Investigation of ZIF-78 Morphology and Feed Composition on the Mixed Gas CO\textsubscript{2}/N\textsubscript{2} Separation Performance in Mixed Matrix Membranes

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In this work, the influence of the zeolitic imidazolate framework 78 (ZIF-78) morphology, with 1D pores, on the mixed matrix membrane (MMM) CO\textsubscript{2}/N\textsubscript{2} mixed gas separation performance is investigated as well as the influence of the feed composition and pressure. Low aspect ratio and a high aspect ratio ZIF-78 particles are synthesized and incorporated in Matrimid with 10 and 20 wt% additive content. High pressure CO\textsubscript{2} and N\textsubscript{2} sorption measurements show that both the low and high aspect ratio ZIF-78 metal–organic frameworks (MOFs) exhibit similar sorption behavior. The incorporation of ZIF-78 into Matrimid results in improved CO\textsubscript{2} permeabilities up to 39%, without compromising the selectivity, relative to native Matrimid membranes. Both at low and high CO\textsubscript{2} partial pressures, the MMMs containing the different ZIF-78 morphologies show equal CO\textsubscript{2} permeabilities, indicating that the ZIF-78 morphology and consequently the aspect ratio are insignificant for these particular MMMs, contradicting previous observations in literature. Thus, depending on the MOF/polymer system, the MOF morphology and aspect ratio can be considered as a design aspect. Finally, a clear influence of feed composition and pressure on the MMM solubility coefficient and diffusivity is observed, emphasizing the importance of the mixed gas composition and measurement conditions.

1. Introduction

Metal–organic frameworks (MOFs) are microporous crystalline materials, where metal nodes are connected by deprotonated organic linkers. The obtained ordered organic–inorganic networks exhibit high surface areas and their pore size, aperture and functionality is highly tunable, due to the variability in available organic linkers.\[3\] For example, a series of iron(II) carboxylate MOFs shows varying framework flexibility, pore size, pore aperture, and 3D structure by varying the carboxylate linker type.\[2–6\] These properties make MOFs very attractive materials in the field of gas storage and separation, since gas sorption and diffusion are tunable by linker variation.\[7,8\] Despite these promising characteristics, MOFs often lack chemical and thermal stability, which limits their practical application. Nonetheless, the number of stable MOFs has been increasing over the years.\[9\]

One subclass of thermally and chemically stable MOFs are zeolitic imidazolate frameworks (ZIFs), which consist out of zinc or cobalt cations and a variety of imidazolate linkers. Since the first reported ZIFs, many new ZIF structures and topologies have been unraveled.\[10\] Due to their versatility, stability, and microporous nature (i.e., high gas uptake), multiple ZIF containing membrane structures have been investigated for gas separation purposes.\[11,12\] By the use of high-throughput synthesis, ZIF structures analogous to the zeolite gmelinite (GME) topology were found, which exhibited extraordinary high CO\textsubscript{2} uptake.\[13\] These hexagonal anisotropic GME ZIF crystals have two 1D channel types (one pore exists out of KNO cages, with pore apertures ranging from 4.5 to 8 Å, the other out of alternating GME and HPR cages, with pore apertures ranging from 3.6 to 4.3 Å) that are oriented parallel along the c-axis of the crystal structure (Figure 1).\[14,15\] GME ZIFs are constructed by linking Zn\textsuperscript{2+} with 2-nitrimidazolate (nIm) and another imidazolate linker, where the other imidazolate linker determines the pore size, aperture, and polarity.\[11,14\] Controlling size and shape of the mixed linker ZIFs is rather difficult, since the difference in p\textsubscript{K}_\text{a} values between the variable imidazoles and 2-nitrimidazolate (nIm) causes different degrees of deprotonation in the reaction mixture.\[16\] Nonetheless, for ZIF-69 and 78 (both with GME topology) it was shown that their size and aspect ratio could be controlled by using specific zinc salts and deprotonating agents and adapting the ratio between zinc and the imidazoles.\[17–19\]
The functionality of the variable imidazolate linker in GME ZIFs strongly impacts the sorption and diffusion behavior. Increasing the size of functional groups on the imidazolate linker (which is located in the KNO cages) resulted in a decrease in pore size, pore aperture, and surface area. However, the CO2 sorption behavior in these ZIFs was not correlated to the surface area, but to the pore polarity (governed by the imidazolate functionality), where ZIF-78 (GME topology, constructed by linking Zn2+ with nIm and 5-nitrobenzimidazolate (nbIm)) with a relatively high pore polarity, due to the nitro functionality in the KNO pore channel, showed the highest CO2 affinity. This nitro functionality and high CO2 affinity stimulated studies about ZIF-78 in several fields, where the ZIF-78 catalytic activity of cyclic carbonate synthesis, the control of the ZIF-78 aspect ratio by triethylamine (TEA) addition and linker ratio and the separation performance of pure ZIF-78 membranes for both liquid and gas separations were investigated. Interestingly, the latter study about gas permeation through pure ZIF-78 membranes demonstrated that the increased pore polarity of ZIF-78 decreased the CO2 permeability, relative to gases with weaker electrostatic interactions, e.g., N2 and CH4.[23] Studies on the sorption behavior in other GME ZIFs underpinned the importance of the presence of polarizable groups for improved sorption of polar molecules. On the other hand, simulations of diffusivities showed that the accounting charge-quadrupole interactions in ZIF-68 (GME topology) significantly decreased diffusivities of CO2 in these materials. For ZIF-68 and 69 (GME topology), both structures exhibit significantly lower CO2, CH4, and N2 sorption than model predictions. Literature shows that the gases cause pore blockage in the HPR channels, making them inaccessible. This behavior was not observed for hydrogen gas, with relatively small dimensions. These observations show that the gas sorption and permeation behavior of GME mixed ligand ZIFs are affected by many parameters.

