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Tailoring CO₂/CH₄ Separation Properties of Mixed-Matrix Membranes via Combined Use of Two- and Three-Dimensional Metal-Organic Frameworks

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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 CO₂/CH₄ separation. The mixed-matrix membrane containing ns-CuBDC alone was capable of improving CO₂/CH₄ selectivity whereas the mixed-matrix membrane containing ZIF-8 alone ensured improved CO₂ permeability. However, by combining both fillers in a mixed-matrix membrane aimed at tailoring the CO₂/CH₄ separation properties, both CO₂ permeability and CO₂/CH₄selectivity 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.

Keywords: Mixed-matrix membrane, CuBDC nanosheet, ZIF-8, polyimide, CO₂/CH₄separation

Graphical abstract

Highlights

- ZIF-8 (3D) nanocrystals and nanosheets of CuBDC (2D) were successfully synthesized.
- Mixed-matrix membranes containing 2D and 3D metal-organic frameworks were successfully fabricated without appreciable defects.
- The 2D and 3D fillers were proved effective in improving CO_2/CH_4 selectivity and CO_2 permeability, respectively.
- Both CO_2 permeability and CO_2/CH_4 selectivity were successfully improved by the combined use of these fillers.

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 CO₂/CH₄ 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 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 CO₂ permeability due to the presence of large pore cavities allowing the rapid transport of CO₂[29, 30]. In contrast, two-dimensional (2D) ns-CuBDC, which possess a high aspect ratio and a pore aperture that can preferentially transport CO₂ over CH₄, are of great interest because CH₄ is forced to adopt a tortuous path that results in a dramatic increase in its diffusion

path in the membrane, which leads to improved CO₂/CH₄ selectivity[31, 32]. More importantly, such 2D filler enhances CO₂/CH₄ 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). In such cases, it may be difficult to tailor the direction of performance enhancement in a specific desired direction on the selectivity-permeability map.

Therefore, in this work, we demonstrate the tailored enhancement of CO₂/CH₄ separation performance of a mixed-matrix membrane via the combined use of 2D and 3D MOF fillers. ODPA-TMPDA (ODPA=4,4'-oxydipthalic 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 purification to increase the molecular weight of the resulting polymer [3, 31, 33]. 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.

2Experimental

2.1 Materials

Copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), 1,4-benzenedicarboxylic acid (H_2BDC), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 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[33]. 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 hours to obtain a viscous solution of 20wt% 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 hours, 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[31, 32]. The bottom layer (3 g of H₂BDC dissolved in 2 ml DMF and 1 ml CH₃CN), middle layer (2 ml, mixture of DMF and CH₃CN in a 1:1 ratio), and top layer (3 g of Cu(NO₃)₂·3H₂O dissolved in 1 ml of DMF and 2 ml of CH₃CN) 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 CHCl₃ (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[34]. In two separate storage flasks, 1.47 g of Zn(NO₃)₂·6H₂O and 3.24 g of Hmim were dissolved in 100 ml methanol. Once the solutions were completely dissolved, the solution containing Zn(NO₃)₂·6H₂O was rapidly added to the solution containing Hmim under strong agitation. The resulting solution was left for 1 hour before separating the ZIF-8 nanoparticles 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 hours. 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 tapping mode. Prior to the measurement, the ns-CuBDC samples were first prepared by subjecting several drops of suspension of nanosheets in DCM onto the silicon wafer and then dried overnight. The crystalline structure of the MOF was investigated using powder X-ray diffraction (PXRD, Bruker D2 phaser) equipped with $\text{Cu K}\alpha$ radiation. The samples were scanned with a step size of 0.02° for the range of 2θ from 5° to 40° at ambient conditions using a zero-background single-crystal silicon sample holder. Thermogravimetric analysis of MOFs was performed on a thermogravimetric/differential thermal analyzer (PerkinElmer, Pyris Diamond TG/DTA), at a heating rate of $10^\circ\text{C}/\text{min}$ over a temperature range of 40 to 800°C , under pure nitrogen purging ($200\text{ ml}/\text{min}$). The morphology of the MOFs

was observed with field-emission scanning electron microscopy (FESEM, JSM-7600F). For sample preparation, several drops of suspensions of ns-CuBDC in DCM or ZIF-8 in methanol were dropped onto a silicon wafer, and the solvent was allowed to dry at room temperature.

