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Mixed matrix membranes using SAPO-34/polyetherimide for carbon dioxide/methane separation

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ABSTRACT

Mixed matrix membranes (MMMs) are hybrid materials prepared by dispersing inorganic particles in a polymeric matrix and are attracting increasing attention for the separation of CO_2/CH_4 mixtures. The zeolite SAPO-34 and polyetherimide were selected as the inorganic filler and the polymeric matrix for the synthesis of the supported MMMs. Two polymer solvents, dichloroethane (DCE) and N-methyl-2-pyrrolidone (NMP), were investigated for the preparation, and the DCE solvent resulted in a membrane with better CO_2/CH_4 selectivity. Various SAPO-34 amounts from 0 to 10 wt% were dispersed in the polymer precursor which was dissolved in DCE. The membrane with 5 wt% SAPO-34 content presented the highest performance with a CO_2 permeance of 4×10^{-10} mol m^{-2} s^{-1} Pa^{-1} and a CO_2/CH_4 ideal selectivity of 60. Based on mixed gas permeances and time-lag measurements, the separation of CO_2 and CH_4 was found to be dominated by the difference in the gas solubilities. The SAPO-34 decreased CH_4 transport by increasing its diffusion pathway. Particle agglomeration was observed at 10 wt% zeolite loading in the polymeric matrix.

1. Introduction

Gas separation membrane technology has been receiving increasing attention because of its potential for reducing the environmental impact and the costs of industrial processes [1–6]. The separation of CO_2 from CH_4 has become a crucial topic because of its importance in the energy and the environmental fields [7–11]. The separation of CH_4 and CO_2 mixtures is particularly relevant in the purification of conventional natural gas and coal seam methane [12], unconventional shale gas [13], the treatment of anaerobic gas from biomass [14], all of which contain fairly high amounts of CO_2.

Membranes are generally classified into three main groups according to materials composition: polymeric, inorganic and mixed organic and inorganic materials. Polymeric membranes are widely used in industrial application because of their low fabrication costs, good mechanical strength, high flexibility, easy processing and robustness compared to inorganic membranes [15,16]. However, polymeric membranes generally suffer from plasticization (swelling and deformation) when placed in contact with highly pressurized CO_2 [17,18]. As a result, processes for CO_2 separation using organic membranes are usually performed at relatively low temperatures [19]. Inorganic membranes have high chemical and thermal stability and do not swell. However, they are brittle and have poor mechanical strength [15]. Mixed matrix membranes (MMMs) are one of the alternatives to overcome the limitations of the aforementioned materials [20]. They are hybrid materials prepared by dispersing inorganic particles into polymers which act as a matrix. Inorganic particles or fillers include various materials such as zeolites [21], carbon molecular sieves [22–24], activated carbons [25], mesoporous materials [26], non-porous silica [27], organic metallic frameworks [28], and graphite [29]. They are classified into porous and non-porous fillers. Porous materials separate gases by molecular sieving, whereas, non-porous materials increase the permeated diffusion path of gas molecules within the polymeric matrix increasing, hence, the selectivity of small molecules compared to larger species [30].

Zhang et al. [31] reported the use of Matrimid® and mesoporous ZSM-5 nanoparticles (20 wt%) for MMMs. The separation selectivity of H_2/CH_4 improved from 83 to 170. Hosseini et al. [32] developed a MMM by mixing Matrimid® with MgO nanoparticles. The membrane was post-treated by immersion in silver solution, and

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Nomenclature

$\overline{P}_i$	permeance of species i (mol m^{-2} s^{-1} Pa^{-1})
$\alpha^*_{i,j}$	selectivity of a species i over j
A	surface area of the membrane (m^2)
Al(O-iPr)$_3$	aluminum isopropoxide
C_0	concentration of dissolved gas (mol L^{-1})
D	diffusivity of gas i (m^2 s^{-1})
DCE	dichloroethane
F_i	molar flow rate of the gas i (mol s^{-1})
H_3PO_4	phosphoric acid
l	length of cylinder (m)
L	thickness of the selective membrane layer (m)
MMM	mixed matrix membrane
MMM-x [$x = 0, 5, 10$]	mixed matrix membranes with 0, 5, and 10 wt% SAPO-34/PEI
NMP	N-methyl-2-pyrrolidone
PEI	polyetherimide
Q	total permeated gas (mol)
r_c	external radius (m)
r_0	internal radius (m)
S	solubility of gas i (mol m^{-3} Pa^{-1})
SAPO-34	silicoaluminophosphate 34
t	time (s)
TEAOH	tetraethylammonium hydroxide
ΔP_i	partial pressure difference of a gas i between the inner and the outer side of the membrane tube (Pa)
ε	porosity