Mixed matrix membranes (MMMs) are membranes consisting of a polymer matrix and a dispersed additive, where the additive improves the permeability and/or the selectivity of the membrane, with respect to the native polymer. One of the additive types that has gained significant attention for MMMs are MOFs, due to their microporosity, high surface area, and matrix compatibility. Depending on the MOF-matrix system, MMMs generally show an increase in permeability due to the MOF microporosity in combination with one of the three possibilities for the selectivity: 1) incompatibility between the MOF and the matrix causes interfacial defects, resulting in a decreased selectivity, 2) proper compatibility between the MOF and the matrix does not influence selectivity, or 3) too much affinity between the MOF and the matrix or pore intrusion of the matrix into the MOF densifies the MOF-matrix interface, resulting in an increased selectivity. Thus far, ZIFs with a GME topology have been investigated for membrane applications, but only as thin, full-MOF films. In general, the morphology of MOFs strongly influences the performance of MOF-based MMMs, but the influence of aspect ratio, which is defined as the length to width ratio of anisotropic MOF particles, is underexposed. For NH2-MIL-53(Al)/Matrimid MMMs (the MOF has 1D channels), a nanoparticle morphology slightly favored the CO2 permeability, while a decrease in CO2 permeability was observed for a nanorod structure, which was ascribed to a higher degree of chain disruption of the polymer around the MOF particles. Moreover, for impermeable additives with a sheet-like morphology, it was shown that an increase in aspect ratio resulted in a lower O2 permeability, due to an increase in diffusion pathway of the gases through the MMM. Thus, the influence of aspect ratio of MOF additives with rod-like morphologies in MMMs has only been investigated to a very limited extent. Since ZIF-78 exhibited a high CO2 uptake and the morphology/aspect ratio of ZIF-78 is controllable by tuning the linker ratio, concentration, and the addition of TEA, this particular ZIF is an excellent starting point to elucidate the effect of the MOF aspect ratio on the gas sorption and mixed gas permeability and selectivity of MMMs. Several aspects of the additive morphology and aspect ratio are important as on one hand a lower aspect ratio provides more entrances into the ZIF, but on the other hand a higher aspect ratio provides a longer highly permeable pathway (compared to the matrix permeability) through the ZIF. For clarity, a schematic overview of these two differences and how the ZIF-78 is defined is shown in Figure 2. Therefore, three scenarios are envisaged for ZIF-78 with a low aspect ratio with a disc-like morphology and a high aspect ratio with a rod-like morphology. L/W < L/W

Figure 1. Top view (perpendicular to the c-plane) of the GME crystal structure of ZIF-78. The KNO cages are located at the lattice corners, while the stacked alternating HPR and GME cages are surrounding the KNO cages (in Figure 6 HPR/GME cages surround the center KNO cage).

Figure 2. Schematic representation of ZIF-78 particles with a low and a high aspect ratio. L represents the length of the crystal and W represents the width of the crystal. The dashed lines represent the actual ZIF-78 crystal morphology. The cylinders illustrate how the pores are oriented parallel to the c-axis in the ZIF-78 crystals.
with different morphologies in MMMs. 1) Either, a lower aspect ratio enhances the permeability more than a high aspect ratio, since relatively more entrances into the GME ZIF pores are present in the same amount of MOF. 2) Either, a low aspect ratio improves permeability less than a high aspect ratio, since the diffusion pathway through the high aspect ratio ZIF is longer, facilitating diffusivity. Or 3) the previously two effects balance each other, resulting in similar performance.

