

Visualizing MOF Mixed Matrix Membranes at the Nanoscale: Towards Structure-Performance Relationships in CO₂/CH₄ Separation Over NH₂-MIL-53(Al)@PI

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Mixed matrix membranes (MMMs) composed of metal organic framework (MOF) fillers embedded in a polymeric matrix represent a promising alternative for CO₂ removal from natural gas and biogas. Here, MMMs based on NH₂-MIL-53(Al) MOF and polyimide are successfully synthesized with MOF loadings up to 25 wt% and different thicknesses. At 308 K and $\Delta P = 3$ bar, the incorporation of the MOF filler enhances CO₂ permeability with respect to membranes based on the neat polymer, while preserving the relatively high separation factor. The rate of solvent evaporation after membrane casting proves key for the final configuration and dispersion of the MOF in the membrane. Fast solvent removal favours the contraction of the MOF structure to its narrow pore framework configuration, resulting in enhanced separation factor and, particularly, CO₂ permeability. The study reveals an excellent filler-polymer contact, with ca. 0.11% void volume fraction, for membranes based on the amino-functionalized MOF, even at high filler loadings (25 wt%). By providing precise and quantitative insight into key structural features at the nanoscale range, the approach provides feedback to the membrane casting process and therefore it represents an important advancement towards the rational design of mixed matrix membranes with enhanced structural features and separation performance.

1. Introduction

Gas separation processes are ubiquitous in the energy and petrochemical industries. As a prime example, CO₂ removal from natural- and bio-gas^[1] accounts for the largest industrial gas separation process. The conventional CO₂ removal method,

which relies on cryogenic distillation and reversible absorption, such as amine scrubbing, is energy intensive and poses serious environmental concerns.^[2] Since the 1980s, polymeric membranes have rapidly become a competitive alternative gas separation technology. The advantages of membrane over traditional gas separation methods include decreasing production costs and equipment size, low-energy consumption, ease of operation and limited environmental impact, supposing an innovative process intensification strategy. However, current commercial polymeric membranes allow for a combination of gas permeabilities and separation selectivities, which are still suboptimal to effectively process large volumes of gas.^[3] In addition, they display insufficient thermal and chemical stability and are susceptible to the so-called plasticization phenomenon.^[4]

Several solutions have been put forward to enhance the performance of polymeric membranes. One of the most promising alternatives comprises the dispersion of a porous filler material within

the polymeric matrix, leading to composite materials referred to as mixed matrix membranes (MMMs).^[5] MMMs constitute a compromise between the optimal mechanical properties and easy processing of the polymeric matrix and the benefits of the particular separation capacities afforded by the sieve filler materials. Many different polymer families, such as polycarbonates, cellulose acetates, polyesters, polypyrrolones, polysulfones and polyimides, have been investigated as gas separation materials, being the latter one of the most widely used for industrial scale applications.^[6] Generally, low-flux glassy polymers are preferred as polymer matrix to highly permeable, but poorly selective, rubbery counterparts.^[7] With regard to the filler, a broad range of materials have been explored,^[8] including zeolites,^[9] clays,^[10] mesoporous silicas and different carbon materials.^[11] Metal organic frameworks (MOFs) are recently attracting a lot of attention as potential filler materials for MMMs since the pioneering work by Yehia et al.^[12] These crystalline nanostructures can be synthesised at mild conditions and display high surface areas and large pore volumes, generally in the micropore range.^[13] Besides, they offer an almost unlimited number

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of design possibilities by selecting the appropriate building blocks^[14] and/or by post-synthetic modifications.^[15] Several MOF structures have been demonstrated efficient for gas separation processes.^[16] Notably, promising results were reported for the separation of CO₂ from methane employing MOF-based MMMs,^[2] which opens a research line with potential applications in processes such as the CO₂ removal from natural gas. In particular, we have previously reported on the outstanding performance of the amino-functionalized MIL-53(Al) framework (NH₂-MIL-53(Al)) in CO₂ capture from CO₂/CH₄ mixtures.^[17] Such unique behaviour, not shown by the non-functionalized counterpart, was ascribed to a delicate interplay of weak dispersion forces controlling the flexibility of the framework. This enables the stabilization of the narrow pore (np) MOF configuration at low adsorbate pressures, while only at high CO₂ partial pressures the framework expands to its large pore (lp) structure (see Supporting Information Figure S1).^[17b,18]

