Investigation of MOF-525 and post-metalated MOF-525 as nanofillers in mixed matrix membranes for CO₂ separation

Nicholaus Prasetya^{*1}, Hasan Can Gülbalkan², Seda Keskin² and Christof Wöll¹

¹ Institute of Functional Interface (IFG), Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344, Eggenstein-Leopoldshafen, Germany.

² Department of Chemical and Biological Engineering, Koç University, Rumelifeneri Yolu, Sariyer, 34450 Istanbul, Turkey

* Corresponding author: nicholaus.prasetya@partner.kit.edu

Abstract

Over the past twenty years, metal-organic frameworks (MOFs) have emerged as extensively developed porous class of materials and are increasingly recognized as promising candidates for membrane-based CO₂ separation. This potential primarily stems from the ability to deliberately customize their structure and functionalities to enhance interactions with guest molecules. In this study, we explore the use of MOF-525, a porphyrin-based MOF, as a nanofiller in a mixed matrix membrane (MMM) composed of 6FDA-DAM (6FDA: 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride; DAM: 2,4,6-trimethyl-1,3diaminobenzene) polymer for CO_2/N_2 and CO_2/CH_4 separations. This particular MOF is chosen because of the possibility to metalate its porphyrin ring to tailor the interaction between the CO_2 molecule and the MOF framework. As a result, the CO_2/N_2 and CO_2/CH_4 separation performance of the MMM loaded with metalated MOF-525 can be significantly improved without the necessity to use a very high nanoparticle loading. When compared to the bare polymeric membrane and 2 wt% non-metalated MOF-525 MMM, around 20% improvement in the membrane permeability and selectivity can be observed for the 2 wt% metalated MOF-525 MMM. Further analysis on the gas transport property of the MMM showed that the improvement mainly results from the enhanced CO₂ solubility in the MMMs and improved interaction between the metalated MOF-525 and the CO_2 molecule. However, it is also found that 2 and 5 wt% are the optimum loading value, above which the interfacial defects between the MOF nanoparticles and the polymers caused by the particle agglomeration starts to appear and thus deteriorating the membrane performance. This is also confirmed through the molecular simulations where some overestimations from the Maxwell model on the membrane permeability is observed particularly at high particle loading, indicating the agglomeration and the build-up of non-selective voids. Despite this, we have successfully shown in this study the high efficacy and efficiency of using metalated porphyrin MOFs for CO_2 separation in a MMM since only relatively low particle loading (around 2 wt%) is required to improve the membrane performance.

Keywords: MOF-525, post-metalated MOF-525, mixed matrix membranes, CO₂ separation

1. Introduction

As the concentration of CO_2 in the atmosphere continues to rise, contributing to the climate crisis, the urgent need to develop effective technologies to tackle this issue becomes increasingly critical. Therefore, separation of the CO_2 from other gases becomes crucial in order to avoid the release of this gas into the atmosphere. In this case, amine absorption technology has been considered as the most mature available technology to fulfill this task [1,2]. However, this approach suffers from several drawbacks such as the large amount of energy needed to release CO_2 again [2]. In order to address the above drawbacks, membrane technology could then offer a number of advantages for CO_2 separation, in particular since it can offer high separation performance while also consuming less energy [3,4].

Despite this huge promise, research and development in the field of advanced membrane materials is still required in order to improve the membrane separation performance [4]. Typically, economic factors and ease of processability make various polymeric materials the preferred choice for membrane construction. However, the performance of a polymeric membrane is usually limited by the permeability-selectivity inverse relationship [5]. As a result, a membrane with high permeability usually exhibits low selectivity and vice versa. Consequently, the last few decades have seen the development of numerous new membrane materials, including polymers of intrinsic microporosity (PIM) [6], thermally-rearranged polymers [7] and metal organic frameworks (MOFs). Compared to other polymeric-based materials, MOFs offer a number of advantages including high porosity, high surface area, the possibility of functionalization, a tailorable architecture and also the possibility to be used as a template for a new material [8–10]. Therefore, during the last two decades, these crystalline coordination networks have been widely investigated to be used for various applications such as water purification and gas separation processes [11,12].

In the field of gas separation processes, one of the main driving forces that stimulates the use of MOFs is the possibility to introduce various functionalities to enhance their gas separation performances. In this case, various functionalities have been identified for being able to effectively improve the CO₂ separation performance of the MOFs such as by introducing polar functional groups [13–16] or by introducing open metal sites [16–19]. In addition to the above strategies, inserting transition metals in the MOF constructed with porphyrin ligand has also been proven for being able to significantly improve the CO₂ separation performance [20,21]. In this case, from theoretical work employing density functional theory (DFT) and Grand Canonical Monte Carlo (GCMC) simulation, it has become evidenced that the metalated porphyrins can act as the selective binding sites for CO₂ by exerting a strong Coulomb interaction with CO₂ and thus resulting in the enhancement of the CO₂ adsorption capacity [21].

