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MIL-53 frameworks in mixed-matrix membranes

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ABSTRACT

The MIL-53 metal–organic framework (MOF) is known to change reversibly from an open-pore framework (MIL-53-ht) to a closed-pore framework (MIL-53-lt) depending on the temperature, pressure, or guest molecules absorbed. Three frameworks of the additive, MIL-53-as synthesized (MIL-53-as), MIL-53-ht, and MIL-53-lt, were prepared, characterized, and combined with Matrimid® to form mixed-matrix membranes (MMMs) for gas separations. The MIL-53-ht/Matrimid® MMMs exhibited higher values of permeability compared to Matrimid® as well as an increased CO_2/CH_4 selectivity suggesting that the open-pore MIL-53 framework was maintained in the polymer matrix. In addition to higher permeability values, MIL-53-as/Matrimid® MMMs showed higher selectivity for gas pairs with kinetic diameters differing by $\geqslant 0.5$ Å, including H_2/O_2, CO_2/CH_4, H_2/CH_4, and H_2/N_2, suggesting the presence of excess benzene dicarboxylic acid molecules within the pores that reduced its diameter enabling the material to discriminate between smaller and larger gases. MIL-53-lt did not retain its closed-pore form in the MMM. Rather, it irreversibly converted to the open-pore form (MIL-53-ht) due to the exchange of water present in the MIL-53 pores with chloroform solvent molecules during membrane casting and to pore penetration and confinement by Matrimid® polymer chains. This finding, that a polymer matrix stabilizes a MOF pore architecture within an MMM, is significant in that the desired selectivity of a MOF-MMM system may be achievable.

1. Introduction

Membranes for use in gas separation applications are gaining importance [1–3]. The challenge is to develop membranes with high permeability and high selectivity under operating conditions appropriate to industrial processes. A potential evolutionary step towards utilizing gas separation membranes is to combine nanoporous particulate materials with polymers to form mixed-matrix membranes (MMMs). MMMs combine the easy processability of polymers with the selective adsorption properties of inorganic additives [4–7].

Metal–organic frameworks (MOFs) are hybrid, inorganic–organic crystals constructed from metal ions that are linked by polydentate ligands [8]. They are being studied for gas separation and gas storage because of their large surface area, pore size variety, pore functionality, and gas affinity [9]. MOFs are being used as additives in MMMs because they have exhibited promising permeability and selectivity performance for gas separation processes [10,11]. The functionalizable frameworks and finite pore sizes of MOFs potentially enable them to act as molecular sieves allowing size exclusion of certain gas molecules. Moreover, the metal ion and organic linkers of the MOFs can help to improve interfacial contact with the polymer matrix in the MMM.

One interesting property of some MOFs is their structural flexibility. The MOF structure can change reversibly as gas or liquid molecules adsorb into the pores [12]. 'Breathing' in MOFs is characterized by a reversible expansion or contraction of the unit cell volume from as little as 40% to as much as 230% upon adsorption or desorption of guest molecules [13]. The breathing ability of MOFs can potentially be exploited in MMMs for the molecular sieving of gas molecules. For example, MOF-Co(1,4-benzenedipyrazolate) undergoes a structural change in the orientation of the benzene rings relative to the pyrazolate rings as well as a transition for Co(II) from square planar to tetrahedral coordination upon adsorption of N_2 [14]. Another MOF known as TetZB, containing tetrakis [4-(carboxyphenyl)-oxamethyl]methane, zinc nitrate hexahydrate, and bipyridine, breathes from a contracted to an expanded framework upon absorption of CO_2 and non-polar hydrocarbons [15].

Among the 'breathing' MOFs, MIL-53 (Materials Institute Lavoisier-53) is one of the most studied because contraction or

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expansion of its framework can be induced by pressure [16], temperature [17], and the adsorption of guest molecules [18,19]. MIL-53 is composed of a 3D network of trans-chains of $MO_4(OH)_2$ octahedra (M = Al [20,21], Cr [13,22,23], Ga [24,25], Fe [26–29], and Sc [30,31]), which are interconnected by 1,4-benzenedicarboxylate groups, creating 1D rhombic-shaped tunnels [32]. Beurroies et al. reported that the volume of MIL-53 decreases with an increase in pressure starting from 1 to 3 MPa [16]. However, at 55 MPa, MIL-53 begins to expand in volume causing the framework to transform from a closed-pore (MIL-53-lt) to an open-pore (MIL-53-ht) form. MIL-53 also responds to a temperature stimulus by transitioning from a closed-pore to an open-pore framework upon heating from 52 to 102 °C, while the transition from the open-pore to closed-pore form occurs from −148 to −123 °C [17]. The expansion or contraction of the MIL-53 framework is accompanied by a temperature hysteresis, which can consequently lead to a biphasic composition upon cooling to room temperature [17]. Serre et al. have shown that MIL-53 is in the open-pore form upon very fast CO_2 uptake at low pressures of 1–4 bars, while at higher pressures of 6–10 bars, it transitions from the open-pore to the closed-pore form with the additional adsorption of ~10 mmol/g of CO_2 [19]. The interplay of temperature, pressure, and molecular absorption can be utilized to bring about MIL-53 framework transitions that can potentially be beneficial in selectively transporting gases.

