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Evaluation of the performance of α-alumina nano-porous ceramic composite membrane for esterification applications in petroleum refinery

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ABSTRACT

The carrier gas permeation performance through α-alumina nano-porous ceramic membrane was investigated in this study. The four carrier gases used for the study were argon (Ar), helium (He), nitrogen (N_2) and carbon dioxide (CO_2). The experiments was carried out at the gauge pressure drop of 0.10–1.00 bar at 80 °C. The α-alumina membrane was prepared using the sol-gel dip-coating techniques. The dip-coated membrane exhibited a higher molar flux with He (0.046 mol $m^{-2}s^{-1}$) and Ar (0.037 mol $m^{-2}s^{-1}$) with a much lower flux for N_2 (0.037 mol $m^{-2}s^{-1}$) and CO_2 (0.035 mol $m^{-2}s^{-1}$) at 0.30 bar. The membrane recorded a huge decrease of permeance with the four carrier gases in the range of 9.81783E-07 mol m^{-2} s^{-1} Pa^{-1} to 1.23237E-06 mol m^{-2} s^{-1} Pa^{-1} at 0.50 bar. The gas flow rate increased with respect to the pressure drop across the membrane. A plot of the inverse square root of the gases molecular weight showed a linear dependence on the gas permeance. The order of the gas flow rate with respect to the mean pressure was He > Ar > CO_2 > N_2. The membrane was characterised using different methods including liquid nitrogen physisorption (Quantachrome instrument 2013) and scanning electron microscopy (Zeiss EVO LS10 SEM). The liquid nitrogen adsorption isotherm were described using the BET and BJH methods The BET surface area of the 7th dip-coated membrane was found to be higher (5.991 m^2/g) in contrast to the 8th dipped (3.840 m^2/g). The BJH pore size distribution of the membrane show a reduction pore size after the modification process. The BET isotherms of the membrane indicated a type IV isotherm with hysteresis on the curve indicating that the membrane can undergo a capillary condensation in the mesoporous region. The SEM/EDAX of support showed a clear surface without evidence of crack while the SEM micrograph of the silica membrane exhibit a bonding on the surface membrane as result of the modification process.

1. Introduction

Membrane separation has shown a lot of advantages such as high efficiency and energy saving in contrast to other conventional methods of separation such as absorption, adsorption and crystallisation. Due to these advantages, membrane separation has been widely accepted in large-scale application during the last decades. Based on the materials, membranes may be classified into two different types: Organic membrane such as polymeric membranes and inorganic membranes such as ceramic membrane. Inorganic membranes possess some outstanding properties such as chemical stability, thermal stability, easy cleaning and non-swelling nature. Hence inorganic membranes are widely used in high-temperature separation processes and as membrane reactors [1]. Gas separation is an important aspect of operation that has attracted a lot of attention in the chemical industries. The separation of air into nitrogen and oxygen and the removal of the volatile organic compounds from effluent streams are examples of gas separation [2]. Recently, membrane-based gas separation has been the topic of the day because of its numerous advantage such as lower energy consumption, ease of operation, low operation and capital cost; compared to tradition method of gas separation. Membrane may be defined as an interphase between two bulk phases. Currently, membrane-based separation are being employed in a lot of applications including nanofiltration, reverse osmosis, ultrafiltration and microfiltration [2]. The use of membranes and membrane technologies for the selective removal of product to shift the equilibrium towards higher yield of the product in equilibrium limiting reaction systems have attracted a lot of attention [3,4]. Generally, esterification reactions are usually limited by equilibrium and therefore do not attain completion [5,3]. The major role of the membrane in esterification in reactions is that it can work both as a catalyst and also in the removal of the product by reacting with the reactants (carboxylic acid and alcohol) and the catalyst and shifting the equilibrium to the product side by selectively removing water from the bulk of the reaction [3]. Solvents are basic consumables in industries such as

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Nomenclature

P	Permeance (mol mm^{-22} s^{-1} Pa^{-1})
P_0	Arrhenius type pre–exponential constant (m^2 s^{-1}),
T	Temperature (K)
Ea	Activation energy (Jmol^{-1}) of surface diffusion or heat of adsorption
R	Gas molar constant (8.314621 Jmol^{-1} K^{-1})
A	Surface area of the membrane (m$_2$)
L	Length of the membrane (m)
r_1	Membrane outer pore diameter (m)
$\langle H1\rangle\langle H1\rangle\langle H1\rangle r_2$	Membrane inner pore diameter (m)
π	Constant (3.142)
J	Flux (mol s^{-1} m^{-2})
Q	Gas flow rate (mol s^{-1})
ΔP	Pressure drop across the membrane (bar)

chemical, pharmaceutical, and agriculture. They are manufactured from petrochemical feedstock obtained from natural gas and crude oil [6]. Studies have shown that the use of some petrochemical solvents may result in serious health and environmental problems. One of the major challenges faced by the petrochemical industry has been the replacement of traditional petroleum-derived solvents [7]. It is therefore essential to develop new solvents with less toxic and hazardous characters [8]. Ethyl lactate (EL) is one of the solvents in high demand in the chemical and petroleum industry and it is a sustainable alternative organic solvent with advantages that include biodegradability, non-carcinogenic, non-corrosive and non-ozone depleting and is miscible with water and hydrocarbons. Because of its outstanding advantages, EL has been described by the U.S Environmental Protection Agency (EPA) as a ”green solvent” [9]. EL is therefore a suitable replacement for a number of hazardous organic solvents including toluene, benzene, chloroform, xylene and hexane in the petroleum industry. It is used in different industries such as food, pharmaceutical, paint, adhesive, agriculture and petroleum refinery [10].

