presents the effect of the molecular weights of the gases on their permeance.

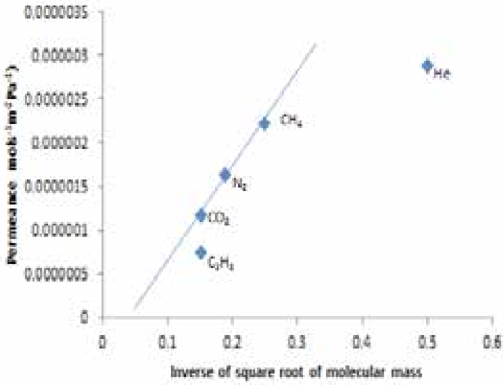


Figure 2: Gas permeance change of various molecules with different molecular weights.

The molecular weights of CO_2 and C_3H_8 are the same at 44 gmol^{-1}, their separation factor calculated using equation (4) at 8 x 10^4 Pa was 1.9 and this shows that molecular sieving mechanism was responsible for the movement of some of the gases.

Effect of viscosity

The effect of the viscosity of the gases on the flux of these gases through the membrane was determined in order to know if the movement of the gases through the membrane could be as a result of viscous flow. Fig. 3 depicts that the gases do not permeate based on their various viscosities.

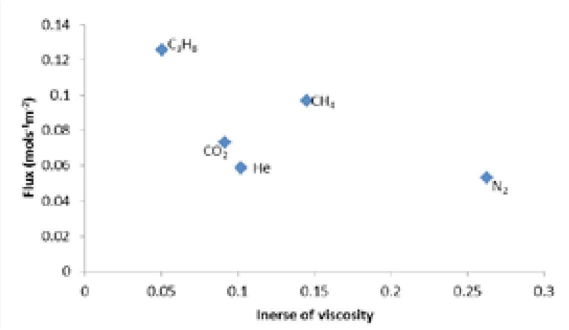


Figure 3: Effect of inverse of viscosity on the flux of gases through a zeolite membrane.

The order of the viscosity is given as He > N_2> CO_2> CH_4> C_3H_8. As expected the gas with the highest viscosity should have the lowest flux, this is exhibited by helium and propane.

Zeolite Membrane Characterisation

SEM image and EDAX spectra of the membrane are shown in Figs. 4 and 5 respectively. The spectrum gives the elemental composition of the membrane and the SEM image shows the layer of zeolite crystals on the ceramic support.

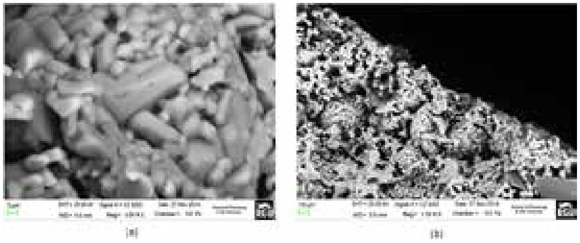


Figure 4: SEM images of the (a) cross sectional view and (b) edge of the zeolite membrane

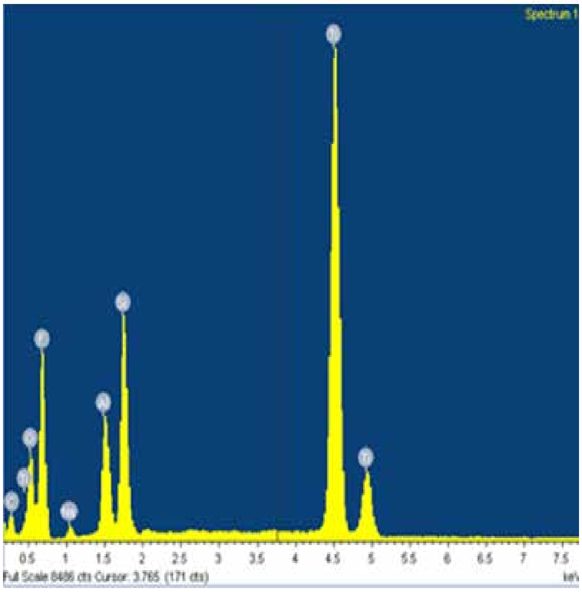


Figure 5: EDAX spectrum of the zeolite membrane

From the cross sectional view image of Fig. 4(a), it can be observed that the pore size of the zeolite layer is not evenly distributed on the membrane support. Using the scale in Fig. 4(b), the thickness of the zeolite layer can be estimated to be less than 10 µm thick. This could account for the transport mechanism of the zeolite membrane. The EDAX spectrum shows the peaks of titanium, silica, aluminium, oxygen and sodium.

CONCLUSION

Y-type zeolite membrane was prepared to determine the separation of lower hydrocarbons from inert gases and from carbon dioxide.The transport mechanism of the gases was studied to determined the feasibility of the membrane to be used to transport carrier gases in the esterification reaction of lactic acid to form ethyl lactate and for use in volatile organic compounds recovery. The membrane has showed evidence of molecular sieving but further modification of the membrane is required to ensure the membrane surface is defect free. This membrane has shown evidence that it could be suitable for the separation of methane, nitrogen and carbon dioxide andfurther work is being carried out to determine the flow mechanism that the membrane exhibits and determine the reproducibility of the preparation technique.

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