Simple Fabrication Method for Mixed Matrix Membranes with in Situ MOF Growth for Gas Separation

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ABSTRACT: Metal organic framework (MOF)/polymer composite membranes are of interest for gas separations, as they often have performance that exceeds the neat polymer. However, traditional composite membranes, known as mixed matrix membranes (MMMs), can have complex and time-consuming preparation procedures. The MOF and polymer are traditionally prepared separately and require priming and mixing to ensure uniform distribution of particles and compatibility of the polymer--particle interface. In this study, we reduce the number of steps using an in situ MOF growth strategy. Herein, MMMs are prepared by growing MOF (UiO-66) in situ within a Matrimid polymer matrix while simultaneously curing the matrix. The gas separation performance for MMMs, prepared using this approach, was evaluated for the CO2/N2 separation and compared with MMMs made using the traditional postsynthesis mixing. It was found that MMMs prepared using both the in situ MOF growth strategy and by traditional postsynthesis mixing are equivalent in performance. However, using the in situ MOF growth allows for a simpler, faster, and potentially more economical fabrication alternative for MMMs.

KEYWORDS: metal organic framework, mixed matrix membrane, in situ growth, Matrimid, UiO-66, CO2/N2 separation

1. INTRODUCTION

Postcombustion carbon capture from fossil energy production is a challenging separation due to the low partial pressure driving force of CO2 in flue gas (~0.10−0.14 bar for coal-derived emissions).1−3 To add to the problem, an enormous volume of gas is emitted by industrial-scale power plants. A typical 500 MW coal-fired power plant emits ~1.5 × 10⁶ m³/h of flue gas, which contains ~200 000 m³/h of CO₂ gas (~3.6 M tonne CO₂ per year).4,5 Because of the scale of gases to be separated in this application, minimizing the cost of the capture media is of critical importance for the successful implementation of a carbon capture technology.

Membrane technology is a promising solution for industrial gas separations because membranes can be engineered for low-cost and high-energy efficiency.6−8 However, postcombustion carbon capture is a particularly difficult separation for membranes as their gas separation performance is limited by the trade-off between permeability and selectivity defined by the Robeson upper bound.9,10 The permeability of gases through the membrane can be described by the solution diffusion model, in which the permeability is the product of the CO₂ gas solubility and diffusivity.11,12 Some researchers have investigated improving the CO₂ permeability to effectively process the large volume of gas with a smaller membrane area.6 Permeability can be improved by increasing the polymer’s free volume or by using structural features to alter the polymer interchain spacing.13−15 Normally, this approach would be at odds with improving selectivity, though, which is defined as the ratio of permeabilities of different gases. By contrast, other research efforts, involving membranes for carbon capture, have focused on improving the CO2/N2 selectivity of membranes to increase the CO₂ purity, for example, by using facilitated transport.14,15 Improving both permeability and selectivity above the Robeson upper bound is desirable, but is difficult to achieve using pure polymeric membranes.

