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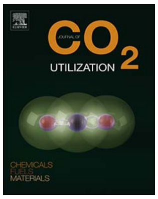

Enhancing the CO_2 plasticization resistance of PS mixed-matrix membrane by blunt zeolitic imidazolate framework

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ABSTRACT

A novel design to synthesize a defect-free mixed-matrix membrane (MMM) exhibiting superior gas separation performance via fully dispersed blunt zeolitic imidazolate framework (ZIF-8) in polymer matrix has been proposed for the first time. The sphericity and interconnected six-membered-ring (6-MR) pore porosity of ZIF-8 was controlled through an aqueous synthetic process by using a non-ionic surfactant (Pluronics, P123) and deionized water as solvent. The use of surfactant in ZIF-8 synthesis resulted in blunt nanocrystals with increased sphericity and 6-MR pore volume as confirmed by scanning electron microscopy (SEM) and nitrogen adsorption–desorption isotherm measurements. Subsequent pure gas permeation tests showed that blunt ZIF-8 increased CO_2/N_2 separation performance through "ideal morphology" in MMMs as a result of the excellent dispersion of ZIF-8 and good ZIF-8-polymer interfacial adhesion within the polymer matrix. A significant increase in CO_2/N_2 separation results were obtained with the MMM containing 10wt% loading of blunt ZIF-8 (P51), CO_2 permeability of 21.5 Barrer (172.6%), and mixed-gas CO_2/N_2 selectivity of 43.9 (205.6%). The MMMs further displayed good aging-resistance properties for over 40 days, with considerable potential for long-term operation.

1. Introduction

Membrane separation is considered one of the most efficient carbon capture technologies currently available for addressing the major challenge of anthropogenic climate change. Thus, owing to their attractive advantages, including simple construction and high energy efficiency [1–3], membrane materials have continued to advance rapidly over the past decades. Significant research effort has been devoted to developing an effective CO_2 separation membrane with high permeability and selectivity that would overcome the Robeson's upper-bound limit [4–6]. Among the potential materials, mixed-matrix membranes (MMMs) that combine polymeric membrane materials with inorganic fillers have been considered as some of the most promising gas separation membranes that might achieve commercial feasibility [7–10]. In terms of the advantages of the polymer and filler phases, the polymeric material-based membrane matrix can be easily fabricated on a large scale, and the inorganic fillers offer special gas-transport pathways to improve the gas separation performance [8,11]. Among the number of inorganic fillers reported for application in MMMs to date, metal-organic frameworks (MOFs) represent a relatively new class of crystalline porous materials, which offer attractive properties, including high porosity, tunable pore size, and well-defined molecular adsorption capacity [12,13].

Zeolitic imidazolate frameworks (ZIFs) are a subclass of MOFs formed through a self-assembly approach, which mimic the structures of aluminosilicate zeolites with transition metals (Co, Cu, Zn, and other elements) as nodes, linked by organic ligands (imidazolate or benzimidazolate) via coordination forces [14–16], as shown in Scheme 1(a1). The ZIF-8 $[Zn(Hmim)_2]$ crystal, for example, was synthesized from Zn^{2+} and 2-methylimidazole (Hmim) ligand, presents a sodalite (SOD)-type framework topology, and exhibits large pore cavities (11.6 Å) connected through six-membered windows with small pore apertures (3.4 Å) [17]. Therefore, ZIF-8 possesses bi-modal pore-size distribution, with two peaks at 11.6 Å and 3.4 Å, which can improve gas permeability and selectivity, respectively. The latter pore window (3.4 Å) is close to the kinetic diameter of CO_2 (3.28 Å) and can thus be beneficial for CO_2 separation from N_2 (3.64 Å) via molecular sieve mechanism [18–20].

As shown in Table 1, ZIF-8 has been already incorporated into a number of polymeric matrices to improve gas separation performance.

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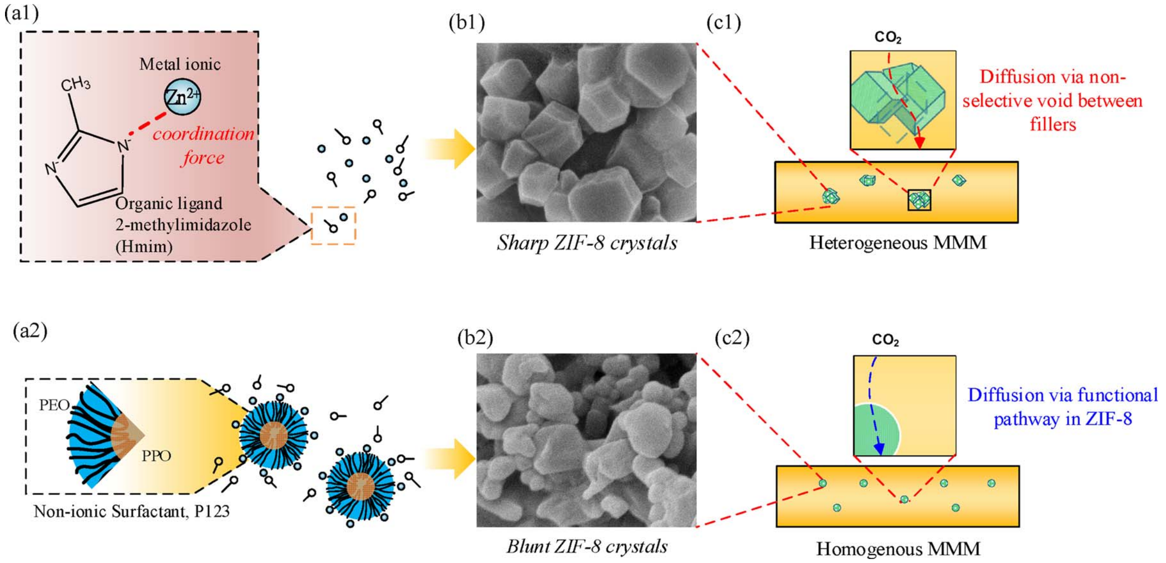

Scheme 1. (a) Synthetic mechanisms for the formation of ZIF-8 filler (1) without and (2) with P123 as a surfactant for (b) shape modification and (c) CO_2 transport properties in MMMs.

