Initial Study of Heterogeneous Catalysts Behaviour and Carrier Gas Permeation with Catalytic Inorganic Ceramic Membrane for Lactic Acid Esterification Applications.

O Edidiong and *E Gobina

***Abstract*—Inorganic membranes continue to attract a lot of attention in various fields including industry and academia, due to the great potential they have shown in various applications. Recently, some studies have focused on the water-permeable metallic membrane reactor involving liquid-phase reversible reactions including esterification reactions. Among the membranes considered, inorganic membrane have been found to be the perfect membrane for the esterification reaction process because they can allow heterogeneous catalysts to be deposited easily on the surface of the membrane; this results in increase in the yield of products. The use of inorganic ceramic to selectively eliminate water from the reaction product during esterification of lactic acid is yet another important application that has attracted a lot of attention. In this work, the initial study of heterogeneous catalyst behaviour and carrier gas permeation with inorganic ceramic membrane for lactic acid esterification applications was carried out. Dowex 50W8x, Amberlyst 36, Amberlyst 15 and Amberlyst 16 cation-exchange resins were used as heterogeneous catalysts. The SEM/EDXA of the resin catalyst was investigated in order to determine the surface morphology of the resin. The EDXA of the catalysts showed the presence of sulphur which confirms the sulfonic acid group in the structure of the polymeric compound. The permeation properties of inorganic ceramic membrane with the carrier gases were also analysed between the gauge pressures of 0.01-1.00 bar at the temperature of 60 ^{o}C (333 K). The membrane was coated twice using silica solution before the permeation experiments. The carrier gas permeance of the silica membrane showed a linear dependence on the inverse square root of the gas molecular weight indicating Knudsen mechanism of transport. Gases with highest viscosity value exhibited the least permeance indicating viscous flow contribution. It was concluded that Knudsen and viscous mechanisms plays a major role in the carrier gas permeation with inorganic ceramic membrane**

***Key words*: Carrier gas permeation, esterification, heterogeneous catalyst, inorganic membrane.**

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I. INTRODUCTION

The simplest hydroxycarboxylic acid with an asymmetric carbon atom is regarded lactic acid. This acid can be obtained from biomass, petroleum and coal. Copolymers and polymers of lactic acid are known to be eco-friendly and are compatible due to their biodegradability, which makes them desirable as an alternative petrochemical polymer [1]. Lactic acid can react with ethanol during esterification process to produce ethyl lactate which is used as flavour chemicals, food additive, perfumery and as solvent.

Ethyl lactate is an important organic solvent produced from biomass and considered to be biodegradable. It can be used as food additives, agricultural processes (used in cadmium and copper removal from the contaminated soil), solvent, flavour chemicals and perfumery. It can also be used in the pharmaceutical industry as a dispersing/dissolving excipient for several biological compounds without destroying the pharmacological activity of the active ingredient. It serves as a desirable coating for polystyrene and can also act as paint remover. This solvent has the ability to dissolve a lot of polyurethane resin because of its high solvency properties which has made it an excellent cleaner for the polyurethane industry [2]. Ethyl lactate can replace environmentally damaging solvents including toluene, acetone, N-methyl pyrrolidone and xylene. Membrane-based separation technologies have shown a wide range of application in food, biotechnology, pharmaceutical and in the treatment of other industrial effluents [3].

Membranes can be classified in two groups including inorganic and organic membranes. Inorganic membranes have shown an increasing interest in the separation of gas mixtures at high temperatures. However, one of the most promising use of inorganic membrane is in the reactors where product purification by separation and chemical conversion occurs in the same device resulting in process intensification. Moreover, it is possible to obtain important enhancement over the equilibrium conversion of the reactor feed stream by selectively separating one or more reaction products across the membrane wall [4].