An additional alleged benefit of using amino-functionalized MOFs as filler material in MMMs is the possibility to improve the adhesion with the matrix phase. Poor filler-polymer compatibilities and filler segregation are highly undesirable as they have a detrimental impact on the mechanical and separation properties of the membranes. Indeed, these major drawbacks have hampered the development of MMMs based on classical inorganic fillers, such as zeolites, up to industrial implementation. As an alternative, the possibility of incorporating certain functional groups, i.e., amino functions, on the surface of MOF crystals could result in enhanced interactions with the functions existing in the polymer chains, e.g., amide, sulfone groups, as reported for MMM comprising NH₂-MIL-53 (Al) and polysulfone that was attributed to hydrogen bonding between the amine and sulfone groups of both constituents at their interface.^[19] In addition, such enhanced filler-matrix contact is expected to result in better filler dispersions within the membrane and to minimize the formation of interfacial voids between both phases, which would represent non-selective bypasses for the permeating gases. However, although filler distribution and filler-matrix contact are considered key parameters for the MMMs, they are also notoriously difficult to assess experimentally.

Here, we report the synthesis of mixed matrix membranes based on NH₂-MIL-53(Al) dispersed in polyimide. The influence of the casting conditions on the final structural properties of the membranes is discussed. Quantitative analysis derived from tomographic focused ion beam scanning electron microscopy (FIB-SEM) is presented as a powerful approach to assess the distribution of the filler and its contact with the polymeric matrix. In addition, the influence of the MOF loading, its framework configuration in the membrane and the operation conditions on the CO₂/CH₄ separation performance are studied.

2. Results and Discussion

2.1. Characterization of NH₂-MIL-53 (Al) MOF

As-synthesized NH₂-MIL-53(Al) consists of rather homogeneous rod-shaped crystals with average dimensions of 650 nm long and 250 nm wide (Supporting Information Figure S2). The

as-prepared MOF shows a diffraction pattern coherent with the np framework configuration (Supporting Information Figure S3).^[20] No diffractions are observed corresponding to the lp structure. The CO₂ adsorption isotherm shows a steep increase in CO₂ uptake at low pressures (<0.01 bar), corresponding to the filling of the micropores of the material (Supporting Information Figure S4). The total micropore volume was determined to be 45 cm³ g⁻¹, in line with previous studies on this MOF structure.^[17a] The low pressure adsorption isotherm shows complete reversibility, i.e., the desorption branch appears superimposed on the adsorption branch, as previously reported.^[18]

2.2. Characterization of MMMs

2.2.1. MOF Loading and Framework Configuration

The MOF loading in the MMMs determined by TGA showed deviations of <0.2% with respect to the intended loading. Therefore, nominal MOF contents are employed in the remaining of the discussion.

Figure 1 depicts the X-ray diffraction (XRD) pattern of selected MMMs with a 25 wt% MOF loading, along with those for the pure MOF and polyimide materials. While the as-synthesized MOF shows exclusively the np configuration, diffractions ascribed to the lp MOF structure dominate the pattern of the casted membranes.