In this work, we investigated a porphyrin-based MOF, namely MOF-525, to be used as a nanofiller in the 6FDA-DAM polymeric matrix to form mixed matrix membranes (MMMs). In addition to the ease of processing and membrane handling, MOF-based MMMs have been shown to significantly improve the performance of a polymeric membrane should the correct MOFs are selected as the nanofillers [22]. As a porphyrin-based MOF, the MOF-525 has the potential to be functionalized through the post-metalation process where its porphyrin center is metalated with other metals, which are cobalt (Co) and zinc (Zn) in our case. We hypothesized that this post-metalation process could bring positive impacts to improve the CO_2 separation performance of the MMMs by enhancing the interaction between the MOF and CO_2 . Therefore, it is expected that the post-metalated MOF-525 could improve the CO_2 separation performance of the 6FDA-DAM polymeric membrane.

2. Materials and methods

2.1 Materials

Benzoic acid, cobalt chloride (CoCl₂), sodium hydrochloride, zinc chloride (ZnCl₂) and zirconyl chloride octahydrate (ZrOCl₂.8H₂O) were purchased from Merck. Meso-tetra(4-carboxyphenyl)porphyrin (H₄TCPP) was purchased from BLD Pharmatech GmbH, Germany. Acetone, dichloromethane, dimethylformamide (DMF), hydrochloric acid 37% was purchased from VWR. 6FDA-DAM with molecular weight around 215,000 was purchased from Akron Polymer Systems, Inc.

2.2 MOF 525 synthesis and post-metalation of MOF-525

MOF-525 was synthesized according to the published procedure using benzoic acid as the modulator [23,24]. Once the synthesis process finished, the product was collected by centrifugation (7000 rpm) and washed thoroughly with DMF and acetone and dried at 80 °C overnight. The obtained nanoparticles (200 mg) were then immersed in a mixture of 20 mL DMF and 1 mL of 8M HCl in an oven at 100°C for 24 h to remove the ligated benzoates from the framework [25]. Afterwards, the MOF-525 was thoroughly washed with DMF and acetone and stored in acetone.

In order to post-metalate MOF-525, cobalt and zinc were used as the metal to be incorporated at the center of the porphyrin ring. Both metals were chosen because of the reproducibility for the post-metalation process. MOF-525 was then post-metalated according to the published procedure [26–29]. In a typical post-metalation process, a 20 mL DMF solution containing 1.24 mmol of the chloride salt of the metal (CoCl₂ and ZnCl₂) was firstly prepared. Afterwards, 100 mg of the MOF-525 was immersed in the solution followed by heating the suspension in a convective oven at 100°C for 48 h. Once the post-metalation process was completed, the samples post-metalated MOF-525 was stored in acetone before being used.

2.3 Mixed matrix membrane (MMM) fabrication

Mixed matrix membranes containing free-base MOF-525, MOF-525(Co) and MOF-525(Zn) were fabricated by using 6FDA-DAM as the polymer matrix. To construct the mixed matrix membranes (MMMs), a suspension was initially prepared using dichloromethane as the solvent. This mixture contained a specific amount of the chosen MOF and 50% of the total polymer. This suspension was continuously stirred overnight to prime the MOF nanoparticles to enhance the MOF-polymer interaction. Afterwards, the rest of the polymer was added to the suspension and the final suspension was continuously stirred overnight. To form a MMM, the suspension was poured on a clean glass petri dish (diameter 40 mm) and was covered with perforated aluminum foil. The petri dish was then kept in a fume hood to let the solvent evaporate. Upon drying, the MMM was

then peeled off from the petri dish and dried in a convective oven at 80°C before the gas separation testing.

2.4 Gas separation performance testing

The gas separation performance of the membranes was evaluated by using the constant-volume variable-pressure method using CO_2 , N_2 or CH_4 as the permeating gases. The gas permeability is calculated based on the gradient of the pressure change on the permeate side.

2.5 Characterizations

UV-Vis spectroscopy. The UV-Vis spectra of the digested samples were recorded by using Cary 5000 UV/Vis Spectrophotometer equipped with Cary Universal Measurement Accessory (UMA). For all cases, the digestion process of the MOF nanoparticles was carried out by immersing them in 1M NaOH solution for 24 h.

X-Ray Diffraction. The powder X-ray diffraction (PXRD) pattern of the non-metalated and postmetalated MOF-525 were collected by using D8 A25 Da-Vinci Bruker XRD. The samples were measured between 2θ 4-20°. The same instrument was also used to record the XRD pattern of the MMMs. In this case, the MMMs were firstly immobilized on the sample holder by using a seal tape before the measurement took place.

Fourier-transformed infrared spectroscopy. The Fourier-transformed infrared (FTIR) spectra of both the nanoparticles and the MMMs were recorded by using Bruker Hyperion - Tensor in Attenuated Total Reflectance (ATR) mode. The measurement took place between the wavenumber 4000 - 400 cm⁻¹

2.6 Computational methodology

To deepen our understanding of the gas separation performance observed in the experiment, we conducted a computational simulation study as well. The aim of this investigation was to compare the experimental results with those derived computationally. To realize this objective, we initially calculated the gas permeability of the MOFs through molecular simulations, followed by combining the results with experimental polymer data, and finally using these values in the Maxwell model [30,31].

