Available online at www.sciencedirect.com

ScienceDirect

Separation and Purification Technology 59 (2008) 34–42

Separation and Purification Technology

www.elsevier.com/locate/seppur

HZSM5-filled cellulose acetate membranes for pervaporation separation of methanol/MTBE mixtures

Xiaocong Ma, Changlai Hu, Ruili Guo, Xin Fang, Hong Wu, Zhongyi Jiang *

Key Laboratory for Green Chemical Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

Received 9 February 2007; received in revised form 21 May 2007; accepted 21 May 2007

Abstract

HZSM5-filled cellulose acetate (CA) membranes were prepared by incorporating HZSM5 into CA for pervaporation separation of methanol/methyl tertiary butyl ether (MTBE) mixtures. The structural morphology, thermal and mechanical stability, and crystallinity characteristics of these filled membranes were investigated. The effects of HZSM5 content on the sorption, diffusion and pervaporation performance were evaluated. The swelling degree of the HZSM5-filled CA membranes decreased compared with that of CA control membrane. With the increase of HZSM5 content, the permeation flux increased continuously, but the separation factor first increased and then decreased. The CA membrane containing 0.2 wt% HZSM5 showed the highest separation factor of 346 with a permeation flux of 226 g/(m^2 h) for 20 wt% methanol in feed at 303 K. The diffusion coefficients of methanol and MTBE for the HZSM5-filled CA membranes were also estimated. The results showed that the membranes were highly methanol selective. Effects of operating conditions on the pervaporation performance have been systematically assessed. It was found that the permeation flux increased while the separation factor decreased with increasing the amount of methanol in the feed. When increasing temperature from 298 K to 323 K, the permeation flux increased significantly while separation factor decreased only slightly. With the increase of feed flow rate, permeation flux first increased and then decreased while separation factor first decreased and then increased.

Keywords: Cellulose acetate; HZSM5; Pervaporation; MTBE; Methanol

1. Introduction

To reduce air pollution from automobiles, it is recommended to use lead-free or low leaded gasoline. Therefore, several fuel additives are currently added to maintain an adequate octane value of gasoline. Methyl tertiary butyl ether (MTBE), an oxygen-containing chemical, has been mainly used as an octane enhancer. It has been shown that an addition of 10–15% MTBE to gasoline increases the motor octane number by 2–5 [1]. MTBE is also used as a reagent in fine chemical production. For these reasons, the market demand for MTBE is rapidly increasing. MTBE is usually produced by the reaction between methanol and isobutylene at moderate temperature and pressure. It is often desired to add methanol up to 20% excess to improve the reaction conversion. Therefore, the separation of methanol/MTBE mixtures constitutes an important unit operation. Another tricky problem is that methanol forms a minimum azeotrope with MTBE at a composition of 14.3 wt% methanol at atmospheric pressure. Pervaporation, due to its distinct advantages such as energy-saving and environmentally benign, has been demonstrated as a novel and efficient method for the separation of methanol/MTBE mixtures.

So far, many polymers such as cellulose acetate (CA) [2–7], triacetate cellulose (CTA) [8,9], chitosan (CS) [10,11], polyvinyl alcohol (PVA) [12,13], acrylamide (AAM) [14] have been used as membrane materials for pervaporation separation of methanol/MTBE mixtures. The suitable match between the liquid mixtures and the polymer can be judged on the basis of the solubility parameters δ of the solvent and of the polymer, taking into account that the smaller the difference between the solubility parameters, the stronger the solvent–polymer interaction is [5]. Hansen divided the conventional solubility parameter into three partial parameters: dispersion (δ_d), dipole (δ_p) and hydrogen bonding (δ_h). All the three partial solubility parameters of CA, methanol and MTBE are listed in Table 1. It can be found that CA membrane should be a competitive candidate for the separation of methanol/MTBE mixtures.

---

* Corresponding author. Tel.: +86 22 27892143; fax: +86 22 27892143.
E-mail address: zhyjiang@tju.edu.cn (Z. Jiang).

1383-5866/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.seppur.2007.05.023

Table 1
Solubility parameters ($MPa^{1/2}$) of CA, methanol and MTBE

	δ_d	δ_p	δ_k	δ
CA	15.54	16.30	12.94	25.97
Methanol	15.13	12.27	22.29	29.60
MTBE	15.48	3.63	5.22	16.73

Recently, zeolite-filled membranes are widely used in view of their better performances over the pure polymeric membranes [15–21]. For instance, Chung et al. [18] had studied the pervaporation separation of zeolite-filled P84 polyimide membranes for dehydration of isopropanol and found that both the separation factor and permeation flux increased simultaneously by modifying the P84 polyimide membrane with the incorporation of zeolite 5A and 13X. The membrane containing 30 wt% of zeolite 13X was found to exhibit the highest separation factor of 4000 with a permeation flux of 75 g/(m^2 h) for 15 wt% of water in the water–isopropanol mixture at 60 °C. Such filled membranes were chemically and thermally more stable and display better potential than polymer membrane in separating liquids by preferential adsorption and molecular sieving effect. Since HZSM5 has an average pore size of about 0.55 nm, which coincidently lies between the kinetic diameter of methanol molecule (0.40 nm) and MTBE molecule (0.62 nm), HZSM5 should be the appropriate filler for the separation of methanol/MTBE mixtures.

