Journal of Membrane Science 557 (2018) 30–37

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Tailoring CO_2/CH_4 separation properties of mixed-matrix membranes via combined use of two- and three-dimensional metal-organic frameworks

S.A.S.C. Samarasinghe[a,b,c], Chong Yang Chuah[a], Yanqin Yang[a,b], Tae-Hyun Bae[a,b,*]

[a] School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore
[b] Singapore Membrane Technology Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, Singapore
[c] Interdisciplinary Graduate School, Nanyang Technological University, Singapore

ARTICLE INFO

Keywords:
Mixed-matrix membrane
CuBDC nanosheet
ZIF-8
Polyimide
CO_2/CH_4 separation

ABSTRACT

Mixed-matrix membranes containing both two-dimensional (ns-CuBDC) and three-dimensional (ZIF-8) metal-organic frameworks were fabricated to investigate their potential capabilities in CO_2/CH_4 separation. The mixed-matrix membrane containing ns-CuBDC alone was capable of improving CO_2/CH_4 selectivity whereas the mixed-matrix membrane containing ZIF-8 alone ensured improved CO_2 permeability. However, by combining both fillers in a mixed-matrix membrane aimed at tailoring the CO_2/CH_4 separation properties, both CO_2 permeability and CO_2/CH_4selectivity were successfully improved by 16.6% and 30.5%, respectively, which indicates a highly desirable method of performance enhancement. Analysis of solubility-diffusivity in the mixed-matrix membranes revealed that the use of both fillers could improve both solubility selectivity and diffusivity selectivity. Our overall results imply that the separation properties of gas separation membranes can be readily adjusted to meet the requirements of real-world applications by the combined use of two fillers with different geometries.

1. Introduction

There has been growing interest in diversifying current conventional energy generation via fossil fuels with natural gas or biogas to cope with the current global energy demand in the coming years [1]. However, the presence of a substantial amount of CO_2 in natural gas or biogas is not optimal for industrial operations in view of the lower caloric value of the feed and the potential corrosive effect on the transportation pipelines. Thus, natural gas sweetening and biogas upgrading are adopted to increase the CH_4 purity in the feed [2,3]. In comparison to conventional purification processes such as amine scrubbing and cryogenic distillation, membrane-based gas separation offers various merits such as small plant footprint, high energy efficiency and ease of operation [4]. However, for conventional polymeric membranes, which are well-established due to their good processability, the separation performance is often limited by the permeability–selectivity trade-off as solution-diffusion is the dominant transport mechanism for gases [5–7]. However, the utilization of pure molecular sieve membranes made up only of microporous materials such as zeolites and a metal-organic framework (MOF) suffer from poor scalability and high production cost [8–10]. Therefore, the development of membranes that can be produced in a scalable manner but that possess a high CO_2/CH_4 separation performance is urgently required [11].

Several methodologies have been developed to overcome the inherent limitations imposed on polymeric membranes. Among them, incorporation of microporous fillers into the polymeric membrane to form a mixed-matrix membrane has been widely adopted. This is generally considered technically viable at the present stage due to the feasibility of fabricating large-scale membrane modules with large packing density [12,13]. In essence, these advantages are based on the utilization of selected materials that are capable of tuning the overall diffusivity and solubility of a particular gas component to allow a membrane with high permeability and/or selectivity. To date, numerous microporous materials such as zeolites [14–16], MOFs [3,17,18], microporous organic polymers [19–21] and graphene (oxide) [22–24] have been widely incorporated into the polymeric membrane to improve the overall CO_2/CH_4 separation performance. In particular, the number of studies on the utilization of MOFs for mixed-matrix membrane fabrication has increased in recent years. This is attributed to the presence of organic moieties on MOFs that allow good compatibility with the polymer matrix, together with large pore volumes and tunable functionalities via pre- or post-synthetic functionalization [25,26]. This poses significant advantages in comparison to other microporous materials, namely zeolites, which typically require

* Corresponding author at: School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore.
E-mail address: thbae@ntu.edu.sg (T.-H. Bae).

https://doi.org/10.1016/j.memsci.2018.04.025
Received 19 January 2018; Received in revised form 7 April 2018; Accepted 16 April 2018
Available online 17 April 2018
0376-7388/ © 2018 Elsevier B.V. All rights reserved.

additional compatibilization to control the filler-polymer interfaces [27,28]. Depending on the properties of the MOFs selected, the diffusivity or the solubility of resulting membrane can be tuned accordingly if appropriate fillers are strategically selected for use in mixed-matrix membrane fabrication.