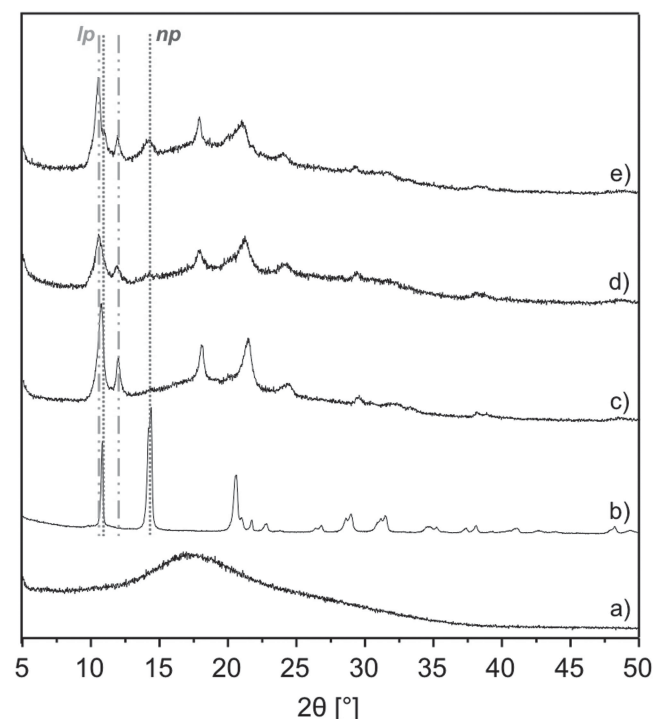


Figure 1. XRD patterns for the neat polyimide MATRIMID (a), the as-synthesized NH₂-MIL-53(Al) MOF (b), and mixed matrix membranes, containing a 25 wt% MOF loading, casted in a Petri dish (thickness 75–105 μm) and dried under free convection conditions at 273 K (c) and at room temperature (d), casted using doctor blade system (thickness 35–75 μm) and dried under free convection conditions at room temperature (e). The most intense diffraction lines for the lp and np MOF configurations are indicated.

We attribute the preferential expanded MOF framework configuration in the MMMs either to the partial penetration of polymer chains in the pore structure of the $\text{NH}_2\text{-MIL-53(Al)}$, or to an impeded framework flexibility in the polymer-embedded MOF, which helps retaining the lp structure as a “frozen” state. Interestingly, as judged from the XRD patterns, the proportion of MOF retaining the original np structure is dependent on the conditions employed for the first step of solvent removal after membrane casting. No reflections ascribed to the np structure are recorded on the membranes casted at 273 K, i.e., when solvent removal is deliberately slowed down. In contrast, albeit weak, diffractions due to the contracted MOF configuration are detected after a faster solvent removal at room temperature. Chloroform present in the pores of the MOF after casting, maintains the structure in its lp configuration. It seems that a longer retention time of the solvent in the pore system after casting, i.e., a lower evaporation rate, increases the chances for the polymer chains to enter the expanded MOF framework, leading to the absence of np $\text{NH}_2\text{-MIL-53(Al)}$ in the MMMs. Fast removal of solvent helps earlier contraction of the MOF structure, partially preventing the polymer chains from penetrating its porous framework. Remarkably, not only the drying temperature can be used to adjust the solvent removal rate. As shown in Figure 1, reducing the membrane thickness by using doctor blade system during casting accelerates solvent removal at room temperature (RT) and leads to a membrane with the highest relative contribution of np $\text{NH}_2\text{-MIL-53(Al)}$. Similar results were observed for membranes with lower MOF loadings (not shown), for which the diffraction lines related to the filler were obviously weaker. Attempts to further accelerate solvent evaporation by applying higher temperatures (323 K) or dynamic vacuum were not successful since partially distorted/folded membranes were obtained. These results highlight the importance of well-controlled conditions during membrane casting, particularly the solvent removal rate, on the ultimate configuration of the metal organic framework in the MMMs. The implications for the gas separation performance will be analyzed in Section 2.3.2.1.

2.2.2. Spatial Distribution of MOF Filler and Filler-Matrix Contact

Structural features of MMMs such as the spatial distribution of the filler crystals and the existence of voids at the filler-matrix boundary are essential in determining the mechanical

properties and gas separation performance. However, these parameters are also particularly difficult to assess experimentally. Generally, the membranes are fractured after immersion in $\text{N}_2(\text{liq})$, often referred to as cryo-fracturing, in order to gain access to the cross-section of the membrane with imaging techniques such as SEM. However, such approach provides only 2D, local information, while the cryo-fracturing approach often results in rough membrane cross-section surfaces. Therefore, a number of surface motifs derived from the fracturing process are imaged, leading to an incomplete or deceptive picture of the structural features of the membrane, most particularly the fraction of voids in the membrane.