By adding filler particles to a polymer matrix to make mixed matrix membranes (MMMs), it is possible to move beyond the performance limitations of conventional polymer films. The use of filler particles can result in increasing the polymer’s free volume, thus increasing the membrane permeability. Furthermore, by combining gas-selective filler particles that possess permeability that matched with the polymer matrix,
it is possible to simultaneously improve both the permeability and selectivity of the membrane. Filler particles, such as porous carbon, metal oxides, silica, zeolites, or metal organic frameworks (MOFs), are among the many different types of additives used to fabricate MMMs. MOFs are of particular interest for MMMs because their properties are easily tailored to yield a strong interaction at the polymer—particle interface. However, defects such as the nonuniform distribution of particles, within the matrix, can reduce the effectiveness of MMMs. Severe agglomerations of particles can lead to nonselective pathways for gases in the membrane. To avoid particle agglomerations and improve the particle—matrix interaction, complex multistep fabrication procedures are used. Using conventional fabrication techniques for MMMs, referred to in this text as the postsynthesis mixing approach, previously synthesized filler particles are first dispersed in the membrane-casting solvent by sonication. Following this, the polymer is gradually added to the filler particle suspension, and mixing times can vary from a few hours to days. These initial steps are referred to as “priming” of the filler particle. Finally, when the filler particle and polymer are successfully combined and properly degassed to avoid air bubble defects in the film, the MMM is cast either as a free-standing film or on the surface of a support. In general, this process can be time-consuming and labor-intensive, which, on a large scale, will lead to increased manufacturing cost. SEOANE et al. first synthesized MIL-68(Al) using the tetrahydrofuran solvent and used the same suspension to dissolve the polysulfone polymer before fabricating the MMM, which reduced the number of steps compared to conventional fabrication. They also fabricated the membranes by synthesizing MOF in the presence of a small amount of polysulfone (3 wt %) as a primer (known as priming technique, as mentioned earlier) during the synthesis of MOF. This polymer usually attaches to the MOF and keeps the small MOF particles dispersed and also results in the improvement of the interaction between the polymer and filler. Zhao et al. further improved the process and reduced the number of MMM fabrication steps by synthesizing Cu4I4-MOF in polymer for sensor applications.

In this study, we have used a simple fabrication scheme for MMMs that involves the in situ MOF growth within the polymer matrix, while simultaneously casting the membrane as a flat sheet. Membranes fabricated using this scheme will be referred to, in this text, as MMMs with in situ MOF growth. Using this strategy, we eliminate the pre-MOF synthesis and priming steps to reduce time and cost. Matrimid was chosen as the polymer matrix because it is a well-characterized material, has high chemical and thermal stability, and typically forms robust free-standing films. A MOF, UiO-66, was employed as the porous filler particle in the Matrimid matrix. UiO-66 is a zirconium-based MOF that is chemically and thermally stable, has a moderate pore size, and is easily tailored. MMMs with UiO-66 in Matrimid (0–11 wt %) were investigated using the in situ MOF growth and were compared to MMMs fabricated using postsynthesis MOF mixing.

In this work, low MOF loadings were used to reduce agglomeration of particles. In many literature reports with higher MOF loadings (>10 wt %), the CO2 permeability increases while the selectivity decreases, which is an indication of particle agglomeration and can be accompanied by other undesirable properties, such as poor mechanical stability or rigidification of the polymer. For example, this has been shown in many reports using the low-permeability polyimide known as Matrimid. Perez et al. investigated MMMs fabricated with MOF-5 in Matrimid for CO2/CH4 separation. They found that using MOF loadings >10 wt % led to a decrease in selectivity, whereas the permeability increased. ORDOÑEZ et al. investigated MMMs consisting of ZIF-8 in Matrimid (MOF loadings of 0–60 wt %) with a similar result. DOROSTI et al. investigated MMMs with a zeolite, ZSM-5, in Matrimid and also a MOF, MIL-53(Al), in Matrimid with 0–30 wt % MOF loadings. They observed that the gas permeance increased with filler loading, but at high loadings (>15 wt %), the selectivity dropped. SHAHID et al. fabricated MMMs with ZIF-8 in Matrimid using a different in situ growth strategy from that described in this text. MATRIMID was modified with an imidazole and then zeolitic imidazolate framework (ZIF) precursors were added, and a film was cast in a solvent-rich vapor environment. They observed a decrease in the selectivity at high ZIF loadings with an increase in permeability, as was reported with traditional MMM fabrication schemes described above by PÉREZ, ORDOÑEZ, and DOROSTI. Other examples of Matrimid-based MMMs with similar performance results have also been reported.