The combination of membrane separation process with chemical reaction process have attracted a lot of attention due to their high selectivity [11,12]. In recent years, silica membranes have been widely investigated for use in gas separations [13]. Silica membranes are normally in the form of a silica layers placed on a ceramic support such as alumina and the deposition is usually carried out by the sol-gel or chemical vapour deposition (CVD) of silica precursors [14]. Generally, the sol-gel process has been widely used for the modification of alumina and silica-based inorganic membranes [2]. Dip-coating is a convenient membrane preparation method which has been widely used to produce ceramic membranes to microporous layers from porous supports [15]. In the dip–coating techniques, a wet layer of ceramic particle is deposited on a porous support by coating the surface of the dry support with a particle-dispersed suspension or a suitable sol such as colloidal boehmite, followed by drying and thermal treatment of the support [15,2]. According to Zhu et al. [15], the conventional dip-coating method involves two steps: support dipping and support withdrawal. However, the dip-coating parameters such as dipping speed, viscosity of the sol, immersion and drying time affect both the thickness and the pore size distribution of the membrane [16]. In the support dipping step, the effect of capillary-filtration dominates, particles are deposited and accumulated on the surface of the support because of the suction of the solvent into the pores of the support under the capillary force. Though a lot of particles gets deposited on the pinhole defect area based on the self-repairing mechanism, the process of the deposition of particles because of the capillary-filtration cannot be controlled and hence needs more repetitions. Similarly, in the case of the support withdrawal, this step is dominated by the film-coating, an adhering particle layer is formed by the drag force applied by the support during withdrawal from suspension [15].

The transport of gases through porous membranes can be explained using various transport mechanisms based on several factors such as the size of the permeating gas molecules, the membrane material, the driving force (pressure and temperature) and the average pore size [17,18]. The different mechanisms of gas transport through porous membranes include surface diffusion, Knudsen diffusion, capillary condensation, viscous flow, and molecular sieving mechanisms [19,20]. Knudsen mechanism occur when the mean free path of the gas molecule is greater than the pore size. In such case, collision of the gas molecule with the pore wall are more frequent than the collision between molecules. Viscous flow mechanism takes place if the mean free path of the gas molecule is smaller than the pore size and diffusion of gases and takes place basically through molecule–molecule interaction than molecule to pore wall. Surface diffusion takes place when the permeating gas molecule exhibit a strong affinity for the membrane surface and adsorb along the pore walls. Capillary condensation occur when the pores are completely filled with the condensed gas at certain critical relative pressures mostly in mesopores and macropores [21]. Gas separation by molecular sieving mechanism takes place when the pore diameter of the inorganic ceramic membrane are roughly the same as those of the permeating gas molecules [22].

Synthesized membranes can be characterised using various methods. Scanning electron microscopy is normally used in order to examine the surface morphology and the x-section of the membrane. Liquid nitrogen physisorption analysis is used to determine the pore structure of the membrane. According to IUPAC (International Union of Pure and Applied Chemistry), the physisorption isotherm can be classified into six different types [23]; Type 1 isotherm is characterised by the adsorption in the non-porous microporous region at a low relative pressure. Type ll is characteristic of non-porous or macroporous adsorbents with the formation of a multilayer of adsorbate (gas molecule) on the surface of the adsorbent. Type III is characteristic of a non-porous or macroporous layer with weak interaction between the gas molecule and the membrane material. Type IV isotherm reflects a macroporous material which involves the coverage of the monolayer–multilayer on the external surface which is followed by capillary condensation in the mesoporous region with the formation of hysteresis loop based on the shape of the pores. Type V isotherm is characteristic of a mesoporous material and involves the weak interaction between the permeating gas molecule and the membrane material. Type V1 isotherm takes place in a highly uniform surface [23,16]. Fourier transform infrared spectroscopy (FTIR) is one of the most useful techniques for the characterisation of the membrane surface [24]. Jin et al. [15], prepared an α-Al_2O_3 microfiltration pinhole-free membrane using a modified dip-coated process to prevent pinhole defects in ceramic membranes. In their results, they found that pinholes in membrane could be effectively avoided by applying a suspension flow velocity of 50 mms^{-1} and a withdrawal speed of 4 mms^{-1} via a single coating-sintering procedure. McCool et al. [13], used the dip-coating method for the membrane fabrication and deposition on a polished surface of an alumina support disk and reported the gas permeation for N_2, Ar, O_2 and He gas to be strongly governed by Knudsen mechanism. Xomeritakis et al. [25] perform an experiment on organic-templated silica membranes. Gas and vapour transport properties. In their results, they found that the silica coated membrane exhibited permeance values as high as 10^{-7}–10^{-6} mol m^{-2}s^{-1} Pa^{-1}.

Although a lot of work has focused on the production of this solvent by the esterification process, no previous work has considered testing the carrier gas with the membrane to check the compatibility of the carrier gas with the GC before being utilised for the analysis of the esterification product. This work incorporates the analysis of the carrier gas with the membrane to see the permeation rate of the gases with the