To elucidate which scenario is of effect, this work will investigate the effect of the ZIF morphology/aspect ratio on the performance of homogeneously dispersed ZIF-78 in dense MMMs. ZIF-78 is used as MOF additive, as it shows the highest CO₂ affinity and has the narrowest pore aperture in the series of isoreticular GME ZIFs and has a properly tunable morphology.[14,19] The polyimide Matrimid 5218 is chosen as polymer matrix, since it is commonly used in MOF-based MMMs for CO₂/N₂ separations and can be regarded as benchmark material for dense gas separation membranes.[29] The CO₂/N₂ gas pair is selected, since a major part of flue gas consists out these gases.[35] Moreover, this separation can serve as a model case for CO₂/CO separation (plasma conversion of CO₂ into CO, i.e., fuel to feedstock), since N₂ and CO have similar properties in terms of kinetic diameter, critical temperature and thermal diffusivity.[36,37] Finally, in addition to the MOF morphology, the influence of the CO₂/N₂ composition on the membrane performance will be investigated.

2. Results and Discussion

2.1. ZIF-78 Analysis

Before analyzing the MMMs with the two different ZIF-78 morphologies, an analysis of the low aspect ratio (LA) and high aspect ratio (HA) ZIF-78 morphologies is performed to identify their structure and sorption behavior. The X-ray diffraction (XRD) patterns of ZIF-78 LA and HA are shown in Figure S1 (Supporting Information) and agree for the majority with literature.[14,19,20,38] However, two discrepancies are observed between the diffractograms of the synthesized ZIF-78 particles and the simulated diffractogram. These are the absence of the (101) peak at 6° and the (002) peak at 8.5°. The presence or absence of certain diffraction peaks or a variation in peak intensity in ZIF-78 as well as other ZIF types is more often observed and can occur due to, e.g., a difference in thermal treatment, used solvent or presence of guest molecules, e.g., an organic base.[19,21,39,40]

Both ZIF-78 LA and HA exhibit high thermal stability (Figure S2, Supporting Information). Up to 200 °C no weight loss is observed. From up to 350 °C a weight loss of ≈6% is observed, which is attributed to the release of solvent (boiling point N,N-dimethylformamide (DMF) = 153 °C) and the carbonization of residual guest molecules (TEA, nlm, and nbIm) in the ZIF-78 structures.[41] Normally, guest molecules are removed by a solvent exchange method.[11,14] However, this method can deteriorate the crystal structure, and was therefore not performed in this work.[48] At 350 °C, a second degradation step is observed, where the organic linkers in both MOFs start to degrade and correspond with the thermal stability of ZIF-78 found in literature.[44]

The Brunauer–Emmett–Teller (BET) surface analysis of ZIF-78 LA and HA (Figure S3, Supporting Information) shows that ZIF-78 LA sorbs a significantly higher amount of N₂ than ZIF-78 HA. With increasing aspect ratio, the inner part of the ZIF channels becomes more difficult to access, due to limited diffusivity through the narrow 1D-pore apertures and capillary condensation and subsequent blockage in channels, which is expressed in a lower N₂ uptake of ZIF-78 HA, relative to ZIF-78 LA.[27,42] The BET surfaces area of ZIF-78 LA and HA are significantly lower than those reported in literature (620 m² g⁻¹).[14] This discrepancy is attributed to a limited nitrogen diffusivity into the narrow 1D channels, lowering the calculated surface area as the aspect ratio increases.[27]

Scanning electron microscopy (SEM) analysis of ZIF-78 LA and HA shows the influence of the mixed linker ratio in the synthesis protocol on the shape and size of the MOF morphology (Figure 3). A 2:1 nIm:nbIm ratio results in hexagonal ZIF-78 crystals with a disc like structure, i.e., the low aspect ratio (LA) ZIF-78. The LA ZIF-78 particles have an average width of 1.49 µm (± 0.60 µm) and a length (along the c-axis of the crystal) of 1.39 µm (± 0.60 µm), resulting in an average aspect ratio of 0.93. Inversing the linker ratio results in hexagonal ZIF-78 crystals with a rod like structure, i.e., the high aspect ratio (HA) ZIF-78. The HA ZIF-78 particles have an average width of 1.14 µm (± 0.43 µm) and a length (along the c-axis of the crystal) of 4.25 µm (± 1.39 µm), resulting in an average aspect ratio of 3.72. Thus, changing the linker ratio (nlm:nbIm) ratio from 2:1 to 1:2 results in a different ZIF-78 morphology and changes the aspect ratio by a factor 3.98. Notably, the particle size of both the ZIF-78 LA and HA was reduced by increasing the relative amount of linker to zinc ions, with respect to literature, which was observed as well for the control of ZIF-8 particle sizes.[39,43]