The crystallographic information of MOF-525 structure was obtained from the literature [32]. Using the "edit structure" tool provided in Mercury 2023.2.0 [33], Co and Zn metals were placed in the center of the porphyrin ring of MOF-525. Subsequently, the Materials Studio Forcite module [34] was utilized to optimize the geometry of the generated structures. The smart algorithm, which uses the steepest descent, adjusted basis set Newton-Raphson and quasi-Newton methods was used to find the lowest energy conformation, with a maximum iteration number of 10,000. The convergence tolerance was set to quality of ultra-fine (energy tolerance value of 2×10^{-5} kcal/mol, displacement tolerance value of 10^{-5} Å, and force tolerance value of 10^{-3} kcal). The cell parameters were allowed to be optimized.

The gas uptakes and self-diffusivities were computed by performing Grand Canonical Monte Carlo (GCMC) and molecular dynamics (MD) simulations, respectively, in MOF-525, MOF-525(Co), and

MOF-525(Zn) using the RASPA [35] simulation code version 2.0.37. Nonbonded interactions were defined using the Lennard-Jones (LJ) potential, with intermolecular interactions truncated at a distance of 13 Å. The potential parameters of the framework structures were obtained using the DREIDING [36] force field. CO₂ was represented as a three-site rigid molecule with a Lennard-Jones 12–6 potential, with partial charges positioned at the center of each site [37]. The TraPPE force field [38] was employed to derive the potential parameters for CO₂. N₂ was modeled as a three-site rigid molecule, where nitrogen atoms occupied two sites, and the third site was located at the center of mass with partial charges [39]. CH₄ was modeled as a single sphere [40]. Pair potentials between different atoms were calculated using the Lorentz-Berthelot mixing rules. The charge equilibration (Qeq) method [41] as implemented in RASPA was utilized to assign partial charges to MOF atoms and to calculate electrostatic interactions between gas molecules and MOF atoms, Long-range electrostatic interactions were accounted for using the Ewald summation method [42].

MD simulations utilized the gas loadings acquired from the results of GCMC simulations conducted at 2 bar and 25°C, which were used as inputs to compute the diffusion of CO₂, N₂, CH₄ gases in each MOF. In addition to 10,000 initialization and 10,000 equilibration cycles, a total of 4 \times 10⁶ production cycles were employed. The temperature was maintained constant using the NVT ensemble with the Nose-Hoover thermostat [43]. The mean square displacement of gas molecules was calculated, and the self-diffusion coefficients of CO₂, CH₄, and N₂ were determined by averaging the diffusivities computed in the x, y, and z directions, following Einstein's relation [44,45]. CO₂, CH₄, and N₂ permeabilities were calculated at the feed condition of 2 bar, presuming the permeate side to be under vacuum [46], using the results of GCMC and MD simulations.

Previous research employing the Maxwell model [30], which depends on an ideal morphology approximation for gas permeation, has shown a good agreement between experimental and simulated gas permeabilities of several MOF-based MMMs [46–48]. Therefore, we predicted the gas permeabilities of MMMs using the Maxwell model, as shown below:

$$\mathsf{P}_{\mathsf{MMM}} = \mathsf{P}_{\mathsf{P}} \left[\frac{\mathsf{n} \times \mathsf{P}_{\mathsf{MOF}} + (1\text{-}\mathsf{n}) \times \mathsf{P}_{\mathsf{P}}\text{-}(1\text{-}\mathsf{n}) \times \Phi \times (\mathsf{P}_{\mathsf{P}} \cdot \mathsf{P}_{\mathsf{MOF}})}{\mathsf{n} \times \mathsf{P}_{\mathsf{MOF}} + (1\text{-}\mathsf{n}) \times \mathsf{P}_{\mathsf{P}}\text{+}\mathsf{n} \times \Phi \times (\mathsf{P}_{\mathsf{P}} \cdot \mathsf{P}_{\mathsf{MOF}})} \right]$$

In the Maxwell model, n is the geometry shape factor taken as 0.3, assuming sphere-like MOF particles and Φ is the volume fraction of the MOF particles in the polymer matrix. P_{MOF} is the gas permeability for the MOF computed by molecular simulations as explained above, P_P is the gas permeability for the polymer and P_{MMM} is the gas permeability for the MMM. Maxwell model is mostly applicable to low filler loadings (Φ <0.2) [49]. To calculate Φ in each wt% loading, densities of MOFs and polymer were used.

3. Results and discussions

3.1 Characterization of MOF and MMMs

First, to ensure the successfulness of the post-metalation process of the MOF-525, the UV-Vis spectrum of the digested MOF-525, MOF-525(Co) and MOF-525(Zn) was collected and the result is presented in Figure 1(A). As can be seen from the result, the successfulness of the post-metalation process can be observed by the change of the UV-Vis spectrum of the MOF-525(Co)

and MOF-525(Zn) from their non-metalated MOF-525, particularly in the wavelength region between 450-650 nm.