Performance limitations based on particle agglomeration also occur in highly permeable polymers, such as polymers of intrinsic porosity (PIM-1). For example, BUSHELL et al. investigated MMMs consisting of ZIF-8 in PIM-1 for CO2/CH4 separation. They found that at low ZIF loadings, the MMM had increased permeability and selectivity; however, at loadings >30 wt %, the selectivity decreased. Similar results were observed by ALVENTIER et al. for MMMs with MIL-101 in PIM-1. SMITH et al. found that MMMs consisting of Ti-exchanged UiO-66 filler particles in PIM-1 had enhanced performance with a filler loading of <5 wt %; however, >5 wt % leads to a decrease in performance. GHALEI et al. found that MMMs with low loadings of MOF (UiO-66 and functionalized UiO-66) in PIM-1 had the best performance; however, >10 wt % MOF in PIM-1 leads to a decrease in permeability. Other types of filler particles also have similar trends. For example, ÅHN et al. investigated Si particles dispersed in PIM-1 for CO2/N2 separation, and at particle loading >10 wt %, the selectivity decreased; at >30 wt %, the membranes had extreme brittleness. Thus, low filler loadings lead to optimum performance and are seen in many examples of both low- and high-permeability polyimide polymers. Several strategies were used to disperse the filler particles in the polymer and to improve the polymer–filler interaction. Among those methods, filler functionalization was the most used strategy and improves the gas separation performance of the resultant MMM. Other methods include polymer functionalization, filler combination, priming technique, and particle–polymer fusion approach.

In this work, UiO-66 (2, 5, and 11 wt %) was successfully synthesized and dispersed in Matrimid using the in situ MOF growth, forming an MMM in a single step. The CO2/N2 gas separation performance for MMMs fabricated using in situ MOF growth was evaluated and compared with MMMs fabricated using postsynthesis MOF mixing (traditional MMMs). We propose that this new method of preparing MMMs may reduce fabrication costs and ultimately lead to a more efficient procedure for large-scale production.

2. EXPERIMENTAL SECTION

2.1. REAGENTS. Matrimid 5218 was obtained from Huntsman. Zirconium(IV) chloride (ZrCl4, CAS No. 10026-11-6), terephthalic acid (99%, Sigma-Aldrich), and terephthalic acid dimethyl ester (98%, Sigma-Aldrich) were used as received.
acid (BDC; CAS No. 100-21-0), and dimethylformamide (DMF; CAS No. 68-12-2) were purchased from Sigma-Aldrich. Methanol (MeOH, CAS No. 67-56-1), hydrochloric acid (HCl, 30–35% w/w; CAS No. 7647-01-0), and chloroform (CAS No. 67-66-4) were purchased from Fisher Scientific.

2.2. Synthesis of UiO-66 MOF. A modified synthesis procedure was used for the synthesis of UiO-66.29,31,52,53 Stock solutions for the MOF reagents were prepared, including 0.1 M ZrCl4 in dimethylformamide (DMF), 0.1 M terephthalic acid (BDC) in DMF, and 0.1 M HCl in DMF. The following were combined: 5 mL of ZrCl4 stock, 10 mL of BDC, and 1.5 mL of HCl stock solution. The MOF solution was heated at 110 °C for 24 h, and then the solid MOF powder was recovered via vacuum filtration and washing with DMF followed by methanol. The MOF solid was activated by drying overnight under vacuum at 120 °C. UiO-66 MOF powder was characterized by powder X-ray diffraction (XRD), scanning electron microscope (SEM), N2 adsorption measurements, and thermal gravimetric analysis (TGA) (see the Supporting Information).

2.3. Fabrication of Neat Matrimid Flat-Sheet Membranes. Matrimid (0.4 g) was cast as a dense membrane by first dissolving it in 3 g of DMF. Then it was left static for 1 h to eliminate air bubbles from the solution. The Matrimid dope solution was then drop-cast onto a 3 in. Pyrex Petri dish and heated to 110 °C for 24 h. The Matrimid membrane was then solvent-exchanged with methanol using Soxhlet extraction for 2 days and then heated at 100 °C for 24 h under vacuum, followed by heating at 340 °C for 4 h. The neat Matrimid films were characterized using TGA and gas permeance measurements (see Supporting Information).