the best performance was obtained at 20 wt% MgO loading after 10 days of silver treatment. The CO_2/CH_4 selectivity slightly increased from 30 to 43. Li et al. [33] treated A zeolite with silver by ion exchange and mixed the modified zeolite (50 wt%) with polyethersulfone. The CO_2/CH_4 selectivity increased slightly from 35 to 44. Sadeghi et al. [34] incorporated silica nanoparticles into a polybenzimidazole matrix. The silica nanoparticles increased the solubility but decreased the diffusivity of gases. The permeabilities of condensable gases such as CO_2 and CH_4 were higher than of non-condensable ones such as N_2 gas. Rojey et al. [35] synthesized MMMs using 4A zeolite (19 wt%) and Ultem ®polyetherimide. The CO_2/CH_4 selectivity improved from 14 to 35. Vu et al. [36] dispersed carbon molecular sieves (36 vol%) in Matrimid ®polyimide and increased the CO_2/CH_4 selectivity from 35 to 52. Anson et al. [37] used a mixture of acrylonitrile–butadiene–styrene copolymer and mesoporous activated carbons particles (62.4 vol%) and increased the CO_2/CH_4 selectivity from 24 to 50.

This work investigates supported mixed matrix membranes prepared by the dispersion of different amounts of SAPO-34 particles in polyetherimide without having covalent bonds between both materials. The use of ceramic supports for the preparation of mixed matrix membranes offers several advantages such as the ease of the preparation process, the decrease of the effective thickness and hence the overall membrane resistance [21]. The silicoaluminophosphate crystals (SAPO-34) were chosen for the separation because they are porous materials selective to CO_2 permeance. The polyetherimide polymer (PEI) was selected since it is thermally and chemically stable. First, two solvents for the PEI, N-methyl-2-pyrrolidone (NMP) and dichloroethane (DCE), were investigated in order to determine the best solvent for the preparation. It was found that membranes using DCE separated the gas pair better than those using NMP and the incorporation of SAPO-34 decreased the CH_4 permeances. Then, various SAPO-34/PEI weight ratios were studied from 0 to 10 wt%. Mixed gas permeances and time-lag measurements showed that the separation of CO_2 from CH_4 was based on the difference in gas solubility.

2. Experimental procedure

2.1. Materials

Porous alumina supports having an average pore size of 5 nm were obtained from the Pall Corporation. The supports with 3 cm length were connected to dense alumina using glass joints. The glass was bought from the Nippon Electric Glass Co., Ltd, and were fabricated by heating the pieces to 1273 K for 10 min using heating and cooling rates of 5 K min^{-1}.

Ludox AS-40 colloidal silica (40 wt% suspension in water, Sigma Aldrich), aluminum isopropoxide (Al(O-iPr)$_3$, >99.99%, Sigma Aldrich), and phosphoric acid (H_3PO_4, 85 wt% in aqueous, Sigma Aldrich) were used as silica, alumina, and phosphoric oxide sources, respectively, to synthesize the SAPO-34 crystals. Tetraethylammonium hydroxide (TEAOH, 35 wt% in H_2O, Sigma Aldrich) was used as a structure directing agent in the crystal synthesis.

Polyetherimide (PEI, MW30,000, Polysciences Inc.) was used as the polymeric precursor (Fig. 1). Dichloroethane (DCE, anhydrous, ⩾99.8%, Sigma Aldrich), and N-methyl-2-pyrrolidone (NMP, anhydrous 99.5%, Sigma Aldrich) were used to investigate the effect of the polymer solvent on the resultant supported hybrid membranes. Pure Ar, H_2, CO_2, N_2, and CH_4 gases with a purity of 99.9% were acquired from Tokyo Koatsu Yamazaki Co., Ltd.

2.2. SAPO-34 synthesis

The SAPO-34 zeolite was prepared using a hydrothermal technique [38]. First, colloidal silica was mixed with TEAOH and hydrolyzed for 16 h at room temperature. Then, Al(O-iPr)$_3$ was vigorously stirred for 15 min in deionized water and H_3PO_4 was added drop wise to form an alumina gel. The mixture was stirred for 5 h. Then, the alumina gel was mixed with colloidal silica and stirred at room temperature for 3 days. The molar composition of the resultant synthesis solution was 1.0 Al_2O_3:1.0 P_2O_5:0.3 SiO_2:1.2 TEAOH:60 H_2O. Crystal formation and growth was promoted by heating the solution to 473 K for 24 h in a Teflon-lined, stainless steel autoclave. The solid product was recovered by repeated centrifugation at 2700 rpm for 10 min and washing with deionized water. The precipitate was dried overnight at 393 K and then calcined at 823 K for 8 h. The heating and the cooling rates of the calcination were 1 K min^{-1}.

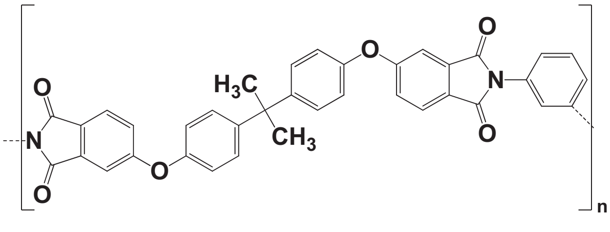

Fig. 1. Chemical structure of polyetherimide.