As an alternative, FIB-SEM is a powerful technique capable of providing three-dimensional information on the structure of solid specimens with nanometer resolution.^[21] The Ga^+ primary focused ion beam is used to controllably sputter a selected area of the specimen, precisely removing thin slices of material and enabling a series of consecutive cross-sections to be studied individually. After alignment of the stack of SEM images, the internal structure of the analyzed volume can be reconstructed in 3D. Here FIB-SEM was used to study the spatial distribution of the MOF filler in the MMMs as well as a mean to quantify the contact between the filler and the matrix phases. The $\text{NH}_2\text{-MIL-53(Al)}/\text{PI}_{25\%}$ membrane was studied as a showcase, given that this membrane showed the best gas separation performance (vide infra, Section 2.3.2.2.).

Two imaging modes were employed for the FIB-SEM study. On the one hand, the backscattered electron (BSE) imaging mode detects electrons, originating in the primary electron beam, which are elastically back-scattered out of the specimen. In this imaging mode, the intensity scales with the atomic number of the elements in the sample specimen and is therefore particularly suitable to detect contrast between areas with different chemical compositions. On the other hand, the in-lens imaging mode detects secondary electrons emitted from the specimen. In particular at low voltages and small working distances, images with high contrast can be obtained.

Figure 2a depicts a low-magnification SEM image of the hole trimmed with the FIB inside the membrane specimen. Figure 2b shows a SEM image of a representative membrane cross-section recorded in BSE mode. As observed, the different constituents of the membrane can be discerned due to their different greyscale levels. MOF crystals appear brighter, while voids between the MOF crystals and the polymer or in-between

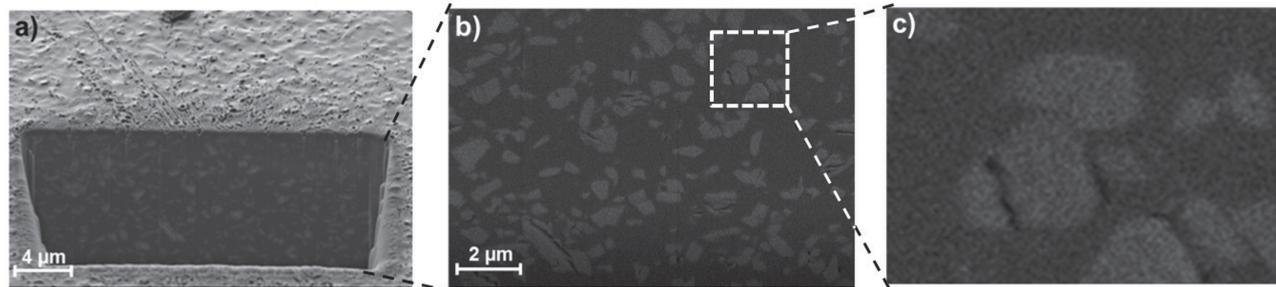


Figure 2. FIB-SEM images of the $\text{NH}_2\text{-MIL-53(Al)}/\text{PI}_{25\%}$ membrane showing a) the hole created by FIB milling of the sample specimen; b) a representative cross-section of the membrane imaged in the BSE mode; and c) enlarged view of the region framed in panel (b) showing the contrast difference between matrix, filler and inter-phase voids.