Recently, the potential utility of ZIF-8 and nanosheets of CuBDC (ns-CuBDC; copper-1,4-benzene dicarboxylate) as a filler of mixed-matrix membranes has been reported. For instance, ZIF-8 nanocrystals possessing three-dimensional (3D) geometry were proved to be an effective filler to significantly enhance CO_2 permeability due to the presence of large pore cavities (ca. 11.6 Å) that allows the rapid transport of CO_2 [29,30]. The presence of narrow 6-membrane ring window (ca. 3.40 Å) that connects to the large cavities allows an efficient molecular separation. It is noteworthy that the effective window size can be extended up to 4.12 Å due to the flexibility of the framework [31,32]. In contrast, two-dimensional (2D) ns-CuBDC, which possess a high aspect ratio and a pore aperture (ca. 5.2 Å) that can preferentially transport CO_2 over CH_4, are of great interest because CH_4 is forced to adopt a tortuous path that results in a dramatic increase in its diffusion path in the membrane, which leads to improved CO_2/CH_4 selectivity [33,34]. More importantly, such 2D filler enhances CO_2/CH_4 selectivity even with a small filler loading (e.g., 2 wt%), whereas the incorporation of a 3D MOF typically requires a high filler loading (e.g., 10 wt% or above) to attain a clear enhancement in performance. However, studies conducted to date have tended to investigate the properties of mixed-matrix membranes containing only one type of MOF (2D or 3D), which can mostly improve either CO_2 permeability or CO_2/CH_4 selectivity. In such cases, it may be difficult to tailor the direction of performance enhancement in a specific desired direction on the selectivity-permeability map. For example, the enhancement in CO_2/CH_4 selectivity by incorporating a 2D filler is typically accompanied by a sacrifice in the permeability [33,34]. In contrast, highly porous 3D fillers that can effectively improve gas permeability often show the limited effect on CO_2/CH_4 selectivity [10,14,27].

Therefore, in this work, we demonstrate the tailored enhancement of CO_2/CH_4 separation performance of a mixed-matrix membrane via the combined use of 2D and 3D MOF fillers. ODPA-TMPDA (ODPA = 4,4′-oxydiphthalic anhydride; TMPDA = 2,4,6-trimethyl-*m*-phenylenediamine) polyimide was selected as the polymer matrix in this study as it is generally more permeable than conventional commercial glassy polymers (e.g., Matrimid®, polysulfone, Ultem®), and it can be readily synthesized with no further purification of monomers, which is highly desirable for potential large-scale production. It is noteworthy that the syntheses of high-performance membrane polymers typically require rigorous monomer purifications to increase the molecular weight of the resulting polymer [3,33,35]. In addition, the effects of 2D and 3D fillers on the solubility and diffusivity of gases in the mixed-matrix membrane are also studied to understand the mechanism behind the enhancement in performance.

2. Experimental

2.1. Materials

Copper(II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$), 1,4-benzenedicarboxylic acid(H_2BDC), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), 2-methylimidazole (Hmim), 4,4′-oxydiphthalic anhydride (ODPA), 2,4,6-trimethyl-*m*-phenylenediamine (TMPDA), triethylamine (TEA), acetic anhydride (Ac_2O), chloroform ($CHCl_3$), N,N-dimethylformamide (DMF), dichloromethane (DCM), acetonitrile (CH_3CN), absolute ethanol, methanol and N,N-dimethylacetamide (DMAc) were used as received without further purifications.