The N₂ and CO₂ sorption isotherms and pressure normalized sorption of ZIF-78 LA and HA are shown in Figure 4. No significant difference in CO₂ and N₂ uptake between the two different aspect ratio ZIFs is observed. At 1 bar ZIF-78 LA and HA have approximately an 18 times higher CO₂ sorption than N₂ sorption, while at 25 bar the CO₂ sorption is approximately only a factor 4 higher than the N₂ sorption (Figure 4A). Thus,
it is expected that the incorporation of ZIF-78 LA and HA into MMMs will enhance the CO$_2$ permeability more significantly at lower partial pressures, with respect to the N$_2$ permeability, since the permeability is governed by the solubility and diffusivity. This expectation is further substantiated by the fact that the sorption behavior in both morphologies shows a stronger Langmuir character for CO$_2$ than N$_2$. Up to 10 bar, a decrease in CO$_2$ in pressure normalized sorption is observed while only a minor decrease in N$_2$ pressure normalized sorption is observed in both ZIF morphologies (Figure 4B). This difference in sorption behavior shows that a high affinity between the ZIFs and CO$_2$ is present and is attributed to difference in quadrupole moments of the respective gases. Similar sorption behavior of ZIF-78 with varying aspect ratios was observed elsewhere in literature.[19] Contrary to the BET surface analysis, no significant difference between ZIF-78 LA and HA is observed for high pressure N$_2$ and CO$_2$ sorption.

2.2. Membrane Analysis

Both Matrimid and the MMMs show excellent thermal stability (Figure S4, Supporting Information). The MMMs start to degrade gradually around 350 °C up to the degradation temperature of Matrimid at 500 °C. In this trajectory, the weight loss is caused by the degradation of ZIF-78 (Figure S2, Supporting Information), with an onset at 350 °C. As expected, similar thermal degradation profiles are observed for the LA and HA MMMs, since both contain equal weight percentages of MOF. The 20 wt% MMMs show a higher weight loss than the 10 wt% MMMs though, since these contain a higher absolute amount of ZIF-78. Once 500 °C is reached, all MMMs show a second degradation step, which is due to the degradation of the polymer matrix.

Cross-sections of the MMMs with the two ZIF-78 morphologies and varying ZIF-78 content are shown in Figure S5 (Supporting Information). All MMMs show that both LA and HA ZIF-78 are homogeneously distributed throughout the polyimide matrices. An increase in ZIF content in the polymer solution from 10 to 20 wt% results in an increased presence in the cross-sections as well.

No difference in CO$_2$ and N$_2$ sorption behavior is observed for the 10 wt% ZIF-78 LA and HA MMMs (Figure 5). Both MMMs show a CO$_2$ sorption that is equal to that of Matrimid and a N$_2$ sorption that is slightly lower than Matrimid. Further increasing the MMM additive content to 20 wt% results in a similar increase in CO$_2$ sorption for both aspect ratios with respect to Matrimid. However, a slight difference between the two aspect ratios in N$_2$ uptake is present (represented by the difference in solubility coefficient between the 20 wt% ZIF-78 LA and HA in Figure 5B). The difference in solubility between the two different gas species is attributed to the

Figure 4. N$_2$ (dash) and CO$_2$ (solid) sorption isotherms A) and pressure normalized sorption B) of ZIF-78 LA (triangle up) and ZIF-78 HA (triangle down) at 35 °C.

Figure 5. High pressure N$_2$ and CO$_2$ sorption A) and solubility coefficients B) of Matrimid, 10 wt% LA, 10 wt% HA, 20 wt% LA, and 20 wt% HA MMMs at 1, 3, 4, and 12 bar at 35 °C (pressures resemble the partial pressures of the corresponding gases in the permeation experiments; values determined by dual mode sorption model fit).
stronger quadrupole moment of CO₂ in comparison with N₂, which causes higher affinity with the matrix and the ZIF. It is clear that, solubility wise, the addition of ZIF-78 to Matrimid not simply results in an weighted average of both pressure normalized concentrations (Figures 4B and 5B) as both aspect ratio ZIFs have a volumetric sorption that is at least two times higher than their sorption per unit mass (due to the density of the ZIF-78 LA and HA particles Figure 4A). This observation indicates that a subtle interplay between the matrix and the ZIFs occurs, i.e., a balance between matrix rigidification in MMMs and an increased sorption capacity due to the incorporation of microporous systems. Moreover, this observation correlates with recently described rigidification/densification in ZIF-8/Matrimid MMMs. In comparison with ZIF-8/Matrimid MMMs (ZIF-8 can be regarded as the ZIF benchmark material), the incorporation of both LA and HA ZIF-78 in Matrimid increases the CO₂ solubility less drastically, relative to Matrimid, which is ascribed to the lower pore volume of ZIF-78 (0.303 cm³ g⁻¹), relative to ZIF-8 (0.49 cm³ g⁻¹). The mixed gas CO₂ permeability of Matrimid and the MMMs at 5 and 15 bar feed pressure for CO₂/N₂ feed compositions of 20/80 and 80/20 is shown in Figure 6. The diffusivities of the Matrimid and the MMMs were calculated by the correlation between permeability, solubility, and diffusivity and are displayed in Figure 7. Based on these figures, the influence of ZIF-78 aspect ratio, ZIF-78 load, and feed composition on the CO₂ permeability will be discussed below and correlated to the sorption data (Figure 5). Although sorption measurements are performed with single gases, while permeation measurements are done with gas mixtures, single gas sorption data are used to effectively support messages extracted from mixed gas permeation experiments.