In the present study, the CA control membrane and HZSM5-filled CA membranes were prepared for pervaporation separation of methanol and MTBE mixtures. The membranes were characterized by Fourier transform-infrared, scanning electron microscope, thermogravimetric analysis, universal testing machine and X-ray diffraction, respectively. The effects of HZSM5 content on pervaporation performance of the membranes were investigated. Effects of methanol concentration in the feed, operating temperature and feed flow rate on pervaporation performance of the membrane were systematically investigated.

2. Experimental

2.1. Materials and membrane preparation

Cellulose acetate (54.5–56.0 wt% acetyl content) was purchased from China National Pharmaceutical Group (Shanghai, China). MTBE was purchased from Huayu Trade Corporation (Tianjin, China). Methanol and acetone were purchased from Tianjin Kewei Ltd. (Tianjin, China). HZSM5 (Si/Al was 50) was purchased from Tianjin Nankai Catalyst Ltd. (Tianjin, China) and grinded by ball mill for 6 h before use.

CA was dissolved in acetone solution stirring for 2 h at room temperature to make 10 wt% CA homogeneous solution. A known amount of HZSM5 was added into the CA solution which was stirred for 3 h then was kept in an ultrasonic bath for about 1 h. The CA solution with HZSM5 loading of 0, 0.1, 0.2, 0.5 and 1.0 wt% (the ratio of HZSM5 weight to weight of CA plus HZSM5) were cast onto a glass plate with the aid of a casting knife and then dried at room temperature for 24 h. The obtained membranes were designated as CA, HZSM5-CA-01, HZSM5-CA-02, HZSM5-CA-05, HZSM5-CA-10, respectively. The thickness of these membranes was measured to be around 30 ± 2 μm by micrometer.

2.2. Membrane characterization

2.2.1. FT-IR measurements

Fourier transform infrared (FT-IR) spectra were obtained by a Nicolet, 5DX instrument equipped with both horizontal attenuated total reflectance (HATR) accessories. The experiments were run with air as the background. Thirty-two scans were accumulated with a resolution of 4 cm^{-1} for each spectrum.

2.2.2. Scanning electron microscopy

Scanning electron micrographs of HZSM5, CA membrane and CA filled membrane were performed on a Philips XL-30M scanning electron microscope (SEM) instrument. All specimens were coated with a thin layer of gold to prevent charging.

2.2.3. Thermogravimetric analysis (TGA) studies

Thermal degradation measurements of HZSM5 and the membrane samples were performed using a Perkin-Elmer TG/DTA thermogravimetric analyzer at a heating rate of 10 K/min and temperature programs were run from 303 K to 1073 K. Nitrogen flow was 20 ml/min in order to remove all corrosive gas involved in the degradation.

2.2.4. Mechanical properties studies

Tensile testing was performed at room temperature using an Instron-type tensile testing machine (testometric/M350-10KN ROCHOALL, England) with a crosshead speed of 1 mm/min. The sample width was 10 mm and the length between the jaws was 25 mm. The measurement was performed at 25 ± 2% RH (relative humidity).

2.2.5. X-ray diffraction

X-ray diffraction spectra of CA membrane and CA filled membrane were obtained using a Rigaku D/max 2500v/pc X-ray diffractometer. The diffractograms were measured at 2θ in the range of 5–60° using Cu Kα radiation ($\lambda = 1.54$ Å) monochromated by means of Parabolic filter, a tube voltage of 40 kV and tube current of 200 mA.

2.3. Pervaporation experiments

Pervaporation experiment apparatus used in this study was shown in Fig. 1. The experiments were performed on the membrane module (CM-Celfa AG Company, Switzerland). The effective membrane area in contact with feed was 25.6 cm^2. The vacuum in the downstream side was maintained at about 0.33 kPa using a vacuum pump, and permeate was collected in liquid nitrogen-cold traps. The compositions of the feed and permeate were measured using Agilent 6890 gas chromatography equipped with a Thermal Conductivity Detector (TCD) and a column packed with GDX102 (Tianjin Chemical Reagent