2.6.2 Characterizations of membrane

The FT-IR spectrum of pure ODPA-TMPDA polymer was obtained using a Shimadzu IR Prestige-21 spectrophotometer. The purity of the polymer was verified using an elemental analyzer (PerkinElmer, CHNS/O 2400). The cross-sections of the mixed-matrix membrane were observed with FESEM (JSM-7600F). Prior to gold sputtering, the samples were prepared by fracturing the membrane in liquid nitrogen. The density of the membrane was measured using a Quantachrome Ultrapyc 1200e pycnometer.

2.7 Gas sorption analysis

The specific surface area and the pore volume of MOFs were quantified using N₂ physisorption at 77 K measured by a Quantachrome Autosorb-1 (AS-1). Prior to the analysis, ns-CuBDC and ZIF-8 were activated at 180 °C for 8 hours under a high vacuum to remove any residual solvents in the sample. Pure CO₂ and CH₄ adsorption isotherms of the MOFs and membranes were measured at 25 °C at the pressure range of 0–1 bar using a volumetric gas sorption analyzer (Quantachrome, iSorb HP1). For the membranes, samples were activated at 160 °C for 8 hours under high vacuum prior to the analysis. The solubility of gas in the membrane, S (i.e., CO₂) was then calculated using the relationship:

$$S = \frac{q\rho}{p} \dots (1)$$

where q is the amount of gas uptake per mass of membrane at pressure p , and ρ is the density of membrane. The diffusivity of gas in the membrane, D , can be calculated by dividing the permeability by the solubility.

2.8 Gas permeation test

The gas permeation test was carried out using the mixed-gas permeation system described in our previous work[26, 27]. Helium (He) and a CO₂/CH₄ (50/50) mixture gas were purchased from Air Liquide. The membrane to be tested was first mounted onto the testing cell, and then the residual gases in the permeation system and membrane were removed under dynamic vacuum. Subsequently, the feed gas was fed to the upstream chamber of the cell at 1 bar, and the gas that permeated through the membrane was swept by He. The composition of gas collected downstream was analyzed by gas chromatography to calculate the permeability of the individual components. The temperature of the entire permeation system was maintained at 25 °C. The measurements were repeated three times to check for experimental errors and ensure reproducibility of the results.

3 Results and Discussion

3.1 Synthesis of ns-CuBDC and ZIF-8

Figure 1(a)PXRD pattern and**(b)**TGA of ZIF-8 and ns-CuBDC

The successful synthesis of ns-CuBDC and ZIF-8 was verified by identification with PXRD as shown in Figure 1 (a). The patterns obtained from our samples matched well with the reference pattern reported in the literature. In particular, a peak broadening was observed for the ZIF-8 nanocrystals, indicating the formation of smaller crystallites, and was further verified by visual observation. As shown in the FESEM image (Figure 2 (a)), the average particle size was estimated to be about 50 nm. However, the ns-CuBDC possess only two characteristic peaks at 17° and 34° that correspond to the ($\bar{2}01$) and ($\bar{4}02$) planes, respectively. Through the analysis of both the FESEM (Figure 2(b)) and AFM images (Figure 2(c)), the lateral dimension and thickness were measured to be around 7 μm and 20 nm, respectively, which translates into a high aspect ratio of 350. Besides, investigation of thermal stability using TGA analysis (Figure 1 (a)) indicated that both ZIF-8 and CuBDC demonstrate reasonable stability up to 300 °C and 600 °C, respectively.