Figure 1. The UV-Vis spectra of the digested MOF-525, MOF-525(Co) and MOF-525(Zn) nanoparticles (A), MOF-525 MMM (B), MOF-525(Co) MMM (C) and MOF-525(Zn) MMM (D).

In addition, we also investigated the UV-Vis spectra of the digested MMMs to ensure that there is no alteration during the membrane fabrication process and the results are presented in the Figure 1 (B)-(D). As can be seen, the UV-Vis spectra of the MMMs are similar with the spectra of their corresponding nanoparticles and thus indicating the absence of the alteration during the membrane fabrication process. Moreover, it can also be seen that the absorbance value of the MMMs corresponds to the loading of the nanoparticles and thus indicating the successfulness of the incorporation of the nanoparticles inside the 6FDA-DAM matrix.

Having successfully proven the post-metalation process, the crystallinity of the MOF-525, MOF-525(Co) and MOF-525(Zn) was also inspected by collecting their PXRD pattern with the result is presented in

(A). As can be seen from the result, the PXRD peak of the non-metalated MOF-525 corresponds well with the simulated pattern. The same case can also be observed on the post-metalated MOF-525, namely MOF-525(Co) and MOF-525(Zn). This case is indeed expected since the post-metalation process is not expected to alter the crystal lattice of the MOF-525. However, it can also be seen that the peak relative intensity of MOF-525(Co) and MOF-525(Zn) is slightly different

from MOF-525. This change of form factor after the post-metalation process is expected because of the change in electron density resulting from replacing the metals. [24,50].



Figure 2. The PXRD patterns of MOF-525, MOF-525(Co), and MOF-525(Zn) and the XRD patterns of the MOF-525 MMM (B), MOF-525(Co) MMM (C) and MOF-525(Zn) MMM (D).

The XRD patterns of the MMMs were also collected in order to examine whether the MOF crystallinity can still be preserved during the MMM fabrication process since it involves impactful steps such as mechanical stirring. As can be seen in the results in

(B)-(D), for all cases, the peaks corresponding to the non-metalated and post-metalated MOF-525 start to appear at the lowest loading, namely 2 wt%, even though these peaks are relatively weak considering the relatively low nanoparticles loading in this case. However, as the nanoparticle loading inside the MMMs increases, the peak intensity also becomes higher and this becoming more prominent in the case of 10 wt% MMM. These results then successfully indicate that the crystallinity of all the MOFs can be well-preserved during the MMM fabrication process. This might then be attributed to the strong coordination bonding established between the Zr as a high-valence metal atom with the carboxylate ligand.

The FTIR spectra of the nanoparticles and the MMMs were also collected, and the results are presented in the Figure 3(A)-(D). Firstly, from the Figure 3(A), it can be seen that almost no difference can be observed between the non-metalated and post-metalated MOF-525. Meanwhile, for the case of the MMMs, it can be generally observed that the FTIR spectra of the

MMMs consist of the FTIR spectra of both MOFs and the 6FDA-DAM. However, differing from the UV-Vis spectra and XRD patterns, almost no difference observed between the MMMs loaded with 2 wt%, 5 wt% or 10 wt% nanoparticles. This might be caused since some of the peaks from the MOFs and the 6FDA-DAM actually overlap.



Figure 3. The FTIR spectra of MOF-525, MOF-525(Co) and MOF-525(Zn) nanoparticles (A), MOF-525 MMM (B), MOF-525(Co) MMM (C) and MOF-525(Zn) MMM (D).

Therefore, in order to have a better perspective for the characterization purpose, the FTIR difference spectra are also obtained at the wavenumber between 1600 cm⁻¹ and 400 cm⁻¹ by subtracting the FTIR spectra of the MMM with the FTIR spectra of the 6FDA-DAM. Figure 4(A)–(C) then presents the results for this analysis. As can be seen, differing from the previous FTIRn spectra, the fingerprint of the MOF-525 and post-metalated MOF-525 in the MMM can be more clearly seen. For all the cases, it can be observed that there is an increase in the peak intensity at the wavenumber around 1410 cm⁻¹, 650 cm⁻¹ and 480 cm⁻¹ as the nanoparticle loading inside the 6FDA-DAM gets higher. As previously observed in Zr-porphyrin MOFs, the peaks at wavenumber around 1410 cm⁻¹ could be attributed to the symmetric stretching of the carboxylate linkers and the stretching mode of the metal-ligand bonding, respectively [24,51].



Figure 4. The FTIR difference spectra of the MOF-525 MMM (A), MOF-525(Co) MMM (B) and MOF-525(Zn) (C)

Lastly, the micrographs of all MMMs were also captured to analyze the MOF nanoparticles distribution inside the 6FDA-DAM polymeric matrix and are shown in Figure 5(A)-(I). From the micrographs, it can be seen that both the non-metalated and post-metalated MOF-525 can be quite homogeneously dispersed inside the polymeric matrix. However, this seems to only happen until the nanoparticle loading is 5 wt%. When the nanoparticle loading is further increased to 10 wt%, it can be observed that nanoparticle agglomeration becomes more prominent. In this case, they are clustered together and are not homogenously dispersed across the polymer matrix. Such conditions could then impart a negative impact to the separation performance of the MMMs, as will be further discussed in the next section.

