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Hydrogen separation and purification using crosslinkable PDMS/zeolite A nanoparticles mixed matrix membranes

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ABSTRACT

The transport properties of gases in polydimethylsiloxane (PDMS)/zeolite A mixed matrix membranes (MMMs) were determined based on pure gas permeation experiments. MMMs were prepared by incorporating zeolite 4A nanoparticles into a PDMS matrix using a new procedure. The permeation rates of C_3H_8, CH_4, CO_2, and H_2 were evaluated through a dense homogeneous pure PDMS membrane and PDMS/4A MMMs to assess the viability of these membranes for natural gas sweetening and hydrogen purification. SEM investigations showed good adhesion of the polymer to the zeolite in MMMs. Permeation performance of the membranes was also investigated using a laboratory-scale gas separation apparatus and effects of feed pressure, zeolite loading and pore size of zeolite on the gas separation performance of the MMMs were evaluated. The MMMs exhibited both higher selectivity of H_2/CH_4 and H_2 permeability as compared with the neat PDMS membrane, suggesting that these membranes are very promising for gas separations such as H_2/CH_4 separation.

1. Introduction

Recent developments in membrane gas separation have heightened the need for materials to have desired separation properties [1–8]. Mixed matrix membranes (MMMs) have been synthesized based on the old idea of polymer compositing in order to improve electrical and mechanical properties [9–12]. The use of two or more different materials with distinct selectivities and fluxes for membrane fabrication provides the possibility of preparation of one type of membrane technology identified as MMMs [13]. The concept of blending two materials (polymer and sieve) has been appeared in two last decades, and many efforts have been carried out by other researchers [14–19]. In MMMs, the selectivity of two incorporating materials for the penetrating molecule(s) must be proportionate. Synthetic polymers have been employed as the matrix of MMMs based on their favorable properties. In many cases, addition of a small amount of a molecular sieve to a polymer matrix enhances the membrane selectivity significantly. This improvement is due to the fact that the molecular sieve separation performance is usually several orders of magnitude higher than the neat polymer and its ability to economically separate the target penetrates is high and this locates the MMM performance above the Robeson upper-bond limit. This achievement is also economical when the capital cost is spent to synthesize large membrane surface compared with little molecular sieve powder [20].

Prior attempts to synthesize MMMs have been published by researchers at UOP. They synthesized CA/silicalite-1 MMMs for CO_2/H_2 separation. The separation factor of MMMs was 6.7 times greater than that of the neat CA membrane [21]. Adams et al. [22] used poly(vinyl acetate) (PVAc) as the polymer matrix to prepare high zeolite 4A loading MMMs. CO_2/CH_4 mixtures were used to investigate the performance of PVAc/

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4A MMMs 50 vol.% zeolite for natural gas separations and substantial improvements in overall the separation performance were observed. The permeation results showed that for high CO_2 partial pressure, CO_2 selectivity increases 63%, while permeability remains effectively unchanged.

Performances of various zeolite filled polymeric membranes in separation of gas mixtures have been further investigated by many researchers. Effect of zeolite particle size on gas permeabilities of the zeolite–polymer MMMs was investigated by Tantekin-Ersolmaz et al. [23]. Hussain and König [24] prepared MMMs with different compositions of ZSM-5 to study CO_2 separation from gas mixtures. The gas separation performance of MMMs was evaluated using the modified Maxwell model. Lin et al. [25] prepared mixed matrix silicone and fluorosilicone/zeolite 4A membranes to dehydrate ethanol by pervaporation in an effort to increase water selectivity and further improve water permeability. Homogeneous poly(trifluoropropylmethylsiloxane) (PTFPMS) as fluorosilicone rubber and PDMS membranes showed good mechanical and solvent stability.