Although the different analogs of MIL-53 are isostructural and have the ability to breathe upon the absorption of various guest molecules, they have different breathing behaviors. For example, in their dehydrated state, MIL-53(Cr) and MIL-53(Fe) have open-pore [22] and closed-pore [26] structures, respectively. The thermal behavior of MIL-53(Al) is similar to that of the MIL-53(Cr), however, MIL-53(Ga) behaves differently with the closed-pore form persisting at higher temperatures [24]. The same phenomenon is observed with MIL-53(Sc), for which a very narrow pore exists at high temperatures [30]. Among these, MIL-53(Al) is the most thermally stable, up to 500 °C, and has the largest Langmuir surface area of 1590 m^2/g [32]. With different treatments, three variants of MIL-53(Al) (-as, -ht, -lt) can exist. The pores of MIL-53-as-synthesized (MIL-53-as) are occupied by unreacted benzenedicarboxylic acid (BDC) molecules. These excess BDC molecules can be removed by heating MIL-53-as at 330 °C. The resulting structure is referred to as MIL-53-high-temperature (MIL-53-ht), which has empty, open pores of 8.5 Å × 8.5 Å in diameter. Upon cooling in air, the structure absorbs water leading to the third form, MIL-53-low-temperature (MIL-53-lt), having smaller or closed pores with dimensions of 2.6 Å × 13 Å [32]. This hydrated form of MIL-53 has contracted pores due to the H-bond interactions between the hydrogen atoms of the absorbed water molecules and the oxygen atoms of the carboxylate functionalities of the linker and the OH-groups associated with aluminum [32]. The absorbed water can be removed by heating, resulting in the MIL-53 open-pore (MIL-53-ht) structure. This transition is fully reversible when water is evacuated from the pores, and no bond breaking or phase transition is observed in the process [13].

Basu and co-workers reported fabricating dense, asymmetric MIL-53(Al)/Matrimid® MMMs and testing them for CO_2/CH_4 and CO_2/N_2 gas separation performance [33]. Enhancements in both selectivity and permeance were observed for a 30 wt% MIL-53 loading compared to Matrimid®. The 18% CO_2/CH_4 and 8% CO_2/N_2 selectivity enhancements were attributed to the breathing of MIL-53 and to the preferentially strong interactions of CO_2 with the hydroxyl groups of MIL-53. Although the study did not specify the MIL-53 framework in the MMM, the 218% increase in CO_2 permeance suggests that the MIL-53 is in the open-pore (MIL-53-ht) form. Another study utilizing MIL-53 in the form of pellets, with polyvinyl alcohol as binder, showed preferential adsorption of CO_2 compared to CH_4 in the 1–8 bar pressure range [34]. The observed CO_2 selectivity was also attributed to framework breathing and to preferential interaction of CO_2 with the hydroxyl groups in the MIL-53 framework.

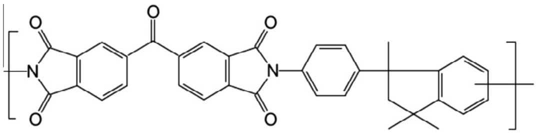

Fig. 1. Structure of Matrimid®.

In the present study, MIL-53(Al) was incorporated into Matrimid® membranes. The MIL-53 ht (open-pore) and lt (closed-pore) forms of MIL-53 were used separately as inorganic additives to determine the effect of pore size on the gas separation efficiency of the membranes as well as to gain insight into the framework transitions of MIL-53 in the MMM. Matrimid® (Fig. 1), a commercially available glassy polymer possessing high gas permeability and selectivity, a high glass transition temperature (T_g), high thermal stability, and solvent resistant properties, was selected as the polymer for the MMMs [35]. MIL-53/Matrimid® MMMs were fabricated, characterized, and tested for gas permeability and separation properties. We anticipated that gas transport would be enhanced with MIL-53 in its open-pore form in the MMM, while in its closed-pore form MIL-53 would act as a gas molecular sieve. Our MIL-53-ht/Matrimid® MMM results corroborate those reported by Basu et al. [33], showing increases in gas permeabilities and a 20% enhancement in CO_2/CH_4 selectivity. The MIL-53-lt form could not be maintained in the MMM, despite exploring ways to stabilize the closed framework. The combined effect of the casting solvent ($CHCl_3$), which exchanged with the water in the pores, and the rigidity of the Matrimid® polymer matrix caused the MIL-53-lt form to irreversibly transform into the MIL-53-ht framework within the MMM. The penetration of the polymer chains into the pores of MIL-53 prevented its ability to 'breathe', thus keeping the MIL-53 in its high temperature framework. Our results demonstrate the stabilizing effect that the polymer matrix of an MMM can have on the framework of a flexible MOF.

2. Experimental

2.1. Materials

Deionized water (H_2O, HPLC grade) and chloroform ($CHCl_3$, 99% purity) were purchased from Fisher Scientific. $CHCl_3$ was dried with activated 4A molecular sieves (Sigma–Aldrich) prior to use. Triethylamine (TEA, 98% purity), aluminum nitrate nonahydrate [$Al(NO_3)_3 \cdot 9H_2O$, 98% purity], and 1,4-benzenedicarboxylic acid (BDC, 99% purity) were purchased from Sigma–Aldrich and used as received. Matrimid® 5218 polymer was generously provided by Huntsman Chemicals, Inc. Prior to use, the Matrimid® was dried in a vacuum oven at 120 °C for 12 h. Mylar® A92 thin films for membrane casting substrates were purchased from Active Industries, Inc. Gases for permeation experiments, including nitrogen (N_2, 99.99% purity), oxygen (O_2, 99.50% purity), hydrogen (H_2, 99.99% purity), methane (CH_4, 99.50% purity), and carbon dioxide (CO_2, 99.99% purity), were purchased from Air Liquide.

2.2. Synthesis of MIL-53

The MIL-53-lt microcrystals were hydrothermally synthesized following a literature procedure [32]. A solution of $Al(NO_3)_3 \cdot 9H_2O$, BDC, and H_2O having a molar composition of 1 Al (1.88 g): 0.5 BDC (0.41 g): 80 H_2O (3.6 mL) in an autoclave vessel was heated in an oven at 220 °C for 3 d. After filtering the product and washing it