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In the esterification reactions of lactic acid with ethanol, both heterogeneous and homogeneous catalyst can be used [5], [6]. The function of these catalysts during esterification of lactic acid is to give a proton (hydrogen) for a chemical reaction between the molecules of the carboxylic acid [7]. Although homogeneous catalysts have shown excellent performance in terms of the rate of reaction, the interest of this catalyst is said to decrease since the recovery and separation of the catalyst are difficult because of the ability of the liquid acid catalyst to mix with the bulk of the reaction [8]. However, metallic membrane can lose their performance easily as a result of being degraded by this acid catalyst. As such, heterogeneous solid catalysts including cation-exchange resin have been suggested for esterification in order to solve the degradation problems of inorganic ceramic membranes [9]. The use of inorganic ceramic membrane to selectively eliminate water from the reaction product during esterification of lactic acid is yet another important application that has attracted a lot of attention [10]. The function of the membrane during esterification reaction is to selectively remove water from the reaction mixture as well as driving the reaction towards completion [11].

Esterification reactions are usually limited by equilibrium and therefore do not reach completion. However, using a membrane can result in higher conversion by shifting the chemical equilibrium towards the formation of the product by removal of water from the reaction mixture [12]. Inorganic porous ceramic membranes with the pore size greater than 0.3nm are normally used as sieve for larger molecules and particles. Materials such as zirconia, zeolite, metals, glass, alumina and carbon membranes are used as commercially porous inorganic membrane. Other materials used for the manufacture of inorganic membrane also include; titania, tinoxide, cordierite and silicon nitride. Although inorganic membranes are generally expensive in contrast to the organic polymeric membrane, they have a lot of advantages in gas separation including well defined stable pore structure, chemical inertness and wear resistant [13]. Inorganic membrane can be prepared using different methods including sol-gel, chemical vapour deposition and sintering methods. Sol-gel method of preparation has been found to be the most suitable method for porous membrane preparation in contrast to chemical vapour deposition and sintering methods [14].

The mechanism of gas transport through membranes is generally divided into 5 groups: surface diffusion, capillary condensation, Knudsen diffusion, viscous flow and molecular sieving mechanisms [15]. 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. Viscous flow mechanism takes place if the pore radius of the membrane is larger than the mean free path of the permeating gas molecule. Gas separation by molecular sieving mechanism takes place when the pore dimensions of the inorganic ceramic membrane approach those of the permeating gas molecules [16]. However, in capillary condensation mechanism, separation can takes place in the pores of the membrane with mesoporous layer in the presence of condensable gas specie. Surface diffusion mechanism occurs when the adsorption of the permeating gas molecule occurs on the pore surface of the membrane material there by increasing the gas transport performance [16].

In this work, the initial study of heterogeneous catalyst behaviour and carrier gas permeation with inorganic ceramic membrane for lactic acid esterification applications will be investigated.

II. EXPERIMENTAL

The four gases used for the carrier gas permeation include; nitrogen (N_2), argon (Ar), helium (He) and carbon dioxide (CO_2). The gases were supplied by BOC, UK. The permeation test was carried out at the feed pressure drop of 0.10 – 1.00 bar and at 413 K. The porous tube support was modified once before the permeation analysis. The effective length of the membrane was 36.6 cm, while the inner and outer radius of the membrane was 7 and 10 mm respectively. The support modification process was carried out based on the procedure developed by Gobina (2006) [17]. Fig. 1 shows the single gas permeation setup [18].