Figure 2(a) and (b) FESEM images of ZIF-8 and ns-CuBDC, respectively; (c)AFM image of ns-CuBDC (red line indicates 1 μm); (d) Height profile for ns-CuBDC

Besides, N_2 physisorption at 77 K was conducted for ZIF-8 and ns-CuBDC to identify the porosity properties of these MOFs. In general, the sorption properties were comparable with the results reported in the literature. As indicated in Figure 3(a), both ZIF-8 and ns-CuBDC show typical behavior of a Type I isotherm due to their high N_2 sorption at low partial pressure. The surface areas and pore volumes determined based on the analysis of N_2 physisorption data are summarized in Table 1. Following this, the CO_2 and CH_4 adsorption isotherms of ZIF-8 and ns-CuBDC were measured at 25 $^\circ\text{C}$ (Figure 3b). As reported elsewhere, the CO_2 adsorption of ns-CuBDC was measured to be higher than that of ZIF-8 despite the higher micropore volume and surface area of ZIF-8 versus ns-CuBDC. However, both MOFs showed a linear CO_2 isotherm in the pressure range tested, indicating that there are no strong binding sites

that can slow down the diffusion of CO₂. As expected, CH₄ uptakes were measured to be far lower than those of CO₂ for both MOFs. However, CO₂/CH₄ sorption selectivity is not that impressive as compared to top-notch MOFs developed for CO₂ capture such as the MOF-74 series and amine-appended MOF [35-38].

Figure 3(a) N₂ adsorption isotherms(adsorption and desorption points are indicated by filled and open symbols, respectively)at 77K and **(b)** pure CO₂ and CH₄adsorption isotherms at 25 °C for ns-CuBDC and ZIF-8

Table 1 Surface areas and pore volumes of ZIF-8 and ns-CuBDC calculated from the N₂ physisorption isotherm at 77 K

Sample	S _{BET} ^[a] (m ² /g)	S _{micro} ^[b] (m ² /g)	V _{micro} ^[b] (m ³ /g)
ZIF-8	1147	1131	0.608
ns-CuBDC	126	49.3	0.0250

Note: [a] BET (S_{BET}) is calculated based on the pressure range of P/P⁰ = 0.05–0.3; [b] Micropore area (S_{micro}) and volume (V_{micro}) are obtained using the *t*-plot method at a pressure range of P/P⁰ = 0.4–0.6.

3.2 Fabrication of mixed-matrix membrane

The successful synthesis of the ODPA-TMPDA polymer was first confirmed via the FTIR spectrum as shown in Figure 4. The characteristic imide peaks(1719 cm⁻¹ and 1774 cm⁻¹), which correspond to the symmetric and asymmetric C=O stretching, were

visible together with the peak associated with C-N stretching at 1358 cm^{-1} . The successful imidization was verified by the disappearance of a peak at 3500 cm^{-1} , which is associated with unreacted polyamic acids. Note that the synthesis of the ODPA-TMPDA polymer comprises two steps, namely, 1) condensation reaction of the monomers to form polyamic acid and 2) chemical imidization of the polyamic acid. Besides, elemental composition of the ODPA-TMPDA polymer as measured by an elemental analysis matched the theoretical calculation well as shown in Table 2. The resulting polymer dissolved well in the various organic solvents including DCM, chloroform and DMF and thus could be easily processed into a film form.

Figure 4 FTIR spectra of the ODPA-TMPDA polymer

Table 2 Elemental analysis of ODPA-TMPDA polymer

Element	Experimental	Theoretical ^[a]
% C	67.37	66.65

% H	3.78	3.87
% N	6.60	6.79

Note: [a]Based on the ratio of elements in the repeating unit of the polymer

With the successful synthesis of the ODPA-TMPDA polymer, mixed-matrix membranes containing ZIF-8, ns-CuBDC and both fillers were fabricated, and the resulting morphologies were observed by FESEM (Figure 5). In general, *sieve-in-a-cage* morphology, which is typically observed when the compatibility between the filler and the polymer is poor, was not observed in this study. This is attributed to the presence of organic moieties in ZIF-8 and ns-CuBDC that allow preferential interaction with the polymer chains in ODPA-TMPDA. It was already shown that downsizing MOF crystals to nanocrystals or nanosheets to increase the polymer/filler contact area is an effective method of fabricating high-quality mixed-matrix membranes in which the fillers are uniformly distributed without forming defects [10, 28].