Table 1
Overview of ZIF-8-based MMMs employed for gas separation to date.

Polymer[a]	Loadings (wt%)	Separation performance			Ref.
		$P(CO_2)$ (Barrer)	$\alpha(CO_2/N_2)$	$\alpha(CO_2/CH_4)$	
PMPS	4.5	827	7	7	[21]
PVAm	9.1–23.1	173–297 (GPU)	72–83	–	[22]
SEBS	30	37.9–42.9	10.6–12.0	5.2–5.4	[23]
Pebax/IL[bmim][Tf2N]	15	104.9	83.9	34.8	[24]
PI	7–30	560–1437	12–20	16–27	[25]
Matrimid5218	5–30	10–28	17.1–21.2	24.9–39.1	[26]
Ultem® 1000	17 vol%	18–34 (GPU at 25–45°)	28–44	–	[27]
PSF (and S1C-PSF)	16	6–12	12–25	15–24	[28]
PSF	5	15–28 (GPU at 25–45°)	–	5.7–28.5	[29]

[a] PMPS: polymethylphenylsiloxane; PVAm: polyvinylamine; SEBS: polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene; IL: ionic liquid ([bmim][Tf2N]); Matrimid5218: polyimide (PI); Ultem® 1000: polyetherimide (PEI); polysulfone (PSF), zeolite silicalite-1 (S1C).

Diestel et al. [21] prepared MMMs consisting of polymethylphenylsiloxane (PMPS) and ZIF-8 at 4.5wt% loading and demonstrated an increase in CO_2 permeability from 305 Barrer to 827 Barrer but a slight decrease in CO_2/N_2 selectivity from 9 to 7. Zhao et al. [22] also observed similar results with poly(vinylamine) (PVAm)/ZIF-8 MMMs. The study reported that the transport of CO_2 was mediated not only by the ZIF-8 pore apertures but also by the intermolecular void of the polymer matrix, arising as a result of the disruption of the polymer assembly due to the incorporation of ZIF-8. Chi et al. [23] further studied the effect of ZIF-8 particle size (ranging from 70 nm to 580 nm) on the gas permeation performance of polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SEBS)-derived MMMs. In their study, ZIF-8 with a particle size of 240 nm achieved effective improvement in performance, namely, the CO_2 permeability increased from 170.6 Barrer to 454.6 Barrer, and the selectivity remained stable due to the elimination of interfacial voids between the polymeric matrix and ZIF-8 fillers. To improve the adhesion between the ZIF-8 filler and polymer matrix, Li et al. [24] and Wang et al. [25] both used interfacial modification to coat an ultrathin polymer layer on the surface of ZIF-8 to improve its compatibility with the polymer matrix and to avoid loss of selectivity.

Despite all of the previous investigations that attempted to combine ZIF-8 with a variety of polymer matrices, the separation performance of ZIF-8-containing MMMs continues to be restricted by structure-related defects at the polymer–filler interfaces, which result in increased permeability for all gases while leaving the selectivity unchanged or reduced [30–32]. In addition, further consideration needs to be given to the influence of the filler's shape on its adhesion with the polymer matrix, which can reduce gas pair selectivity.

The shape usually adopted by ZIF-8 is that of rhombic dodecahedra or cubes. However, the polyhedron properties of ZIF-8 in the polymer matrix are the main reason for the formation of interfacial voids as a result of the poor adhesion between the polymer and ZIF-8 as the inorganic filler [33,34]. MMMs are typically prepared through solution casting, followed by solvent evaporation. The formation of interfacial voids during the solvent evaporation process [35] has been reported to occur as a result of the differences in the thermal expansion coefficients of the polymer and filler. This issue is of particular importance for glassy polymers with hard properties [36,37]. As shown in Scheme 1(c1), the polyhedral filler can result in aggregation in the polymer matrix to form a heterogeneous MMM. Consequently, gas molecules will be able to pass through the nonselective (less resistant) void between fillers instead of passing through the functional pathways in the filler. Thus, an improvement in the interfacial adhesion properties is essential to achieving high performance ZIF-8-containing MMMs.

Up until now, the solvothermal synthesis of ZIF-8 was the most widely adopted synthetic approach [38]. To reduce the environmental impact, green synthetic processes have been developed for the fabrication of ZIF-8 crystals at room temperature [39–41]. Bustamante et al. [42] used water as a green solvent to replace organic solvent (e.g., DMF, acetone, *n*-propanol, or other solvent). Kida et al. [39] reported a controlled, low stoichiometric molar ratio of the metal and organic ligand (Zn:Hmim = 1:2) as a way of reducing excessive organic ligand waste. McCarthy et al. [43] employed amines (triethylamine and NH_4OH) as promoters to improve the reaction efficiency by enhancing the deprotonation of organic ligands. Furthermore, previous studies utilized surfactants, including Pluronic® (triblock copolymer) [44] and CTAB (cetrimonium bromide) [41,45] in aqueous solution systems, which act as capping agents to control the stability of the reaction system and as promoters to increase the product yield. Yao et al. [44] added Pluronic® P123 surfactant [poly(ethylene glycol)-*b*-poly(propylene glycol)-*b*-poly(ethylene glycol)] to improve the yield of ZIF. The