2.4. Fabrication of MMMs using the in Situ MOF Growth. Nano-Uio-66 synthesis involves combining precursors in a DMF solution at high temperature. Therefore, we chose to fabricate MMMs using our new approach with a glassy polymer that is stable at those synthesis conditions. Matrimid is soluble in DMF and is thermally stable to ~400 °C. Three different MMMs were fabricated with MOF loadings of 2, 5, and 11 wt % in Matrimid. MMMs with 2 and 5 wt % MOF loadings were prepared by dissolving 0.4 g of Matrimid in 16.5 mL of MOF solution (as described in Section 2.2). MMMs with 2 wt % MOF were prepared by dissolving Matrimid in 1 g of MOF solution with 2 g of DMF. MMMs with 5 wt % MOF used 3 g of MOF solution to dissolve the polymer. For MMMs with 11 wt % MOF, a higher concentration of MOF precursor solution was prepared, consisting of 0.15 M ZrCl4 in DMF and 0.15 M BDC in DMF. Then, 5 mL of 0.15 M ZrCl4 stock was combined with 10 mL of 0.15 M BDC stock and 1.5 mL of 0.1 M HCl stock. The 11 wt % MMM dope solution was then prepared by dissolving 0.4 g of Matrimid in 16.5 mL of MOF solution with an additional 0.5 g of DMF. Once dissolved, all MMM solutions (2, 5, and 11 wt %) were drop-cast into 3 in. Pyrex Petri dishes. MMM solutions with 2 and 5 wt % MOF were heated in an oven at 110 °C for 24 h, whereas the 11 wt % solution was heated at 100 °C for 24 h. The DMF in the MMM solution slowly evaporated as the MOF formed, and the clear yellow MMM solution transformed into an opaque yellow MMM solution slowly evaporated as the MOF formed, and the clear yellow MMM solution transformed into an opaque yellow film. The 11 wt % MOF MMM formed a uniform film using a slightly lower reaction temperature as compared to the 2 and 5 wt % MOF MMMs. Above 100 °C, MMMs with 11 wt % MOF had some defects and were brittle. All MMMs were solvent-exchanged with methanol using Soxhlet extraction for 2 days and then heated at 100 °C for 24 h under vacuum, followed by heating at 340 °C for 4 h. All MMMs were characterized by powder XRD, SEM, TGA, and gas permeation measurements (see the Supporting Information).

2.5. Fabrication of MMMs Using Postsynthesis MOF Mixing. MMMs with 3, 6, and 10 wt %UiO-66 were prepared using traditional postsynthesis mixing techniques of MOF and the polymer dope solution. First, a polymer dope solution was prepared by dissolving 0.4 g of Matrimid in chloroform. Then, UiO-66 MOF particles, synthesized according to Section 2.2, were dispersed in chloroform using ultrasonication. Next, UiO-66 particles were primed by adding 30% of the total polymer dope solution to the MOF/chloroform mixture, and then were roller-mixed and sonicated for 2 h. The rest of the polymer dope solution was added slowly in two more steps, with roller mixing and sonication performed after each step. The MMM solutions were then cast on a glass plate in a glovebag using a casting knife. The glovebag was purged with N2 prior to MMM casting to ensure limited humidity and was saturated with chloroform to slow down solvent evaporation from the membrane. The MMMs were kept for 48 h in the glovebag. MMMs were then heated at 100 °C under vacuum for 24 h, followed by heating at 340 °C for 4 h to eliminate any unevaporated solvent. The resulting films had a thickness of ~100 μm.

3. RESULTS AND DISCUSSION

3.1. Metal Organic Framework Characterization. UiO-66 MOF was successfully synthesized using a modified solvothermal procedure and characterized using powder XRD, SEM, N2 adsorption, and TGA. The powder XRD of UiO-66 matched the simulated XRD powder pattern obtained from crystallographic information39 (Figure S1). The particle size of UiO-66 was found to range from ~200 to 300 nm using SEM imaging (Figure S2), as a result of the modulator HCl under the synthesis conditions.31 The as-synthesized UiO-66 has a type I isotherm and a high Brunauer–Emmett–Teller surface area of 1583 m2/g, calculated using N2 adsorption at 77 K. The pore size distribution showed pores of 6.3, 7.4, 11.6, and 15.6 Å, calculated using the density functional theory method (Figure S3). The micropore volume was determined to be 0.56 cm3/g, calculated using the t-plot method. All gas adsorption results were compared with literature data and were within a reasonable agreement.53 TGA was used to identify and compare the thermal decomposition of the as-synthesized UiO-66 to literature reports (Figure S4). UiO-66 first loses the residual moisture at ~100 °C, followed by a loss of residual physisorbed solvent molecules, and finally degrades at 500 °C to become zirconium oxide (ZrO2).54,55 The resulting films had a thickness of ~100 μm.