Figure 5 Cross-sectional FESEM images of mixed-matrix membranes containing (a) 2wt% ns-CuBDC nanosheets (b) 10 wt% ZIF-8 and (c) both 10 wt% ZIF-8 and 2 wt% ns-CuBDC

3.3 Gas permeation results

The transport properties of an equimolar mixture of CO₂/CH₄ in the pure and mixed-matrix membranes prepared in this work were evaluated at 25 °C and 1 bar of total upstream pressure (Table 3). It was observed that incorporation of ZIF-8 alone can increase CO₂ permeability by about 30% as compared with that of pure polymer with no significant change in selectivity. Such a result is consistent with the data reported in the literature in which the utilization of ZIF-8 is only capable of increasing the CO₂ permeability and not CO₂/CH₄ selectivity [39-41], mainly because the CO₂/CH₄ selectivity of ZIF-8 is not sufficiently high to increase the selectivity of ODPA-TMPDA which is already as high as 36. However, utilization of ns-CuBDC alone can increase CO₂/CH₄ selectivity (by about 20%) as compared to pure polymeric membrane although the filler loading was only 2 wt%. However, such enhancement derived from ns-CuBDC filler also caused an undesirable result. A slight decrease in CO₂ permeability was observed, which is consistent with results

reported elsewhere [32, 42]. Nevertheless, as two fillers can improve the performance of membrane in totally different ways, the combined use of these fillers may allow us to tweak the direction of performance enhancement in a desirable direction.

Table 3 Gas permeability and CO₂/CH₄ selectivity of pure and mixed-matrix membranes measured at 1 bar upstream pressure and 25 °C

Membrane	CO ₂ permeability (Barrer)	CO ₂ /CH ₄ selectivity
Pure ODPA-TMPDA	112 ± 3	36 ± 1
10 wt% ZIF-8	144 ± 9	37 ± 4
20 wt% ZIF-8	231	30
30 wt% ZIF-8	322	27
2 wt% ns-CuBDC	99 ± 7	43 ± 4
4wt% ns-CuBDC	95 ± 3	40 ± 2
6wt% ns-CuBDC	91 ± 1	39 ± 2
10 wt% ZIF-8 & 2 wt% ns-CuBDC	131 ± 6	47 ± 3
20wt% ZIF-8 & 2wt% ns-CuBDC	164	46
10wt% ZIF-8 & 4wt% ns-CuBDC	113	39

To validate this idea, we fabricated mixed-matrix membranes containing both fillers and measured the CO₂/CH₄ permeation property. As depicted in Table 3, the combined use of these two fillers together could increase both CO₂ permeability and CO₂/CH₄ selectivity by 17% and 31%, respectively. Such results are more desirable and more attractive than performance realized by incorporating a single filler alone in the membrane. As shown in Figure 6, the performance of the membrane moves toward

the upper bound limit when both fillers are incorporated together. Furthermore, it is noteworthy that this approach is readily applicable to typical mixed-matrix membrane fabrication procedures without any resistance.

We also demonstrated the performance of MMM with higher loadings to investigate the optimum performance conditions.

According to the results, it seems that 2wt% ns-CuBDC is the optimum amount to be incorporated into the polymer matrix. As the filler loading increase, decrease in CO₂ permeability becomes more prominent than the decrease in CH₄ permeability. It seems that tortuosity path for CH₄ diffusion is not affected much due to increase of ns-CuBDC loading. On the other hand significant increase in CO₂ permeability could be observed with the increase in ZIF-8 loading however at the cost of CO₂/CH₄ selectivity.