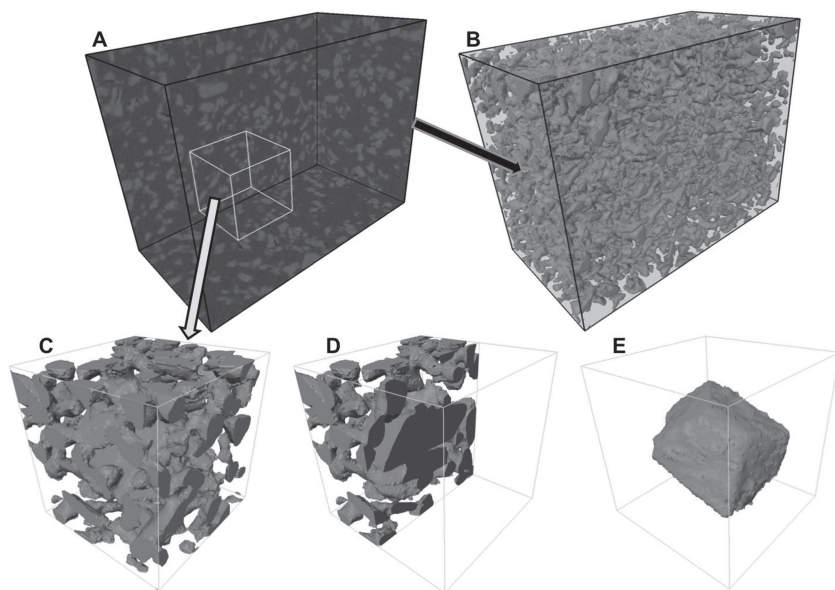


Figure 3. 3D reconstructed volume of the portion of the $\text{NH}_2\text{-MIL-53(Al)/PI}_{25\%}$ membrane studied with FIB-SEM (a); the corresponding surface-rendered view of the volume corresponding to the MOF crystals (b). Panel (c) shows a detail of the volume indicated in the yellow frame in panel (a). In panel (d), half of the material in (c) has been removed to improve visualization. And (e) shows the surface-rendered view of the volume corresponding to the voids. Box size (a,b,e): $14.3\ \mu\text{m} \times 10.7\ \mu\text{m} \times 7.5\ \mu\text{m}$.

agglomerated MOF crystals are observed darker than the polymer matrix, which shows an intermediate greyscale value. Such assignment was confirmed by performing local EDX analysis on the different observed phases (see Supporting Information Figure S5).

In addition, the BSE and in-lens imaging modes, at high-magnification, have been compared on the same selected area within the membrane cross-section (Supporting Information Figure S6). The in-lens detection mode offers less background noise and higher contrast of the embedded MOF crystals with respect to the PI matrix, as compared to the BSE mode. However, using in-lens detection, charging effects result in excessively bright regions and thereby marked changes in contrast within individual objects. Therefore, although it provides a comparatively lower contrast difference between different constituents, the BSE image mode was selected for further image analysis by segmentation due to the more homogenous greyscale level within each phase.

After alignment of the stack of SEM images, the 3D structure of the analyzed volume was reconstructed in 3D (Supporting Information Figure S7 and video) and depicted along three orthogonal cross-sections.

Segmentation of the individual phases, i.e., PI matrix, MOF filler and voids, was performed by image thresholding. **Figure 3** shows the 3D surface-rendered view of the MOF and void volumes, respectively.

Despite the relatively high filler loading, a homogeneous distribution of the MOF crystals within the polymer matrix is observed, indicating adequacy of the procedure employed to cast the MMMs. In addition, quantification of the segmented volume (showed in Supporting Information Figure S7) allows

determining the mass based MOF loading. For this calculation, volume densities of 1.66 and $1.24\ \text{g cm}^{-3}$ were assumed for the MOF and the polyimide phases, respectively. As shown in **Table 1**, the MOF weight loading determined from the image analysis is in remarkably good agreement with the bulk MOF loading (as derived from TGA), which validates the image analysis results.

Similarly, the volume corresponding to the voids between filler and matrix was segmented as depicted in **Figure 3e**. The volume fraction of voids determined by image analysis amounted 0.11% (**Table 1**). This result evidences the excellent match between the filler crystals and the polymeric matrix. Such a good contact might be related to the interaction between the amino groups of the MOF crystals with the amide groups of the polymer chains.^[22] DRIFT spectroscopy provides additional evidence for these interactions (Supporting Information Figure S8).

2.3. Gas Separation Performance

2.3.1. Transitory and Steady States

The performance of selected MMMs has been evaluated by long-term gas permeation experiments, studying the evolution of the CO_2 permeability and the separation factor within the first ca. 50 h of operation (Supporting Information Figure S9).

During the first few hours of operation the CO_2 permeability increases circa threefold, while the separation factor decreases notably. Such transition period is likely related to the accumulation of CO_2 in the membrane and the aging of the polymer. In addition, it does not result in permanent structural modifications in the membranes as the same transient period was observed for separation runs carried out with membranes previously operated for 50 h followed by flushing with He and exposure to ambient conditions for 12 h. A steady state is reached for longer run-times, where the separation performance does not change appreciably in the timescale studied. Notably, while transient periods longer than 8 h are registered for MMMs casted in Petri dish, the steady state performance is reached in a shorter period (<6 h) for thinner membranes casted with the doctor blade method. Although generally overlooked, this transient behavior must be considered to ensure comparison

Table 1. Volume and mass fraction of the different phases in the $\text{NH}_2\text{-MIL-53(Al)/PI}_{25\%}$ membrane as derived from the image analysis of the reconstructed FIB-SEM tomogram.