3.2. Characterization of MMMs with in Situ MOF Growth. MMMs of 2, 5, and 11 wt % UiO-66 were fabricated using in situ MOF growth and were yellow in color and appeared opaque with higher MOF loadings (Figure S5A). MMMs prepared with 2 and 5 wt % MOF were opaque with a glossy appearance. In contrast, MMMs with 11 wt % MOF had a matte appearance and were more difficult to handle due to brittleness.

XRD results revealed that all MMMs contained distinctive peaks associated with UiO-66 (Figure 1). MMMs with 2 wt % UiO-66 contain two reflections that overlay with d-spacings of 2.26, 2.83, 3.31, 5.71, and 7.35 Å. The MMMs with 5 wt % UiO-66 presented similar reflections with increased intensity. MMMs with 11 wt % UiO-66 presented additional peaks at 2.72, 4.38, and 5.31 Å. These peaks correspond to the UiO-66 structure, indicating the successful incorporation of UiO-66 into the MMMs.

Figure 1. XRD results for pure Matrimid (orange), UiO-66 powder (black) with d-spacing identified, and MMMs fabricated using the in situ MOF growth: 2 wt % UiO-66 (green), 5 wt % UiO-66 (red), and 11 wt % UiO-66 (blue).
111 and 200. The same reflections are also observed in the XRD patterns for MMMs with 5 and 11 wt % MOF. As the loading of UiO-66 MOF increases to 5 and 11 wt %, more XRD reflections are observed at 2θ > 10°, including 12.0, 17.3, 25.1, 25.6, and 30.8° 2θ. These reflections overlay with reported UiO-66 XRD results, but are likely below the detectable limit for the 2 wt % MMMs.

SEM images demonstrate the morphologies of a neat Matrimid film and MMMs fabricated using the in situ MOF growth (Figure 2). The neat Matrimid has a uniform morphology with no obvious defects. In MMMs with 2 wt % UiO-66, the polymer matrix shows a scalloped vein structure around the MOF particles, which is an indication that there is a strong interfacial interaction between the polymer and filler particles. No gaps were observed between the polymer and filler particles, commonly referred to as the “sieve in a cage” effect. Increasing the MOF loading to 5 wt % also produced a relatively uniform distribution of MOF particles (Figure 2C), whereas 11 wt % of UiO-66 caused particle agglomeration (Figure 2D). White clumps of MOF particles are visible in the SEM images, which appear to cause residual stress cracking in the film. The Young’s modulus of the in situ grown 10 wt % MMM is much less than the pure Matrimid, as shown in the Supporting Information.

3.3. Characterization of MMMs Fabricated by Postsynthesis MOF Mixing. MMMs fabricated using traditional postsynthesis MOF mixing were made with MOF loadings close to those of MMMs fabricated using the in situ MOF growth. MMMs with 3, 6, and 10 wt % UiO-66 were fabricated and were yellow in color and became increasingly opaque with increasing MOF loadings (Figure S5B). XRD results showed that all films contained distinctive peaks associated with UiO-66 (Figure 4). MMMs with 3 wt % MOF exhibited three reflections with UiO-66 d-spacings of 111, 200, and 220. MMMs with 6 and 10 wt % MOF exhibited decomposition profiles that were least like Matrimid and resembled those of UiO-66 (Figure 3). On the basis of the final weight of the ZrO2 remaining after complete decomposition, we determined the percent MOF loading for each of these MMMs. TGA calculations used to determine the MOF wt % loading in MMMs are described in detail in the Supporting Information.