Today, the major direction of membrane separation research is oriented to introduce a new type of membranes having relatively high permeabilities and selectivities. It has been proven that introduction of zeolite may increase permeabilities and selectivities of neat polymer membranes when the right zeolite–polymer pair is selected. Zeolite filled polymeric membranes seem to be promising for many applications. Jia et al. [26] used zeolite-filled silicone rubber membranes in gas permeation. In another similar study, Duval et al. [27] investigated carbon molecular sieve and zeolite gas separation properties of poorly selective rubbery polymers towards a mixture of CO_2/CH_4. Clarizia et al. [28] used PDMS as the host matrix to prepare different MMMs with various surfaces and molecular sieving (silicalite-1, NaX, NaA and graphite) on the gas transport properties of MMMs were investigated. These MMMs exhibited higher selectivities and lower permeabilities for some gas pairs compared with pure PDMS membrane. Vankelecom et al. [29] incorporated several types zeolites in silicone rubber membranes and studied the tensile strength, xylene sorption, and density of the MMMs.

Crystalline structures of zeolites with their pores angstrom size dimensions enable them to be processable in gas separation. Zeolite was thus chosen as inorganic filler in current work to provide more discrimination based upon its pore size and/or shape for gas molecules to preferentially transport.

So far, however, in development of PDMS membranes, many studies have been carried out regarding their transport properties for pure and binary gas mixtures because PDMS is well known most frequently used polymer in membrane preparation [30–39]. Indeed, of all elastomers, mechanical properties of PDMS upon addition of inorganic fillers show the greatest improvement [25]. Hence, PDMS, with its repeating unit of [–$Si(CH_3)_2$–O–], was selected as the polymer matrix in this study.

As a result, this study provides a new proof of concept for preparation of the novel MMMs made using PDMS as the base polymer matrix and zeolite A nanoparticles as fillers using a new procedure and the pros and cons of various operational conditions in natural gas sweetening and hydrogen purification processes. The individual gas permeabilities and ideal selectivities of the MMMs were reported and compared with those of the neat PDMS membrane under the same conditions. The focus of the current work was to evaluate the effects of zeolite A nanoparticles loading on MMM performance. Furthermore, the effects of upstream feed pressure and zeolite type on performance of PDMS MMMs were investigated. The experiments were carried out to investigate whether zeolite A is beneficial to the relatively poor performance of PDMS membrane for CO_2/CH_4 and H_2/CH_4 separation applications.

2. Experimental

2.1. Materials

Dehesive 944 silicone as a solvent-based addition crosslinkable silicone (RTV 615A en B, density 1.02 g/mL) was purchased from Wacker Silicones Corporation, Adrian; MI. Component A is a prepolymer with vinyl groups, terminal at long PDMS chains. The proprietary crosslinker (polyhydrogenmethylsilane under the trade name V24, Wacker), contains SiH groups in the polymer chains, forms the much less viscous component B, together with platinum, acting as a catalyst (1,3-divinyl-1,1,1,3-tetramrthyldisiloxane platinum complex under the trade name OL, Wacker) in the hydrosilylation reaction [29]. Toluene was purchased from Merck and used as received. Zeolite nanoparticles (particle size = 80–250 nm and Si/Al molar ratio = 1) were dedicated from Research Institute of Petroleum Industries. H_2, CO_2, and CH_4 gases with purity of 99.5% were supplied by Technical Gas Services, Inc., and C_3H_8 gas with purity of 99.9% was supplied by Air Products and Chemicals, Inc.

2.2. Mixed matrix membrane preparation

This study especially contributes to provide a proof of concept regarding the current state-of-art technologies for preparation methodology of novel PDMS/zeolite A mixed matrix membranes. Preparation of MMMs is considerably complex. PDMS/zeolite A nanoparticles MMMs were synthesized via the conventional solution-casting technique, as the most applicable method to form void-free MMMs. Following the literature [40,41], to prepare MMMs with higher selectivity, the method by means of applying high processing temperature during mixed matrix membranes formation was employed to eliminate the voids between the zeolite and the polymer phases in this work. The flowchart of preparation methodology for PDMS/zeolite A MMM is shown in Fig. 1.

Pretreatment of zeolites (activation) is considered as a significant factor affecting gas permeation results. A more efficient water removal from zeolite surface can be achieved at higher activation temperature resulting in an improvement in zeolite permeation properties [42]. As a result, zeolite A nanoparticles were placed in a beaker and activated for 24 h in vacuum condition at 200 °C to activate the zeolite for gas permeation. The dried zeolite A nanoparticles were cooled to room temperature and then quickly weighed. The zeolite weight was about 20% after activation. The zeolite