2.2.1. Morphology and Aspect Ratio

Minor differences in CO₂ permeability are observed between the LA and HA MMMs for 20/80 CO₂/N₂ feed compositions at both 10 and 20 wt% ZIF load. The HA MMMs shows a slightly higher CO₂ permeability than the LA MMMs (Figure 6A), where the differences are more pronounced for the 10 wt% MMMs, both at 5 and 15 bar feed pressure. As a consequence of the MMM CO₂ permeability, the HA MMMs have higher CO₂ diffusivities at the 20/80 CO₂/N₂ feed composition than the LA MMMs (Figure 7A), since the CO₂ solubility of the different ZIF-78 morphology MMMs is approximately equal over the measured pressure range (Figure 5B). However, as deviations between the CO₂ permeability of the two types of MMMs are overlapping (t-tests show statistical insignificance), it is concluded that no difference is present between the two different ZIF-78 morphology MMMs with 20/80 CO₂/N₂ feed composition, by means of permeability, solubility, and diffusivity. Increasing the CO₂ partial pressure results in a further leveling of the CO₂ permeability of the different aspect ratio MMMs, as no influence of the ZIF-78.
morphology on the MMM CO₂ permeability is observed for the 80/20 CO₂/N₂ feed composition (Figure 6B). Correspondingly, the CO₂ diffusivities of both aspect ratio MMMs are approximately the same (Figure 7B). Thus, the different morphologies of the ZIF-78 particles in the MMMs result in comparable CO₂ permeabilities and diffusivities both at low and high CO₂ partial pressures. Interestingly, this observed CO₂ permeation behavior contrasts with literature, where the investigation of NH₂-MIL-53 (Al) (consisting of 1D channels)/Matrimid MMMs showed that a lower aspect ratio increased the CO₂ permeability, while higher aspect ratios showed CO₂ permeabilities similar to the native polymer membrane.[13] This discrepancy shows that the insignificance of the aspect ratio for the ZIF-78/Matrimid MMMs cannot simply be extrapolated to other MMMs and still should be considered as a design aspect for MMMs.

2.2.2. ZIF Load

The CO₂ permeability increases with increasing ZIF load for both the LA and HA MMMs at all operating conditions (up to 39%), relative to the Matrimid CO₂ permeability (Figure 6A,B), which exhibits CO₂ permeabilities that lie within the range of reported literature values.[48,51–53] An increase in CO₂ permeability is often observed for ZIF-based MMMs with increasing MOF content, relative to the native matrices, due to the microporous nature of MOFs.[48,54–56] In comparison with ZIF-8/ Matrimid MMMs, both the LA and HA ZIF-78 MMMs enhance the CO₂ permeability less significant, relative to Matrimid, which is attributed to the previously observed difference between CO₂ solubility of the ZIF-78/Matrimid MMMs and the ZIF-8/ Matrimid MMMs.[48,54] For the 10 wt% MMMs, the increase in permeability, relative to Matrimid, is solely caused by an increase in diffusivity (Figure 7A,B), since the CO₂ solubility coefficient of the 10 wt% MMMs is equal to Matrimid at all operating compositions and pressures (Figure 5B). This indicates that, at 10 wt% additive content, the microporous nature of the MOF only promotes diffusivity in the MMMs, while an increment in CO₂ solubility might be prevented by matrix rigidification and pore blockage. Interestingly, incorporating both 20 wt% ZIF-78 LA and HA in Matrimid results in an increased CO₂ permeabilities, relative to Matrimid, but these increased permeabilities are caused by both an increase in CO₂ solubility and as well as diffusivity (Figures 5B, and 7A,B). This observation indicates the presence of a trade-off between MOF-induced matrix rigidification and enhancement in CO₂ permeability.