Figure 5. SEM micrographs of 2 wt% (A), 5 wt% (B), 10 wt% (C) MOF-525 MMM, 2 wt% (D), 5 wt% (E) and 10 wt% (F)MOF-525(Co) MMM, 2 wt% (G), 5 wt% (H) and 10 wt% (I) MOF-525(Zn) MMM. The 5 μm scalebar for all the figures is given in (A).

3.2 CO₂ separation performance of MMMs

Having fully characterized the MOF nanoparticles and the MMMs, the CO_2/N_2 and CO_2/CH_4 separation performance of all MMMs were then evaluated and the results are given in the Figure 6. Firstly, as can be seen from the Figure 6(A) and (B), the CO_2 , N_2 and CH_4 permeability of the bare polymeric membrane is found to be around 450, 27 and 25 Barrer, respectively. Therefore, the CO_2/N_2 and CO_2/CH_4 selectivity of the bare polymeric membrane is found to be around 17 and 18, respectively, which are also comparable with other reports [52–54].



Figure 6. The gas permeability (A) and CO_2/N_2 and CO_2/CH_4 selectivity (B) of the membranes. Figure (C) and (D) show the change of the CO_2 permeability and selectivity against N₂ and CH₄, respectively, of the MMMs against the 6FDA-DAM.

Once the polymer is loaded with 2 wt% of MOF nanoparticles, the increase of CO_2 permeability in all MMMs can be observed, which could be attributed to the additional gas pathway contributed by the MOF nanoparticles as they are embedded in the 6FDA-DAM. Therefore, such a trend becomes more prominent as more MOFs are added into the polymer matrix to reach 10 wt%. However, as can also be seen in the Figure 7(A), differing from the trend of the CO_2 permeability, there is a tendency for the permeability of both gases to be stagnant when the MOF loading inside the MMMs is 5 wt% before a slight increase in their permeability occurs when the MOF loading is further increased to 10 wt%.

As a consequence of the differing trend of the gas permeabilities increase, a differing trend is also observed regarding the CO_2/N_2 and CO_2/CH_4 selectivity. As presented in the Figure 7(B), higher MOF loading does not necessarily lead to improved CO_2/N_2 and CO_2/CH_4 selectivity. For all the cases, it can be seen that the CO_2/N_2 and CO_2/CH_4 selectivity for all MMMs reaches plateau at 5 wt% MMMs. Once the MOF particle loading inside both MMMs is further increased to 10 wt%, a decrease in gas selectivity can be observed and more prominent in the case of MOF-525(Co) and MOF-525(Zn) MMMs rather than MOF-525 MMM.

The diffusivity and solubility coefficient of the MMMs are then calculated to further analyze the gas transport and the results are depicted in Figure 7. First, it can be seen that the CO₂ diffusivity

of the bare 6FDA-DAM is found to be around 6.4×10^{-7} cm² s⁻¹. Once loaded with the nanoparticles, a differing trend can be seen for each case of the MMM. For the MOF-525 MMM, an increasing trend of CO₂ diffusivity from the bare polymeric membrane can be observed from around 6.7×10^{-7} cm² s⁻¹ for the 2 wt% MOF-525 MMM to be around 8.2×10^{-7} cm² s⁻¹ for 10 wt% MOF-525 MMM. Meanwhile, in the case of MOF-525(Co) and MOF-525(Zn), such an increasing trend is not very prominent. In fact, for 2 wt% MOF-525(Co) and MOF-525(Zn) MMM, the CO₂ diffusivity slightly decreases from the bare polymeric membrane to be around 5.5×10^{-7} cm² s⁻¹ and 5×10^{-7} cm² s⁻¹, respectively. The CO₂ diffusivity of the 5 wt% MOF-525(Co) and MOF-525(Zn) MMM then increases to be around 5.8×10^{-7} cm² s⁻¹ and 6.3×10^{-7} cm² s⁻¹, respectively. A significant increase in the CO₂ diffusivity for the post-metalated MOF-525 MMM can be observed at the highest particle loading when it reaches 8.2×10^{-7} cm² s⁻¹ and 1×10^{-6} cm² s⁻¹ for MOF-525(Co) and MOF-525(Zn) MMM then increase in the CO₂ diffusivity for the post-metalated MOF-525 MMM can be observed at the highest particle loading when it reaches 8.2×10^{-7} cm² s⁻¹ and 1×10^{-6} cm² s⁻¹ for MOF-525(Co) and MOF-525(Co) MMM, respectively.



