Chemical Engineering Journal 279 (2015) 273–276

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Enhanced CO_2 separation performance of polymer composite membranes through the synergistic effect of 1,3,5-benzenetricarboxylic acid

Yeji Choi [a,1], Young Rae Kim [b,1], Yong Soo Kang [b,*], Sang Wook Kang [a,*]

[a] Department of Chemistry, Sangmyung University, Seoul 110-743, Republic of Korea
[b] Department of Energy Engineering, Hanyang University, Seoul 133-791, Republic of Korea

HIGHLIGHTS

- The utilization of 1,3,5-benzenetricarboxylic acid for synergy effect in CO_2 separation membrane.
- The enhanced solubility of CO_2 by 1,3,5-benzenetricarboxylic acid.
- The barrier effect of 1,3,5-benzenetricarboxylic acid on the transport of N_2.

ARTICLE INFO

Article history:
Received 21 March 2015
Received in revised form 2 May 2015
Accepted 8 May 2015
Available online 14 May 2015

Keywords:
1,3,5-Benzenetricarboxylic acid
Polymer
Membrane
CO_2

ABSTRACT

To achieve enhanced CO_2/N_2 separation performance, 1,3,5-benzenetricarboxylic acid (H_3BTC) was utilized in polymer composite membranes. Since H_3BTC has three carboxylic acids on the benzene ring, the separation performance was expected to be enhanced by the synergistic effect of (1) the increased solubility of CO_2 by dipole–dipole interactions between CO_2 and carboxyl groups in H_3BTC and (2) the barrier effect of H_3BTC on the transport of N_2. Actually, when H_3BTC was incorporated into poly(vinylpyrrolidone) (PVP), the selectivity of CO_2/N_2 increased to 8.5 with a CO_2 gas permeance of 1.2 GPU, while the neat PVP did not show separation performance. The chemical and physical behaviors of H_3BTC in PVP were further investigated by FT-IR and TGA analyses.

1. Introduction

Global warming caused by greenhouse gases is a major environmental problem [1]. In order to solve this problem, the separation of CO_2 is of great interest because the effective capture of CO_2 can reduce greenhouse gas emissions [2–6]. Therefore, many CO_2 separation processes have been developed, including cryogenic separation, adsorption, and membrane separation [7–12]. Compared to other methods, membrane separation technology has many advantages such as energy efficiency and ease of operation [13–16]. However, high selectivity and high permeability remain challenges to be overcome for practical applications [17]. Recently, Hanioka et al. reported the use of a supported liquid membrane (SLM) based on a task-specific ionic liquid to achieve selective and facilitated CO_2 transport using amine-terminated ionic liquid. At 2.5 kPa of CO_2, SLMs based on $[C_3NH_2mim][Tf_2N]$ and $[C_3NH_2mim][CF_3SO_3]$ showed selectivities of approximately 100 and 120, respectively [18]. Bai and Winston Ho reported CO_2 facilitated transport membranes based on a sulfonated polybenzimidazole (SPBI) copolymer matrix. The membrane showed a CO_2/H_2 selectivity of 64.9 and a CO_2 permeability of 2539 barrer in an optimized composition [19]. Ren et al. prepared multilayer PEI/PDMS/PEBA1657/PDMS composite membranes using a dip-coating method. For CO_2/N_2 separation, CO_2 permeance was enhanced by increasing the pressure ratio, resulting in an increase in selectivity [20]. Our group reported a facilitated CO_2 transport membrane by in situ preparation of copper nanoparticles using 1-hexyl-3-methylimidazolium nitrate ($HmimNO_3$). The separation of CO_2/CH_4 and CO_2/N_2 showed ideal selectivities of 6.2 and 7.4, respectively [21]. Furthermore, we reported the CO_2 separation performance of poly(vinylpyrrolidone) (PVP)/potassium fluoride (KF) membranes in order to utilize the interactions between K^+ ions and CO_2 molecules, and we observed a CO_2 permeance of 28.0 GPU and an ideal selectivity of 4.1 for CO_2/N_2 [22]. Very recently, we also reported the CO_2 separation performance of

* Corresponding authors. Tel./fax: +82 2 2287 5362.
E-mail address: swkang@smu.ac.kr (S.W. Kang).
[1] These authors contributed equally to this work as first authors.

http://dx.doi.org/10.1016/j.cej.2015.05.027

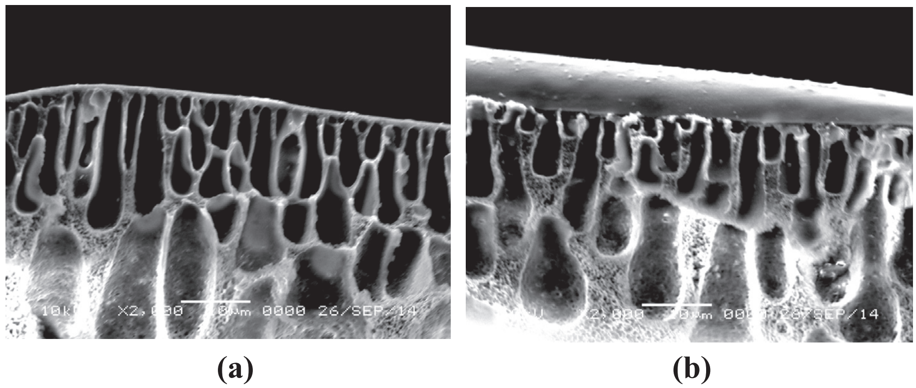

Fig. 1. SEM images of (a) polysulfone support and (b) coated polysulfone membrane.