Material	Volume fraction [%v/v]	Mass fraction [wt%]
MOF	19.5	24.5
PI matrix	80.4	74.5
Voids	0.11	—

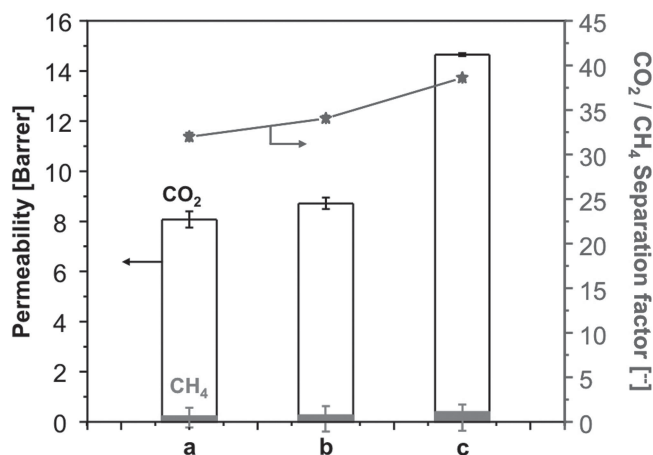


Figure 4. CO₂/CH₄ separation performance of mixed matrix membranes containing a 25 wt% MOF loading and a) casted in Petri dish and dried at 273 K; b) dried at 298 K; and c) cast using doctor blade system and dried at 298 K. Operation conditions: gas feedstock mixture of CO₂:CH₄ = 1:1, $T = 308$ K, $\Delta P = 3$ bar. Error bars correspond to the standard deviation.

of steady gas separation performances. All separation results discussed hereafter were determined after at least 10 h of operation.

2.3.2. Influence of the Membrane Structural Parameters

2.3.2.1. Influence of the MOF Framework Configuration: As discussed in Section 3.2.1., the rate of solvent removal from the just-cast membranes is determinant for the final structure of the MOF filler. Faster solvent removal leads to a higher percentage of the MOF filler in its narrow pore configuration. This might have implications for the gas separation performance, given that the framework flexibility of the NH₂-MIL-53(Al) MOF has proven to be essential for the selective separation of CO₂.^[18] **Figure 4** summarizes the separation performance of MMMs containing a 25 wt% MOF loading differing in their thickness and the drying temperature applied after casting.

After casting, increasing the drying temperature during the natural evaporation step from 273 to 298 K results in an increment in both the CO₂ permeability and the separation factor. Further enhancement in both separation parameters takes place when the thickness of the membrane is reduced by using the doctor blade casting system. Notably, this trend matches with the increase in the relative proportion of the np MOF configuration in the membranes, as earlier discussed on the basis of XRD results (vide supra). These results suggest the key role of framework configuration for the gas separation performance and the fact that polymer penetration into the MOF pores is detrimental for MMM performance. Remarkably, the final configuration of the MOF filler in the membrane can be adjusted to some extent by controlling the membrane casting conditions. XRD analysis of selected membranes after operation for 10 h revealed no noticeable modification of the MOF configuration during the gas separation experiments, not even under the highest applied trans-membrane pressure difference of 12 bar. Unlike for the bare MOF crystals, these results suggest the rigidity of the MOF structure when embedded in the polymer