2.2.3. Feed Composition and Pressure

The feed composition and pressure significantly influence the performance of all tested membranes (Figure 6A,B). For both compositions, the CO₂ permeability of all membranes decreases with increasing feed pressure. This is mainly due to the decrease in CO₂ solubility coefficient of the membranes as function of pressure (Figure 5B), as the CO₂ diffusivity in both Matrimid and the MMMs decreases slightly (20/80 CO₂/N₂, Figure 7A) or even increases (80/20 CO₂/N₂, Figure 7B). Thus, the influence of feed pressure on the CO₂ permeation behavior of Matrimid and the MMMs is predominantly determined by the CO₂ solubility coefficient. Regarding the feed composition, the CO₂ diffusivity is clearly lower for the 20/80 CO₂/N₂ composition (Figure 7A) than the 80/20 CO₂/N₂ composition (Figure 7B), indicating a suppression of CO₂ diffusivity due to relatively high N₂ partial pressures. The difference in performance between the different feed compositions is further substantiated by comparing the CO₂ permeability of the 20/80 CO₂/N₂ composition at 15 bar feed pressure (3 bar CO₂ partial pressure) with the 80/20 CO₂/N₂ composition at 5 bar feed pressure (4 bar CO₂ partial pressure), as the CO₂ partial pressures are in a comparable range but have significantly different N₂ partial pressures. The CO₂ solubility of Matrimid and the MMMs decreases within the range of 10–20% for all membranes when the CO₂ pressure is increased from 3 to 4 bar (Figure 5B), while the CO₂ diffusivity increases at these conditions within the range of 60–70% (Figure 7). These opposing trends are expressed in an increase in CO₂ permeability of ≈50% for all membranes at the 80/20 CO₂/N₂ composition at 5 bar feed pressure, relative to the 20/80 CO₂/N₂ composition at 15 bar feed pressure. Thus, in contrast with the effect of feed pressure on the CO₂ permeability, the effect of the feed composition on the CO₂ permeability of Matrimid and the MMMs is predominantly determined by the influence of the N₂ partial pressure on the CO₂ diffusivity.

The separation factor of Matrimid and the MMMs at 5 and 15 bar feed pressure for CO₂/N₂ feed compositions of 20/80 and 80/20 is displayed in Figure 8.

![Figure 8](https://www.advancedsciencenews.com/doi/abs/10.1002/admi.202001478)

Figure 8. Separation factor of Matrimid (M), 10 wt% LA, 10 wt% HA, 20 wt% LA, and 20 wt% HA MMMs for CO₂/N₂ feed compositions of 20/80 (A) and 80/20 (B) at 5 and 15 bar feed pressure. All measurements are performed at 35 °C.
As can be seen in Figure 8, with the incorporation of both ZIF-78 morphologies in Matrimid matrices the MMM CO₂/N₂ selectivity hardly changes with respect to Matrimid, indicating that the MOF and the matrix are properly compatible, and no difference in selectivity is observed between the LA and HA MMMs.

This similar selectivity of both aspect ratio MMMs indicates that the MOF-matrix interaction is independent of the ZIF-78 aspect ratio, since MOF-matrix interactions are a determining factor for the MMM selectivity.[8] All membranes show a higher CO₂/N₂ selectivity at 20/80 CO₂/N₂ with 5 bar feed pressure in comparison with the other conditions. This behavior is linked to the relatively high CO₂ solubility coefficient in Matrimid and the MMMs at low CO₂ partial pressures of 1 bar, in comparison with the CO₂ solubility coefficients for conditions with higher CO₂ partial pressures (Figure 5).

3. Conclusion

ZIF-78 with two distinctly different morphologies, due to their different aspect ratios, was incorporated into Matrimid at 10 and 20 wt% additive load. The resulting MMMs were evaluated for their mixed gas permeability of the CO₂/N₂ gas pair at different feed ratios. The ZIF-78 particles showed different BET surface area, where the MOF with the low aspect ratio showed a higher surface area than the MOF with the high aspect ratio. Contrarily, the low and high aspect ratio ZIF-78 showed similar high pressure sorption behavior. The incorporation of ZIF-78 into Matrimid resulted in improved CO₂ permeabilities, while no significant loss in selectivity was observed, relative to native Matrimid without additives. Increasing the ZIF-78 content in the MMMs from 10 to 20 wt% increased the CO₂ permeability due to an increase in both the CO₂ solubility coefficient and diffusivity. Both at low and high CO₂ partial pressures both aspect ratio MMMs showed equal CO₂ permeabilities, indicating that the MOF morphology, by means of aspect ratio, is insignificant for the ZIF-78/Matrimid MMMs, which contrasted with literature. Thus, depending on the MOF/polymer system, the MOF morphology should be considered as a design aspect. Finally, a clear influence of feed pressure and composition was observed for all membranes, where an increase in feed pressure predominantly lowered the CO₂ solubility coefficients, lowering the permeability, and a decrease in N₂ partial pressure at similar CO₂ partial pressures increased the CO₂ diffusivity, increasing the permeability.