Figure 2. SEM images of (A) neat Matrimid and MMMs fabricated using the in situ MOF growth, including (B) 2 wt % MOF, (C) 5 wt % MOF, and (D) 11 wt % MOF.

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Figure 3. TGA results for neat Matrimid, MMMs fabricated using the in situ MOF growth, and UiO-66 MOF. Top graph: (A) full complete data collection. (B) Zoomed-in section of MMM data from 700−900 °C.

Figure 4. XRD results for MMMs fabricated using the postsynthesis mixing technique. Neat Matrimid (orange), UiO-66 MOF (black) with d-spacing identified, and MMMs with 3 wt % MOF (green), 6 wt % MOF (red), and 10 wt % MOF (blue).
more XRD peaks matching than those of UiO-66. This confirms that the fabrication of the MMMs did not alter the structure of the MOF.

SEM images of MMMs fabricated using postsynthesis MOF mixing exhibit the same veinlike morphology, as observed for MMMs made using the in situ MOF growth (Figure 5).

However, MMMs fabricated using postsynthesis MOF mixing had an agglomeration of particles at all MOF loadings studied. In Figure 5B, MMMs with 3 wt % MOF have one-particle agglomeration, shown in the magnified inset. Increasing the MOF loading to 6 wt % (Figure 5C) produced more particle agglomerations. Finally, MMMs with 10 wt % MOF had the most particle agglomerations, with white clumps visible under the surface of the polymer, as was observed for MMMs fabricated using the in situ MOF growth strategy (11 wt % MOF).

3.4. Gas Separation Results. The gas separation performance for MMMs fabricated using the in situ MOF growth and by postsynthesis MOF mixing was measured and compared. In Figure 6A, the CO₂ gas permeability is displayed at MOF loadings of 0–11 wt %. Figure 6B shows the CO₂/N₂ selectivity of MMMs at MOF loadings of 0–11 wt %. MMMs fabricated using the in situ MOF growth demonstrate an increase in CO₂ permeability and CO₂/N₂ selectivity with increasing MOF loadings similar to MMMs fabricated using postsynthesis MOF mixing. In this case, the MOF loadings were small enough that performance increased even at the highest loadings tested, despite some observations of particle agglomeration. At the highest MOF loading tested, MMMs fabricated using the in situ MOF growth had more than twice the CO₂ permeability of the neat polymer and an increase in CO₂/N₂ selectivity of about 17%. Interestingly, the results of the two fabrication techniques are highly consistent with each other. On the basis of these data, it appears that either fabrication route results in a membrane that is functionally the same in terms of gas-transport properties.

4. CONCLUSIONS
In this work, we have successfully fabricated UiO-66/Matrimid MMMs using an in situ MOF growth strategy. Here, UiO-66 was simultaneously grown within Matrimid, while it was cast as a film. MMMs with MOF loadings of 2, 5, and 11 wt % were characterized and confirmed to be a successful MMM, using XRD, SEM, TGA, and gas separation. The gas separation performance for MMMs fabricated using the in situ growth approach was investigated and compared to traditional cast MMMs of the same formulation. The results show that both MMMs perform consistently and offer a performance enhancement as compared to the neat polymer. The one-step approach used to fabricate UiO-66/Matrimid MMMs is a promising alternative for large-scale MMM production.

ASSOCIATED CONTENT
S Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b06592.

Material characterization techniques and their results for UiO-66; thermal gravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), gas adsorption analysis, gas separation analysis, mechanical properties (PDF)

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ACKNOWLEDGMENTS

We thank Michael Gipple of Smart Data Solutions (NETL) for the table of contents graphic. This work was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees makes a warranty, express or implied, or assumes any legal liability or account of work sponsored by an agency of the United States Government. We thank Michael Gipple of Smart Data Solutions (NETL) for the table of contents graphic. This work was prepared as an account of work sponsored by an agency of the United States Government.

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