Journal of Natural Gas Science and Engineering 34 (2016) 509–519

Contents lists available at ScienceDirect

Journal of Natural Gas Science and Engineering

journal homepage: www.elsevier.com/locate/jngse

CO_2 and CH_4 gas permeation study via zeolitic imidazolate framework (ZIF)-8 membrane

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ARTICLE INFO

Article history:
Received 28 March 2016
Received in revised form
8 June 2016
Accepted 2 July 2016
Available online 7 July 2016

Keywords:
ZIF-8 membrane
CO_2
Microwave
Gas separation
Solvent evaporation

ABSTRACT

In the present work, the effects of CO_2 feed composition (15%–90%), pressure difference (100 kPa –700 kPa) and temperature (303 K–343 K) on the separation of CO_2 from CH_4 via ZIF-8 membrane were investigated. The membrane was synthesized through a simple, feasible and reproducible solvent evaporation seeding method coupled with microwave-assisted secondary solvothermal growth. Subsequently, the membrane was characterized by using scanning electron microscopy. The results showed that, for single gas permeation, CO_2 permeances remained constant while CH_4 permeances increased slightly with the increasing pressure differences at temperature of 303 K. Besides, CO_2 permeances decreased while CH_4 permeances increased slightly with the increase in temperature at pressure difference of 100 kPa. For binary gas separation, maximum CO_2/CH_4 separation factor of 5.07 and CO_2 permeance of 6.595×10^{-8} mol m^{-2} s^{-1} Pa^{-1} were obtained at CO_2 feed composition of 15%, pressure difference of 100 kPa and temperature of 303 K. Besides, CO_2 fluxes approached constant value with the increasing CO_2 partial pressure differences at CO_2 feed composition of 15%, which was mainly attributed to the competitive adsorption between CO_2 and CH_4. On the other hand, CH_4 fluxes increased with increasing CH_4 partial pressure differences even at higher CO_2 composition in the feed, owing to its adsorption capacity and gas transport pathway via membrane intercrystalline pores.

1. Introduction

Natural gas presents to be a cleaner fuel as compared to the other fossil fuels. Natural gas has wide application for industry usage, such as heating, air-conditioning, power generation, fuel cells, and natural gas vehicles (NGV), etc (King, 2013). It contains mainly CH_4 and non-hydrocarbon components, such as CO_2. However, CO_2 needs to be removed from natural gas because it can corrode the pipelines in the presence of water and reduce the energy content of the natural gas (Zhu et al., 2006). Recently, metal organic frameworks (MOFs) demonstrate high potential in CO_2 separation owing to its exceptional high porosity, large surface areas and tunable pores size (Li et al., 2011). Meanwhile, zeolitic imidazolate frameworks (ZIFs) is a subcategory of MOFs. Unlike MOFs, ZIFs exhibit exceptionally high stability due to the strong bonding between metal cations and imidazolate anions (Xu et al., 2011). Among ZIFs, ZIF-8 is one of the most studied materials for gas separation due to its high affinity towards CO_2 (Venna and Carreon, 2010), excellent chemical and hydrothermal stability and frameworks flexibility (Park et al., 2006). ZIF-8 possesses large pore sizes of 11.6 Å and small apertures of 3.4 Å with zinc metal center coordinated by imidazole-type of organic linkers and resembles neutral zeolitic sodalite (SOD) topology (Huang et al., 2006). Several researchers have reported CO_2 separation from CH_4 using ZIF-8 membrane. For instance, for an equimolar gas mixtures of CO_2/CH_4, Venna and Carreon (2010) reported CO_2/CH_4 separation factor of 7 for ZIF-8 membrane with CO_2 permeance up to ~1.69×10^{-5} mol m^{-2} s^{-1} Pa^{-1} at feed pressure of 139.5 kPa. Meanwhile, CO_2/CH_4 separation factor of 3.4 and CO_2 permeance of 2.60×10^{-8} mol m^{-2} s^{-1} Pa^{-1} was reported by Bux et al. (2009) (Bux et al., 2010) at feed pressure of 200 kPa over ZIF-8 membrane. Besides, Yeo et al. (2014) reported CO_2/CH_4 separation factor of 3.2 and CO_2 permeance of 33.80×10^{-8} mol m^{-2} s^{-1} Pa^{-1} using ZIF-8 membrane at 100 kPa feed pressure. To the best of our knowledge, the effect of the separation process parameters, including CO_2 feed composition, pressure difference and temperature, on the removal of CO_2 from CH_4 using ZIF-8 membrane has not been studied in detail so far. In this paper, ZIF-8 membrane was grown on an inert α-alumina disk support via microwave-assisted secondary growth.

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http://dx.doi.org/10.1016/j.jngse.2016.07.005
1875-5100/

Prior to the solvothermal growth of the membrane, the support was seeded with ZIF-8 through solvent evaporation method. It is noted that, this seeding method showed high feasibility and reproducibility as it did not require complicated steps for support or seeding solution modifications. This was due to the highly supersaturation condition created under the reducing volume of solvent, which enhanced the nucleation and crystallization process, and subsequently, formed pure phase and small size of ZIF-8 particles on the porous support. Then, the membrane was solvothermally grown on the seeded support under microwave heating. The resultant membrane was characterized by using scanning electron microscopy and tested for single gas permeation and binary gas separation involving CO_2 and CH_4.