4. Experimental Section

Chemicals: 2-Nitroimidazole (nim, 98% purity) and 5-nitrobenzimidazole (nblm, 95% purity) were purchased from Fluorochem Ltd. Zinc nitrate hexahydrate (Zn(NO₃)₂·6 H₂O, 98% purity), triethylamine (TEA, ≥ 99% purity), N,N-dimethylformamide (DMF, ≥ 99.9%), and tetrahydrofuran (THF, ≥ 99.0% purity, 250 ppm BHT inhibitor) were purchased from Sigma-Aldrich. Matrimid 5218 (Matrimid) was kindly provided by Huntsman. The gases He (5.0 grade), N₂ (4.5 grade), and CO₂ (4.5 grade) for sorption measurements were purchased from Linde gas (the Netherlands). For permeation measurements, the gases N₂ (5.0 grade) and CO₂ (5.0 grade) were purchased from Air Liquide (Belgium). All chemicals were used as received.

ZIF-78 Synthesis: ZIF-78 with low and high aspect ratio (abbreviated as LA and HA) were synthesized by a protocol similar to literature with some minor adaptations, in terms of reactant concentrations and synthesis time.[19] For the synthesis of ZIF-78 LA nmI (0.226 g, 2 mmol) and nblm (0.163 g, 1 mmol) were dissolved in DMF (20 mL) (2:1 linker ratio). After dissolution, TEA (0.693 mL, 5 mmol) was added to deprotonate the imidazoles and the solution was stirred for 10 min. Meanwhile, Zn(NO₃)₂·6 H₂O (0.300 g, 1 mmol) was dissolved in DMF (10 mL). The zinc solution was added to the imidazole solution and the mixture was heated at 120 °C and stirred at 130 rpm for 18 h. The resulting suspension was centrifuged with a VWR CompactStar CS 4 for 20 min at 6500 rpm and washed with DMF three times. The precipitate was dried with a rotary evaporator and further dried in a vacuum oven at 125 °C and 1 mbar for 24 h. ZIF-78 HA was synthesized, also following the above described protocol, only the amounts of nmI and nblm were adapted to 0.113 and 0.326 g (1:2 linker ratio), respectively.

Membrane Preparation: Native Matrimid and MMMs containing 10 and 20 wt% ZIF-78, LA and HA, were synthesized according to a protocol mentioned elsewhere.[19] Matrimid casting solutions were made by dissolving Matrimid (0.42 g) in THF (5.58 g), where Matrimid was added in three steps of -0.14 gram. MMM suspensions were made in a similar fashion, but 10 and 20 wt% ZIF-78 (0.047 and 0.105 g, respectively), both LA and HA, were first added to THF. Before each addition of Matrimid, the MOF MMM suspensions were sonicated for 15 min in a Branson 3510 sonication bath. The MMM suspensions were continuously stirred. All casting solutions were made in a similar fashion, but 10 and 20 wt% ZIF-78 (0.047 and 0.105 g, respectively), both LA and HA, were first added to THF. Before each addition of Matrimid, the MOF MMM suspensions were sonicated for 15 min in a Branson 3510 sonication bath. The MMM suspensions were continuously stirred. All casting solutions were made in a similar fashion, but 10 and 20 wt% ZIF-78 (0.047 and 0.105 g, respectively), both LA and HA, were first added to THF. Before each addition of Matrimid, the MOF MMM suspensions were sonicated for 15 min in a Branson 3510 sonication bath. The MMM suspensions were continuously stirred. All casting solutions were cast in Teflon evaporating dishes (d = 6 cm) and were put in a N₂ atmosphere for 24 h. The solidified membranes were further dried and annealed in a muffle oven, where a temperature of 110 °C was reached by heating with 5 °C min⁻¹ and held for 2 h. Subsequently, the temperature was increased to 180 °C by heating with 5 °C min⁻¹ and was hold for 6 h.

Characterization: XRD patterns of ZIF-78 LA and HA were obtained with a Rigaku Miniflex 600 (15 mA, 40 kV, Cu Kα radiation (λ = 1.5406 Å)), in the 2θ range from 2° to 35° with a scanning rate of 1° min⁻¹. N₂ physisorption of ZIF-78 LA and HA was performed with a Micromeretics Tristar II at -196 °C (liquid N₂) to determine the BET surface area. The samples were dried in a vacuum oven at 150° and 0 mbar overnight before the measurement. Moreover, due to a long equilibrium time, the measurement was programmed to start with 40–50 cm³ (STP) N₂.