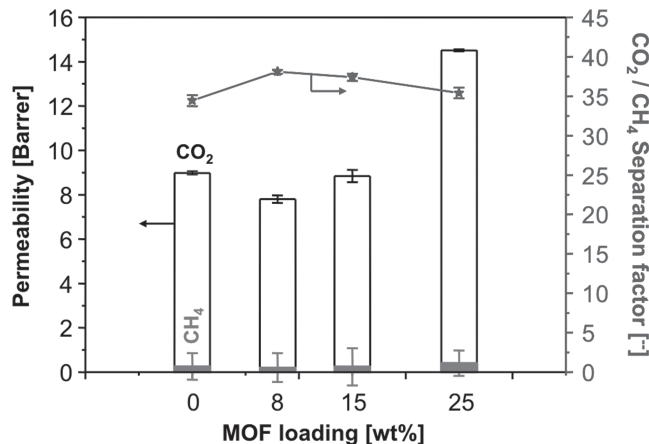


Figure 5. CO₂/CH₄ separation performance of NH₂-MIL-53(Al)/PI membranes, cast by the doctor blade system and dried at 298 K under natural convection conditions, as a function of the MOF loading. Operation conditions: gas feedstock mixture of CO₂:CH₄ = 1:1, $T = 308$ K, $\Delta P = 3$ bar. Error bars correspond to the standard deviation.

matrix. Thinner membranes casted with doctor blade and dried at 298 K offered the best results and were used to elucidate the influence of the MOF loading and the operation conditions on the gas separation performance.

2.3.2.2. Influence of MOF Loading: **Figure 5** depicts the evolution of the CO₂ permeability and the separation factor with the weight loading of MOF in the membrane. Upon MOF incorporation, only a marginal increase is achieved in the separation factor with respect to the membrane based on the neat polymer. This result is in good agreement with previous reports showing minor improvements over the already outstanding separation factor offered by PI MATRIMID upon incorporation of different filler materials.^[23] In addition, for a relatively low MOF loading of 8 wt%, a lower CO₂ permeability is observed than for the pure polymer. However, CO₂ permeability increases upon further increasing the MOF loading in the MMMs. The membrane with a 25 wt% MOF loading displays a 50% increment in the CO₂ permeability with respect to the MOF-free counterpart, while, remarkably, retaining the separation selectivity. It is therefore evident that a relatively high filler loading is required in order to benefit from the incorporation of MOF crystals in the polymeric matrix. Unfortunately, MOF loadings beyond 25 wt% resulted in MMMs with insufficient mechanical stability, hampering a stable operation in the gas separation experiments under the applied conditions.

2.3.2.3. Influence of the Trans-Membrane Pressure Difference: The influence of the pressure difference over the membrane (ΔP) on the gas separation performance was studied for NH₂-MIL-53(Al)/PI₂₅. The range of ΔP studied lies below the onset of plasticization, which for PI takes place above 12 bar of CO₂ at 295 K.^[24] **Figure 6** compares the performance of this membrane at increasing ΔP with that of the neat polymer membrane. For the MOF-free membrane, the CO₂ permeability and the separation factor drop with 17% and 57%, respectively, upon increasing ΔP from 3 to 9 bar. Further increase of ΔP to 12 bar led to structural damage due to insufficient mechanical stability of the polymeric membrane. On the contrary, incorporation of

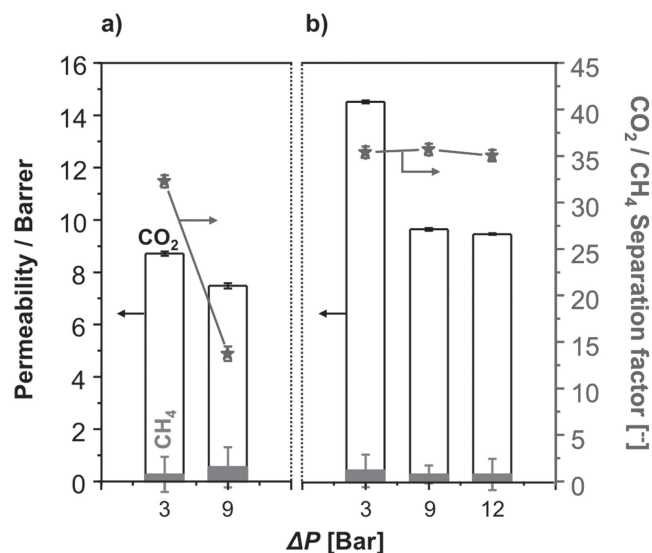


Figure 6. CO_2/CH_4 separation performance of neat PI membrane (a) and $\text{NH}_2\text{-MIL-53(Al)-25\%}$ membrane (b) as a function of the trans-membrane pressure difference. Operation conditions: gas feedstock mixture of $\text{CO}_2:\text{CH}_4 = 1:1$, $T = 308$ K. Error bars correspond to the standard deviation.