2.2. Synthesis of ODPA-TMPDA polymer

The synthesis of ODPA-TMPDA was conducted based on the experimental procedures described in a previous work with modifications [35]. The synthesis of ODPA-TMPDA was conducted in an inert environment. First, 1.63 g of TMPDA was added to a round-bottom flask followed by 20.0 g of DMAc, and the mixture was stirred vigorously. Next, 3.36 g of ODPA was added to the mixture, whereupon the resultant mixture was stirred continuously for 24 h to obtain a viscous solution of 20 wt% polyamic acid. The imidization process was conducted by adding 4.44 g of Ac_2O and 4.39 g of TEA into the solution. The mixture was allowed to agitate for 24 h, whereupon the resultant polymer solution was poured slowly into a beaker containing 300 ml of absolute ethanol to precipitate the ODPA-TMPDA polymer. The precipitated ODPA-TMPDA polymer was then washed with copious amounts of fresh ethanol before drying in a vacuum oven at 200 °C overnight.

2.3. Synthesis of CuBDC nanosheets (ns-CuBDC)

ns-CuBDC were synthesized using the three-layer method as described elsewhere using a glass tube with an inner diameter of 13 mm [33,34]. The bottom layer (3 g of H_2BDC dissolved in 2 ml DMF and 1 ml CH_3CN, middle layer (2 ml, mixture of DMF and CH_3CN in a 1:1 ratio), and top layer (3 g of $Cu(NO_3)_2{\cdot}3H_2O$ dissolved in 1 ml of DMF and 2 ml of CH_3CN) were cautiously poured to the tube to avoid premature mixing. The tube was then placed in a convection oven at 40 °C for 24 h under a static condition. The blue precipitate was collected by repetitive centrifugation-redispersion cycles with DMF (3 times) and $CHCl_3$ (3 times). The resulting material was left suspended in DCM for the subsequent characterizations and composite membrane fabrication.

2.4. Synthesis of ZIF-8

ZIF-8 nanocrystals were synthesized according to the method reported in a previous work [36]. In two separate storage flasks, 1.47 g of $Zn(NO_3)_2{\cdot}6H_2O$ and 3.24 g of Hmim were dissolved in 100 ml methanol. Once the solutions were completely dissolved, the solution containing $Zn(NO_3)_2{\cdot}6H_2O$ was rapidly added to the solution containing Hmim under strong agitation. The resulting solution was left for 1 h before separating the ZIF-8nanoparticles from the mother liquid and performing repetitive centrifugation-redispersion cycles with fresh methanol. The ZIF-8 nanocrystals were eventually dried in a vacuum oven at 60 °C for subsequent characterizations and composite membrane fabrication.

2.5. Membrane fabrication

All membranes were fabricated using the solution casting method. The pure ODPA-TMPDA membrane was fabricated from a dope solution made by dissolving 0.5 g of polymer into 4 g of $CHCl_3$. However, to make the dope solutions for the composite membranes, a specified amount of the (ZIF-8 [10 wt%] and/or ns-CuBDC [2 wt%]) was dispersed into 4 g of $CHCl_3$ with the aid of sonication. Next, 0.25 g of polymer was added to the resulting suspensions, which were then gently shaken with a laboratory shaker at room temperature for about 3–4 h. Subsequently, 0.25 g polymer was again added, and the resulting suspension was shaken continuously for 1 day. Thereafter, the dope solution was cast on a glass plate with a casting knife in a glove bag that was filled with $CHCl_3$ vapor, and the nascent membranes were left undisturbed at room temperature for 1 day. The resulting membranes were annealed in a vacuum oven at 160 °C for 1 day prior to gas permeation testing.

2.6. Characterization

2.6.1. Characterizations of ns-CuBDC and ZIF-8

The height profile of ns-CuBDC was measured using atomic force microscopy (AFM, Veeco Multimode Nanoscope 3A microscope) in the

Download English Version:

https://daneshyari.com/en/article/7019838

Download Persian Version:

https://daneshyari.com/article/7019838

Daneshyari.com