Figure 7. The CO₂ (A), N₂ (B) and CH₄ (C) diffusion and solubility coefficient and the CO₂/N₂ and CO₂/CH₄ diffusivity and solubility selectivity (D) of the membranes

As in the case with CO₂ diffusivity, there is also a differing trend regarding the N₂ and CH₄ diffusivity of the MMMs. For the 2 wt% MOF-525 MMM, the diffusion coefficient of both N₂ and CH₄ increases from 2.7 x 10^{-7} cm² s⁻¹ and 1.2 x 10^{-7} cm² s⁻¹ to be around 4 x 10^{-7} cm² s⁻¹ and 1.5 x 10^{-7} cm² s⁻¹, respectively. Differing from the MOF-525 MMM, there is no significant change observed regarding the N₂ and CH₄ diffusivity for both MOF-525(Co) and MOF-525(Zn) MMM. Upon further increase of the MOF loading to 5 wt%, the N₂ and CH₄ diffusivity for both MOF-

525(Co) and MOF-525(Zn) MMM starts to increase to be around 4.3 x 10^{-7} cm² s⁻¹ and 1.4 x 10^{-7} cm² s⁻¹, respectively. At the highest particle loading, the N₂ and CH₄ diffusivity of all the MMMs show a significant increase from its bare polymeric membrane to be around 4.5 x 10^{-7} cm² s⁻¹ and 2 x 10^{-7} cm² s⁻¹, respectively.

Meanwhile, the CO₂ solubility of the 6FDA-DAM is found to be around 7 x 10⁸ cm³STP cm⁻³ cmHg⁻¹. Differing from the CO₂ diffusivity trend, an increase in the CO₂ solubility for all the cases of 2 wt% MMM can be observed. In this case, the CO₂ solubility of 2 wt% MOF-525, MOF-525(Co) and MOF-525(Zn) MMM is found to be around 7.8 x 10⁸ cm³STP cm⁻³ cmHg⁻¹, 9.1 x 10⁸ cm³STP cm⁻³ cmHg⁻¹ and 9.5 x 10⁸ cm³STP cm⁻³ cmHg⁻¹, respectively. However, such an increasing trend can no longer be observed at higher nanoparticle loading. At 5 wt% nanoparticles loading, the CO₂ solubility for MOF-525, MOF-525(Co) and MOF-525(Zn) MMM decreases to be around 7.1 x 10⁸ cm³STP cm⁻³ cmHg⁻¹, 8 x 10⁸ cm³STP cm⁻³ cmHg⁻¹ and 7.7 x 10⁸ cm³STP cm⁻³ cmHg⁻¹, respectively. A further decrease can then be seen for all the cases of 10 wt% MMM where the CO₂ solubility for MOF-525(Co) and MOF-525(Zn) MMM is found to be around 7 x 10⁸ cm⁻³STP cm⁻³ cmHg⁻¹, 5.5 x 10⁸ cm³STP cm⁻³ cmHg⁻¹ and 5.4 x 10⁸ cm⁻³STP cm⁻³ cmHg⁻¹, respectively.

In contrast to the CO₂ solubility trend, both N₂ and CH₄ solubility show a decreasing trend for all the case of the MMMs. The N₂ and CH₄ solubility of the bare 6FDA-DAM is found to be around 9.6 x 10⁷ cm³STP cm⁻³ cmHg⁻¹ and 2.1 x 10⁸ cm³STP cm⁻³ cmHg⁻¹, respectively. For the 2 wt% MMMs, the N₂ and CH₄ solubility decrease to be around 8.8 x 10⁷ cm³STP cm⁻³ cmHg⁻¹ and 2 x 10⁸ cm³STP cm⁻³ cmHg⁻¹, respectively. When the particle loading is increased to 5 wt%, the decrease in N2 solubility is more pronounced in the case of MOF-525(Co) and MOF-525(Zn) MMM to be around 5.6 x 10⁷ cm³STP cm⁻³ cmHg⁻¹. Meanwhile, the CH₄ solubility for all the 5 wt% MMMs is found to be around 1.5 x 10⁸ cm³STP cm⁻³ cmHg⁻¹. At the highest particle loading, the N₂ and CH₄ solubility of the MOF-525 MMM is found to be around 6.5 x 10⁷ cm⁻³ cmHg⁻¹ and 1.6 x 10⁸ cm⁻³STP cm⁻³ cmHg⁻¹, respectively. Meanwhile, the N₂ and CH₄ solubility values are found to be around 6 x 10⁷ cm⁻³STP cm⁻³ cmHg⁻¹ and 1.2 x 10⁸ cm⁻³STP cm⁻³ cmHg⁻¹, respectively. Meanwhile, the N₂ and CH₄ solubility values are found to be around 6 x 10⁷ cm⁻³STP cm⁻³ cmHg⁻¹ and 1.2 x 10⁸ cm⁻³STP cm⁻³ cmHg⁻¹, respectively. Meanwhile, the N₂ and CH₄ solubility values are found to be around 6 x 10⁷ cm⁻³STP cm⁻³ cmHg⁻¹ and 1.2 x 10⁸ cm⁻³STP cm⁻³ cmHg⁻¹, respectively. Meanwhile, the N₂ and CH₄ solubility values are found to be around 6 x 10⁷ cm⁻³STP cm⁻³ cmHg⁻¹ and 1.2 x 10⁸ cm⁻³STP cm⁻³ cmHg⁻¹, respectively. In the case of MOF-525(Co) and MOF-525(Co) and MOF-525(Cn) MMM.