Thermogravimetric analysis (TGA) was conducted with a PerkinElmer TGA 4000 under N₂ atmosphere (flow 20 mL min⁻¹) from 50 to 800 °C with a heating rate of 20 °C min⁻¹ for ZIF-78 LA and HA, Matrimid and the MMMs to elucidate the thermal stability.

The morphology of the ZIFs and cross-sections of MMMs were analyzed by a JEOL JSM-IT100 SEM. The cross-sections of the MMMs were obtained by cryogenic fracture in liquid N₂ after immersion in a 50:50 water/isopropanol mixture. All samples were sputter coated with a Jeol JFC-2300 HR with gold source prior to the measurement, to prevent sample charging.

High pressure CO₂ and N₂ sorption measurements were performed for ZIF-78 LA and HA, Matrimid and all MMMs with a Rubotherm series IsoSorp sorption instrument at 35 °C up to 25 bar. Since the principle of operation of the sorption instrument is based on a magnetically suspended balance, helium pycnometry was performed first on every sample to determine the weight and volume of the sample in the same apparatus. Thereafter, the CO₂ and N₂ sorption measurements were all corrected with the density of the used gas at operating temperature and pressure by Archimedes' principle, i.e., a buoyancy correction to the measured sorbed weight (Equation (1)). In Equation (1) m_corrected is the corrected weight (g), m_measured is the measured weight (g), ρ_gas is the density of the measuring gas (g cm⁻³), and V_sample is the sample volume (cm³). The acquired data were fitted according to the dual sorption model

\[
m_{\text{corrected}} = m_{\text{measured}} + \rho_{\text{gas}} \cdot V_{\text{sample}}
\]
The CO₂/N₂ mixed gas permeability and separation factor of Matrimid and the MMMs were measured in a high-throughput gas separation system (HTGS).\(^\text{[38,39]}\) This system allows the measurement of 16 different membranes, while pressure, feed ratio, and temperature can be varied throughout the measurement. In this work, feed pressures of 5 and 15 were applied. The CO₂/N₂ mixture composition was set to 20:80 or 80:20 and the temperature was kept constant at 35 °C. Prior to each measurement, all membranes were conditioned for 6 h. The mixed gas permeability was obtained by the pressure increase method, i.e., the increase in permeate pressure in a calibrated volume was measured over time. The total permeability was determined according to Equation (2), where \(P_{\text{total}}\) is the total gas permeability (Barrer), \(\Delta P_{\text{permeate}}\) is the increase in permeate pressure (Pa) per time interval \(\Delta t\) (s), \(V_c\) is the calibrated permeate volume (m³), \(R\) is the gas constant (J K\(^{-1}\) mol\(^{-1}\)), \(T\) is the temperature (K), \(V_m\) is the molar volume at STP (cm³ mol\(^{-1}\)), \(L\) is the membrane thickness (cm), \(A\) is the membrane area (cm²), and \(\Delta P\) is the transmembrane pressure (cm Hg).

\[
P_{\text{total}} = \frac{\Delta P_{\text{permeate}} \cdot V_c \cdot V_m}{A \cdot \Delta t} \cdot 10^{10}
\]  

(2)

Subsequently, the permeate composition was analyzed with a gas chromatograph (Interscience), where the mixed gas separation factor was calculated according to Equation (3). In Equation (3) \(\alpha_{\text{CO2/N2}}\), is the separation factor (\(\alpha\)), \(P_{\text{CO2}}\) is the CO₂ permeate fraction (\(\alpha\)), \(P_{\text{N2}}\) is the N₂ permeate fraction (\(\alpha\)), \(x_{\text{CO2}}\) is the CO₂ feed fraction and \(x_{\text{N2}}\) is the N₂ feed fraction (\(\alpha\)). \(P_{\text{CO2}}\) is the CO₂ permeability (Barrer), and \(P_{\text{N2}}\) is the N₂ permeability (Barrer).

\[
\alpha_{\text{CO2/N2}} = \frac{P_{\text{CO2}}}{P_{\text{N2}}} = \frac{x_{\text{CO2}}}{P_{\text{CO2}}} \cdot 10^{10}
\]  

(3)

The combination of Equations (2) and (3) results in Equation (4), where the component permeability was calculated.

\[
P_{\text{overall}} = x_{\text{CO2}} \cdot P_{\text{CO2}} + x_{\text{N2}} \cdot P_{\text{N2}}
\]  

(4)

Finally, the diffusivity was calculated by dividing the permeability with the solubility coefficient (obtained from the high pressure sorption experiments) according to Equation (5), where \(D\) is the diffusivity (cm² s\(^{-1}\)), \(P\) is the permeability (Barrer), and \(S\) is the solubility coefficient (cm² STP cm³ mol⁻¹ cm Hg⁻¹).

\[
D = \frac{P}{S}
\]  

(5)

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

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