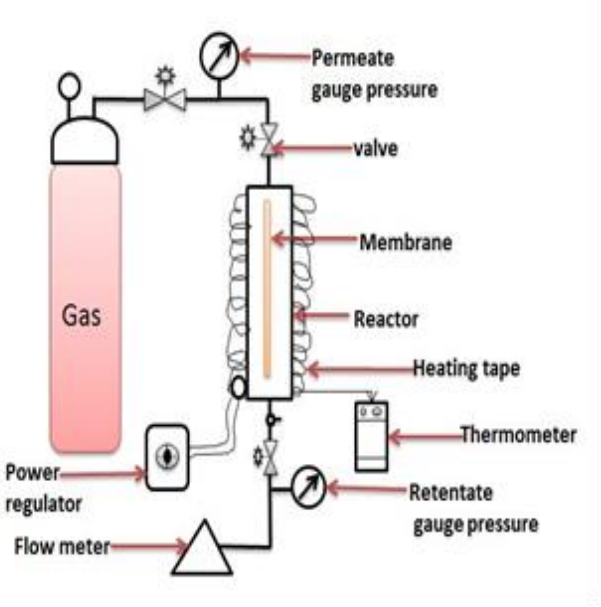

Fig. 1. Schematic diagram of the membrane dip-coating process.

The surface area analysis of the resin was examined using Scanning electron microscopy coupled with energy dispersive x-ray analyser (SEM-EDXA) instrument as

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shown in Fig. 2. Dowex 50W8x, Amberlyst 36, Amberlyst 15 and Amberlyst 16 cation-exchange resins were used as heterogeneous catalysts. The SEM/EDXA of the resin catalyst was investigated in order to determine the surface morphology of the resin.

Fig. 2. Pictorial diagram of the SEM-EDXA

III. RESULT AND DISCUSSION

Fig. 3 presents the relationship between the gas flow rate (mols s^{-1}) and the gauge pressure (bar). From the result, it can be seen that the gas flow rate increases with increase in gauge pressure. It was also found that He gas with the least molecular weight recorded the highest permeability.

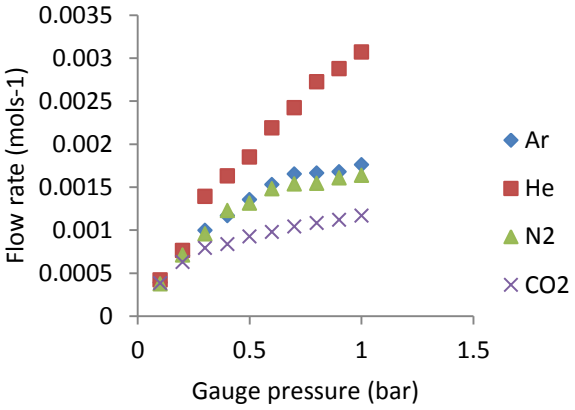

Fig. 3. Flow rate (mols s^{-1}) against Gauge pressure (bar)

Fig. 4 shows the relationship between the gas permeance ($molm^{-2}\ s^{-1}\ Pa^{-1}$) and the gas kinetic diameter (Å). From the result obtained in figure 4, it was found that although the gases followed the order of their kinetic diameter; N_2 (3.64 Å) > Ar (3.43 Å) > CO_2 (3.30 Å) > He (2.60 Å), the gas flow through the silica membrane was not based on the molecular sieving mechanism. For the gas flow to be described by molecular sieving mechanism, N_2 with the highest kinetic diameter would have exhibited a lower permeance in contrast to Ar, CO_2 and He gas. Also CO_2 would have been close to He rather Ar since their kinetic diameter are close as shown in table 1, however, the reverse was the case which, implies that the gas flow was controlled by another mechanism of gas transport.

Table 1 describes the respective gases with their kinetic diameter and molecular weight.

TABLE 1: GAS MOLECULAR WEIGHT AND THEIR RESPECTIVE KINETIC DIAMETER

Gases	**Molecular weight (g/mol)**	**Kinetic diameter (Å)**
Helium (He)	4	2.60
Argon (Ar)	40	3.43
Nitrogen (N_2)	28	3.64
Carbon dioxide (CO_2)	44	3.30