The differing trend of the diffusion and solubility coefficient exhibited by the MOF-525, MOF-525(Co) and MOF-525(Zn) MMMs then also result in the differing trend of their diffusivity and solubility selectivity, which is presented in the Figure 7 (C) and (D), respectively. The CO_2/N_2 and CO_2/N_2 diffusivity selectivity of the bare 6FDA-DAM is found to be around 2.3 and 5.3, respectively. Meanwhile, the CO_2/N_2 and CO_2/CH_4 solubility selectivity of this membrane is found to be around 7.3 and 3.3, respectively. Once loaded with 2 wt% of the nanoparticles, there is barely any change observed regarding the diffusivity selectivity of all the MMMs. In contrast, a significant change can be observed in the solubility selectivity, more prominently in the postmetalated MOF-525 MMMs. In this case, the CO_2/N_2 and CO_2/CH_4 solubility selectivity of 2 wt% MOF-525(Co) can be significantly increased to be around 10 and 4.5, respectively. The same trend is also exhibited by the 2 wt% MOF-525(Zn) MMM where the values increase to be around 11.16 and 4.8, respectively.

When the particle loading is further increased to 5 wt%, it can be firstly seen that the diffusivity selectivity of the MOF-525 MMM changes slightly from the bare 6FDA-DAM. However, a

significant improvement on the solubility selectivity can now be observed. In the case, the CO_2/N_2 and CO_2/CH_4 solubility selectivity of the 5 wt% MOF-525 MMM increases to be around 9.7 and 5.3, respectively. Meanwhile, in the case of 5 wt% MOF-525(Co) and MOF-525(Zn) MMM, the diffusivity selectivity is significantly lower than the bare 6FDA-DAM. The CO_2/N_2 and CO_2/CH_4 diffusivity selectivity for both MMMs are found to be around 1.4 and 4.3, respectively. In contrast, the solubility selectivity of both MMMs continues to increase in comparison to the 2 wt% MMM. The CO_2/N_2 and CO_2/CH_4 solubility selectivity are then found to be around 14 and 4.9, respectively.

Upon further increasing the nanoparticle loading to be 10 wt%, both the diffusivity and solubility selectivity of MOF-525 MMM show only a slight change in comparison to the 5 wt% MOF-525 MMM. A contrasting situation, on the other hand, can be seen in both 10 wt% MOF-525(Co) and MOF-525(Zn) MMM. In both cases, it can be seen that, although the diffusivity selectivity of both membranes barely changes, there is a significant decrease on the CO_2/N_2 and CO_2/CH_4 solubility selectivity for both membranes. For the 10 wt% MOF-525(Co) MMM, both values drop to be around 9.4 and 4.6, respectively. Meanwhile, the values for 10 wt% MOF are found to be around 8.6 and 4.5, respectively.

Analyzing from these results, it could then be firstly inferred that the improvement of CO_2/N_2 and CO_2/CH_4 selectivity for all the MMMs is likely caused by the improvement of CO_2 solubility. This is evident by the prominent increase of the solubility selectivity while the value of the diffusivity selectivity barely changes or even decreases for some cases, such as in the case of 5 wt% MOF-525(Co) and MOF-525(Zn) MMM. The improvement of CO_2 solubility then becomes more prominent in the case of post-metalated MOF-525 MMMs since this positive impact can readily be observed at low particle loading, namely 2 wt%. This then highly indicates the beneficial aspect of employing post-metalated MOF as nanofillers in a MMM.

However, when the nanoparticles loading inside the polymeric matrix is increased to 10 wt%, the positive impact coming from the CO_2 solubility improvement is now impaired by the presence of non-selective defects in the MMM. This is more prominent in the case of MOF-525(Co) and MOF-525(Zn) MMM rather than in the case of MOF-525 MMM as the former experiences a more significant decrease in CO_2 solubility selectivity than the latter. Consequently, the overall selectivity of the 10 wt% MOF-525(Co) and MOF-525(Zn) is the lowest when compared with the MMMs loaded with 2 wt% and 5 wt% MOF-525(Co) and MOF-525(Zn).

We then also performed a molecular simulation as a resource to offer valuable insights into gas permeation through MOF-based MMMs. Validating computational methodologies for predicting gas permeation through membranes necessitates comparing simulation results with experimental measurements for various separations. Molecular simulations of MOFs were conducted under identical pressure and temperature conditions as the experiments and then gas permeabilities were computed. The comparison of experimental CO₂, CH₄, and N₂ permeabilities of MMMs with the predictions of the Maxwell model are presented in the Figure 8. From the results it can be seen that the Maxwell model overestimates the experimental gas permeabilities particularly at 5 wt% and 10 wt% loadings since particle agglomeration was observed in the experiments after 5 wt%. This is attributed to the assumptions that MOFs were modeled as defect-free crystals during molecular simulations and perfectly compatible within MMMs as considered in the Maxwell model [31]. Recent studies have demonstrated that when the gas permeability of a polymer

(approximately 450 Barrer for CO_2) is significantly lower than that of pure MOF (4.36 x 10^4 Barrer for MOF-525), the maximum gas permeability of the MMM calculated using the Maxwell model is up to two times higher than the permeability of the pure polymer [47,89], which aligns with the results presented in the Figure 8.