Table 1
Selectivity and CO_2 permeance of neat PVP and 1/0.05 PVP/H_3BTC membranes.

	Selectivity (CO_2/N_2)	CO_2 permeance (GPU)
Neat PVP	Not measurable	Not measurable
PVP/H_3BTC	8.5	1.2

$BMIM^+BF_4^-$/cyanuric chloride membranes for use of cyanuric chloride as a carrier. This membrane showed a CO_2 permeance of 19.2 GPU and an ideal selectivity of 11.0 for CO_2/N_2 and 10.7 for CO_2/CH_4. The high selectivity was generated by a barrier effect against CH_4 and N_2, while the amine groups on the imidazolium ring and cyanuric chloride selectively interacted with CO_2 molecules [23]. In the present study, we report a PVP/1,3,5-benzenetricarboxylic acid (H_3BTC) membrane for CO_2 separation. In this membrane, it was expected that the carboxyl groups in H_3BTC would facilitate the transport of CO_2 through the membrane, and the barrier effect against N_2 caused by the benzene ring in H_3BTC would prevent the transport of N_2. To investigate the effect of H_3BTC on separation performance, poly(vinylpyrrolidone) (PVP) was utilized as matrix since it was known not to be effective for CO_2 separation.

2. Experimental

Poly(vinylpyrrolidone) (PVP) (Mw = 40,000) and 1,3,5-benzenetricarboxylic acid (H_3BTC) were purchased from Sigma–Aldrich and TCI, respectively, and were used without further purification. A polymer solution was prepared by dissolving PVP in ethanol (20 wt%). To prepare the PVP/H_3BTC solution, H_3BTC was added to the polymer solution at various mole ratios. These solutions were coated onto macroporous polysulfone membrane supports (Toray Co. Ltd, Japan) using an RK Control Coater (Model 101, Control Coater RK Print-Coat Instruments Ltd., UK). Gas flow rates were measured using a bubble flow meter at room temperature and 2 atm. The unit of gas permeance is GPU, where 1 GPU = 1×10^{-6} cm^3 (STP)/(cm^2 s cm Hg). To confirm the effect of H_3BTC concentration in PVP/H_3BTC on the chemical and physical properties, FT-IR, thermal gravimetric analysis (TGA) and DSC were performed. Thickness of the membrane was measured by scanning electron microscopy (SEM).

3. Results and discussion

Scanning electron microscope (SEM) images were obtained to investigate the thickness of the coated film, as shown in Fig. 1. The used polysulfone support was observed to have a finger-like structure. The average thickness of the coated selective layer on the polysulfone support was 6.5 μm. To investigate the effect of H_3BTC concentration in PVP/H_3BTC membranes on CO_2 separation performance, the gas permeance of N_2 and CO_2 through the PVP/H_3BTC membrane was measured with increasing mole ratios of H_3BTC, as shown in Fig. 1.

It was confirmed that the presence of H_3BTC in the solutions increased both N_2 and CO_2 permeance. The best separation performance is described in Table 1.

In the case of a neat PVP membrane, permeance was not detected using a bubble flow meter because of the slow permeation. The low permeance of neat PVP was attributable to the high rigidity of chains in glassy polymer. On the other hand, the ideal

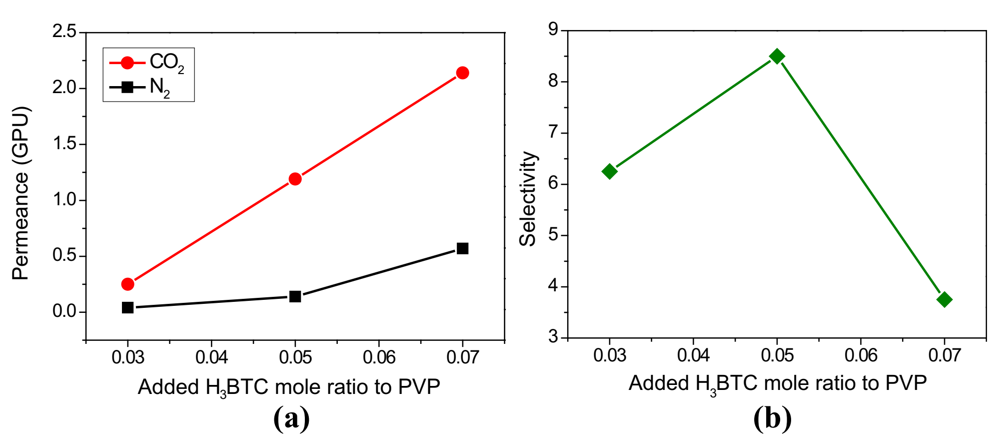

Fig. 2. Gas separation performance of PVP/H_3BTC membranes: (a) pure gas permeance and (b) ideal selectivity of CO_2/N_2.