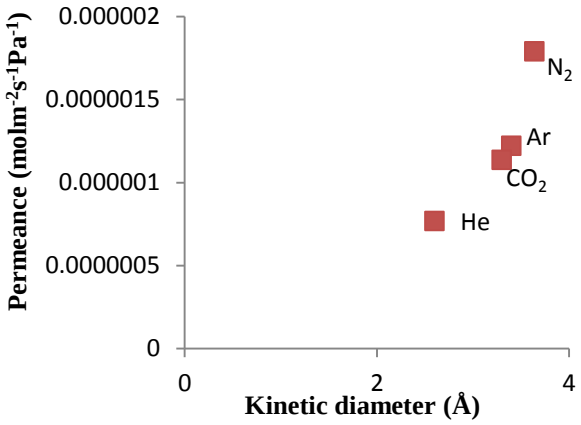

Fig. 4. Permeance ($molm^{-2}s^{-1}Pa^{-1}$) against kinetic diameter (Å) at 0.4 bar and at 333 K.

Fig. 5 presents the relationship between the gas flow rate (mols s^{-1}) and inverse square root of molecular weight for CO_2, Ar, N_2 and He gases. It was found that the membrane exhibited a linear dependence of flow rate on the inverse square root for CO_2, N_2, and Ar gases as expected for Knudsen flow mechanism of gas transport, whereas He gas was suggested to be controlled by another mechanism of transport.

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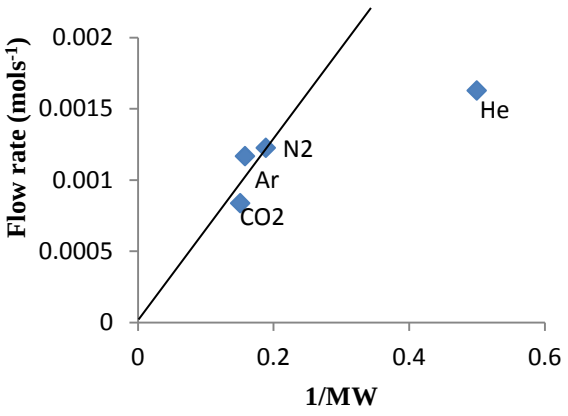


Fig. 5. Flow rate (mols s^{-1}) against inverse square root of molecular weight at 0.4 bar and at 333 K.

The relationship between the gas permenace ($molm^{-2}\ s^{-1}\ Pa^{-1}$) and the gauge pressure drop (bar) was also obtained as shown in Fig. 6. From Fig. 6, it was found that permeance decreases with respect to gauge pressure indicating mass transfer limitation of transport for the four gases. The order of the gas permeance with respect gauge pressure was He > Ar > N_2 > CO_2 .

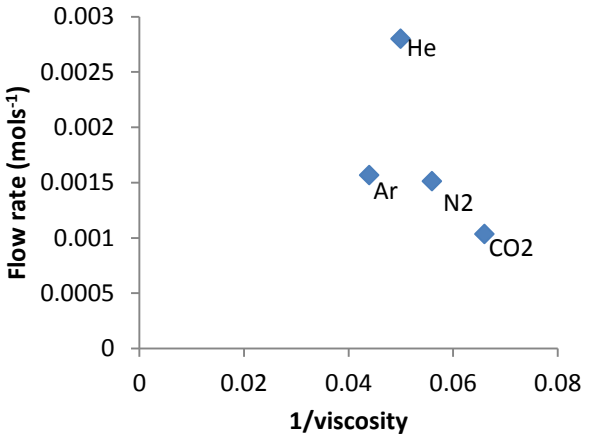
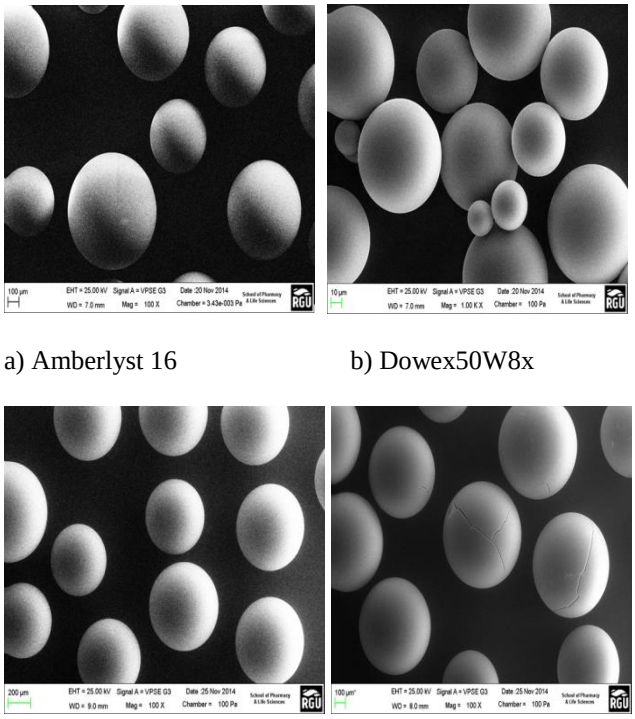