Figure 8. Comparison of experimental pure gas permeabilities of CO₂ (A), CH₄ (B), and N₂ (C) in MOF-525, MOF-525(Co), and MOF-525(Zn)/6FDA-DAM MMMs with the predictions acquired from Maxwell model.

Lastly, to put the performance results of the MMMs used in this study into a perspective, their performance in relation to the upper bounds is also given in the Figure 9 [5,55] and compared with other MOF MMMs used for CO_2/N_2 and CO_2/CH_4 separation [56–87]. First, from the Figure 9(A) and (C), it can be seen that the MMMs in this study is located at the lower right corner of the diagram and thus indicating a satisfactory CO₂ gas permeability, which is indeed an intrinsic feature of the 6FDA-DAM and thus can perform better than other MMMs fabricated with other glassy polymers such as Matrimid [59,72,83,88] or polysulfone [66,76] that usually show a relatively low CO₂ permeability. Looking closely on the separation performance of the MMMs, it can be seen from the Figure 9(B) and (D) that both the CO_2/N_2 and CO_2/CH_4 selectivity of the bare polymeric membrane can be enhanced so they are closer to the both 2008 and 2019 Upper Bound. However, the enhancement obtained by embedding the MOF-525 inside the matrix is not sufficient to surpass both upper bounds. This might then indicate that higher MOF loading might be necessary to simultaneously increase the gas permeability and selectivity. However, as has been previously discussed, there is a tendency for interfacial imperfections once the MOF loading reaches 10 wt% and thus a deterioration in membrane performance is very likely to be seen when the MOF loading is made higher. Despite this, it is worth to note that, in our case, only a relatively low loading of MOF nanoparticles in the range of 2-5 wt% is necessary to improve the performance of the bare polymeric membrane and thus resulting in the simultaneous improvement of gas permeability and selectivity. For example, as also illustrated in the Figure 6

(C) and (D), in the case of 2 wt% post-metalated MOF-525 MMM, the CO₂ permeability and selectivity against N₂ and CH₄ can be simultaneously improved up to 10% and 25%, respectively, to be around 494 Barrer and in the range of 20-22, respectively. Using the same polymer and ZIF-301, as an example, around 20 wt% of the particle loading is required to increase the CO2 permeability and CO₂/CH₄ selectivity around 37.5% and 31%, respectively [81]. In another investigation using polysulfone as a polymer, even though the CO₂ permeability of the membrane can be significantly increased up to more than 100% using 16 wt% of ZIF-8 and HKUST-1, an improvement in CO₂ selectivity against N₂ and CH₄ can be barely observed [66]. This then might indicate the high efficiency of using post-metalated MOF-525 nanoparticles to simultaneously improve the CO₂ permeability and selectivity of a polymeric membrane because of the presence of the metal center in the porphyrin ring to increase the CO₂ solubility of the MMMs. Therefore, if the interfacial defects issue can be solved, it could be expected that the performance of the resulting MMM could also be further enhanced by incorporating these nanoparticles.



Figure 9. The CO₂/N₂ (A and B) and CO₂/CH₄ (C and D) separation performance of the membranes used in this study evaluated against the 2008 and 2019 upper bound [56–87]. The data for this graph can be seen in the Table S1 in the Supporting Information.

4. Conclusions

In summary, our study demonstrates that incorporating MOF-525 and its post-metalated variants, MOF-525(Co) and MOF-525(Zn), positively impacts the CO_2/N_2 and CO_2/CH_4 gas separation performance of 6FDA-DAM membranes. For the post-metalated MOF-525 MMM, an initial

improvement in performance is observed at a relatively low nanoparticle loading of 2 wt%. However, the positive trend of the gas separation performance does not continuously increase with increasing nanoparticle loading. For the highest nanoparticles loading of 10 wt%, a slight decrease in the gas separation performance from the 5 wt% MMMs can be observed, indicating the presence of non-selective voids in the MMMs. Using molecular simulations and the Maxwell permeation model, gas permeabilities of the MMMs were theoretically predicted and shown to overestimate the experiments, particularly at high particle loading. We speculate that the discrepancies between the experimental results and those predicted by the Maxwell model at high particle loading result from non-ideal conditions within the MOF MMM at the maximum loading used in this study. This observation underscores the importance of keeping the particle loading under 5 wt% for these specific MMMs, where conditions remain near-ideal, thereby allowing the Maxwell model to more accurately predict their gas separation performance. Despite this, it can also be seen that the metalated MOF-525 are very efficient to simultaneously improve the CO_2 permeability and selectivity of the bare polymeric membrane since this can be incorporating them at relatively low loading at 2 wt%. If the issue of interfacial defects can be effectively addressed, the CO₂ separation performance of the MMMs using these metalated MOF-525 could then be further increased.

5. Acknowledgements

N. P acknowledges the funding from the Alexander von Humboldt Postdoctoral Fellowship (Ref 3.3 – GBR – 1219268 – HFST-P).

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