2. Methodology

2.1. Preparation of seeded support

Solvent evaporation method was applied in the present study for the preparation of ZIF-8 seeded support. The seeding solution was prepared by dissolving 1.06 g of zinc chloride ($ZnCl_2$, >97%, Fisher brand), 0.99 g of 2-methylimidazole (Hmim, 99%, Fisher brand) and 0.54 g of sodium formate (HCOONa, 99%, Acros brand) in 80 mL of methanol (MeOH, >95%, Merck) under stirring. Then, the polished α-alumina porous support (Nishimura Porcelain) with thickness of 2 mm and diameter of 18 mm was placed horizontally at the bottom of a 100 mL vessel. The solution was then poured into the vessel and the vessel was sealed with small holes for slow evaporation of solvent. After that, the solution was subjected to heating at 338 K–343 K for the complete solvent evaporation within 2.5 h. Then, the seeded support was dried in the desiccator at room temperature overnight prior to the solvothermal synthesis.

2.2. ZIF-8 membrane synthesis

The synthesis precursor was prepared by mixing 2.12 g of $ZnCl_2$, 1.98 g of Hmim and 1.08 g of HCOONa in 160 mL of MeOH under stirring until clear solution was obtained. The seeded α-alumina porous support was placed vertically in the Teflon-lined vessel. The synthesis precursor was then poured into the vessel. The vessel containing the seeded support and the synthesis precursor was heated in a microwave oven (MARS 6, CEM Corporation) at 413 K for 5 h, with ramping rate of 287 K min^{-1}. After heating, the membrane was washed with fresh MeOH. The other side of the membrane was polished with fine sand paper to avoid the deposition of ZIF-8 crystals. Then, the resultant membrane was dried in the desiccator at room temperature overnight.

2.3. Membrane characterization

The surface morphology and cross section view of the ZIF-8 membrane were observed using scanning electron microscopy, SEM (Hitachi TM3030). The elements of the membrane were determined using Energy-Dispersive X-ray Spectroscopy, EDX and the distribution of the elements was scanned through EDX mapping.

2.4. CO_2 and CH_4 gas permeation

For the gas permeation and separation studies, the membrane was firstly mounted onto a stainless steel module and silicone gasket was used as seal to prevent the leakage of gas. The total feed flow rate was set to 200 mL min^{-1}. The feed pressure was set accordingly with the total pressure difference ranging from 100 kPa to 700 kPa, while the pressure at the permeate side was maintained at atmospheric pressure. The temperature was controlled using oven, ranging from 303 K to 343 K and the gas was fed into the system using mass flow controller. For binary CO_2/CH_4 gas separation, the CO_2 feed composition in the feed was changed from 15% to 90%. After attaining steady state condition, the gas permeance was measured by using bubble flow meter. Then, the sampling gas was collected at the permeate side using nitrogen as sweep gas at

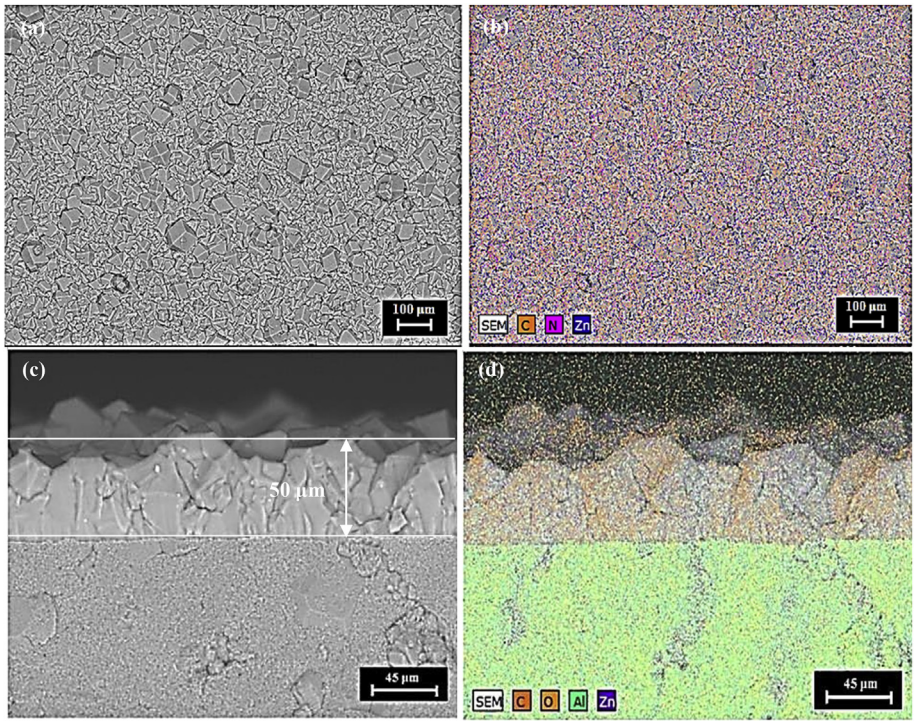

Fig. 1. SEM images of ZIF-8 membrane: (a) Top view and (c) cross section view; EDX mapping of ZIF-8 membrane: (b) Top view and (d) cross section view (Lai et al., 2016).