Figure 1 Performance of pure polymeric membrane and mixed-matrix membrane with respect to the Robeson upper bound established in 2008

3.4 Gas adsorption properties in mixed-matrix membrane

Figure 2 (a) CO₂ and (b) CH₄ gas adsorption isotherms for ODPA-TMPDA and mixed-matrix membrane measured at 25 °C

Subsequently, to understand the mechanism behind the improved CO₂/CH₄ separation performance, the diffusivity and solubility of CO₂ and CH₄ in the mixed-matrix membrane were quantified. To do this, the CO₂ and CH₄ adsorption properties of the pure ODPA-TMPDA and mixed-matrix membrane were measured at 25 °C, and the results are shown in Figure 7. The solubility and the diffusivity of CO₂ and CH₄ that were computed are also shown in Table 4. In general, both fillers could improve the solubility selectivity as the MOFs used in this work can selectively take up CO₂ over CH₄ as depicted in Figure 3(b). Thus, the major difference between the two fillers can be found in how they changed the diffusivity of CO₂ and CH₄ in the mixed-matrix membrane. The effective diffusivity of CO₂ in the ns-CuBDC mixed-matrix membrane decreased substantially compared to that in the neat polymeric membrane, indicating that the 2D filler significantly inhibited the CO₂ within the membrane resulting in a decrease in CO₂ permeability of the ns-CuBDC mixed-matrix membranes. However, the CH₄ diffusivity decreased even more than that of the CO₂,

which resulted in an increase in the CO₂/CH₄ diffusion selectivity. In contrast, an increase in CO₂ diffusivity was clearly observed upon incorporation of ZIF-8 in the membrane, which reveals that ZIF-8 can improve CO₂ permeability by improving the diffusivity. Besides, incorporation of both ZIF-8 and ns-CuBDC does not significantly sacrifice CO₂ solubility as compared to the mixed-matrix membrane containing ZIF-8 alone. Hence, by incorporating the two fillers together, the drawback of the 2D filler, the sacrifice of CO₂ diffusivity, can be easily overcome as ZIF-8 can increase CO₂ diffusivity to a greater extent. Indeed, as shown in Table 4, the mixed-matrix membrane containing both fillers exhibited a higher CO₂ diffusivity than that of the pure polymer membrane. Meanwhile, the mixed-matrix membrane containing the two fillers together incorporated the benefit of the 2D filler, which is the effective enhancement of CO₂/CH₄ selectivity. Overall, owing to such synergistic effects of the 2D and 3D fillers mentioned above, performance of the mixed-matrix membrane was

improved in a desirable direction on the selectivity-permeability map (Figure 6).

Table 4 Solubility and diffusivity data for ODPa-TMPDA and mixed-matrix membranes

Membrane	Density (g/cm ³)	CO ₂ uptake, x 10 ⁻⁴ (mmol/g)	CO ₂ solubility (mol/m ³ -bar)	CO ₂ diffusivity, x 10 ⁻¹² (m ² /s)	CH ₄ uptake, x 10 ⁻⁴ (mmol/g)	CH ₄ solubility (mol/m ³ -bar)	CH ₄ diffusivity, x 10 ⁻¹³ (m ² /s)
Pure ODPa-TMPDA	1.35	9.91	1340	1.29	2.02	273	1.77
2 wt% ns-CuBDC	1.47	9.07	1337	1.15	1.68	248	1.45
10 wt% ZIF-8	1.25	9.04	1131	1.98	1.61	202	3.00
10 wt% ZIF-8 + 2 wt% ns-CuBDC	1.23	8.87	1099	1.84	1.38	171	2.52

4 Conclusions

In conclusion, both CO₂ permeability and CO₂/CH₄ selectivity in mixed-matrix membranes can be improved by adding both ns-CuBDC and

ZIF-8 into ODPA-TMPDA membranes, such that the resulting membrane becomes more attractive for practical applications. The addition of both fillers enhances the overall performance in a more favorable direction as compared to the incorporation of only one type of filler (ns-CuBDC or ZIF-8), which are only capable of improving either CO₂/CH₄ selectivity or CO₂ permeability. Detailed analysis of the diffusivity and solubility revealed that the drawback of an individual filler could be overcome by the positive effect of its counterpart. Our results suggest that the combined use of 2D and 3D fillers is a facile approach to tweak the direction of performance enhancement of a mixed-matrix membrane in a desirable direction.

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