Fig. 7: Gas permeance against 1/viscosity (Pa s^{-1}) at 0.4 bar gauge pressure (bar) and 333 K.

SEM/EDXA OF THE RESIN CATALYST

The four resin catalysts were analysed using SEM/EDXA at the magnification of 100 x and the scale of 100 µm. Fig. 8a, b, c and d, presents the SEM images of the fresh commercial resin catalysts before being used for the esterification experiments. In these Fig., the surfaces of Amberlyst 16 (8a), Amberlyst 36 (8b) and Dowex 50W8x (8c) showed a very smooth surface although there was a bit of crack on the surface of Amberlyst 15 (8d) indicating that the resin catalysts were defect-free. A similar result was obtained by Zhang et al. 2004 [19].



a) Amberlyst 16 b) Dowex50W8x

c) Amberlyst 36 d) Amberlyst 15

Fig. 8: 8a (Amberlyst 16), 8b (Dowex 50W8x), 8c (Amberlyst 36) and 8d (Amberlyst 15): SEM surface morphology of the resin catalyst before esterification.

The elemental composition of the resin catalysts was also analysed using EDXA instrument. From Fig. 9, it was found that the EDXA of the resin catalyst consist of the elements such as oxygen, carbon and sulphur. It was also found that sulphur (S) exhibited the highest peak in contrast to other elements suggested to arise as a result of sulfonic acid group from the structure of the resin catalyst. However, these results will be compared with the images of resins after being used for the esterification experiment.

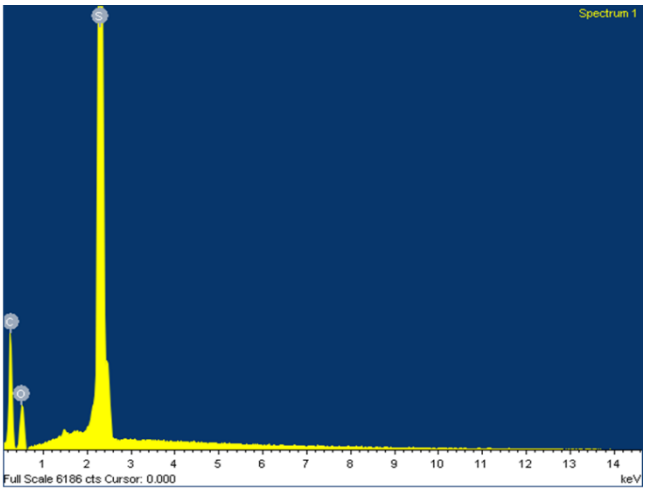


Fig. 9. EDXA of the resin catalyst

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IV. CONCLUSION

The behaviour of carrier gases with catalytic inorganic membrane for lactic acid esterification applications was achieved using viscous, Knudsen and molecular sieving mechanisms. It was found that viscous and Knudsen mechanism of transport plays a major role with respect to carrier gas transport. However, the membrane exhibited a linear dependence of permeance on the inverse square root of molecular for CO_2, N_2 and Ar indicating Knudsen flow mechanism except for He gas.

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