the MOF filler increases the mechanical stability of the membrane, enabling operation with a ΔP of up to 12 bar. Even though an increment in ΔP results in a decrease in the CO_2 permeability, the flux still increases (it has to be considered that permeability is already corrected by ΔP), while the presence of the MOF filler affords a remarkable insensitivity of the separation factor with ΔP in the range of 3–12 bar.

2.3.2.4. Influence of the Operation Temperature: The impact of the operation temperature on the separation performance was assessed for a membrane based on the neat PI and a membrane incorporating 25 wt% filler. As summarized in **Figure 7**, decreasing the operation temperature from 308 to 273 K results in up to a threefold increment in the separation factor for both the neat polymer membrane and a mixed matrix membrane with 25 wt% MOF loading. This enhancement in separation factor, however, is at the expense of the permeability of both gases. At 273 K, the methane concentration in the permeate fell below the detection limit. The membrane with MOF filler shows a larger decrease in CO_2 permeability upon decreasing the operation temperature. We attribute this stronger temperature sensitivity of the MOF containing membrane to the higher heat of adsorption of CO_2 in $\text{NH}_2\text{-MIL-53(Al)}$ (40 kJ mol^{-1})^[25] than in the PI matrix (10 kJ mol^{-1}).^[25] Such strong difference in ΔH_{ads} results in a much higher CO_2 loading in the MOF phase and in slower diffusion.

3. Conclusions

In this work we have studied in detail the influence of preparation conditions and internal structure of mixed matrix membranes based on the flexible filler $\text{NH}_2\text{-MIL-53(Al)}$ MOF on the separation performance. Using this functionalized filler, it is possible to successfully prepare MMMs with MOF loadings

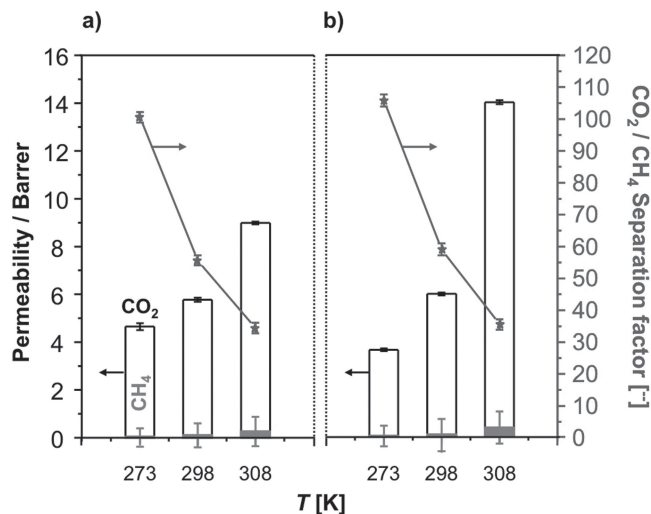


Figure 7. CO_2/CH_4 separation performance of neat PI membrane (a) and $\text{NH}_2\text{-MIL-53(Al)-25\%}$ membrane (b) as a function of the operation temperature. The membranes were casted using Doctor Blade system and dried at 298 K under natural convection conditions. Operation conditions: gas feedstock mixture of $\text{CO}_2:\text{CH}_4 = 1:1$, $\Delta P = 3$ bar. Error bars correspond to the standard deviation.

as high as 25 wt%. Casting conditions determine the performance of the membrane, in particular when casting favours the narrow pore MOF configuration, these membranes show promising performance in the separation of CO_2/CH_4 mixtures as compared to neat polymer counterparts, such as up to 70% enhancement in CO_2 permeability combined with a slightly better separation factor and improved mechanical stability. While CO_2 permeability and gas separation factor decrease upon increasing the trans-membrane pressure difference for neat PI membranes, the incorporation of the MOF filler helps reducing the dependence of the separation performance on the pressure difference. In addition, the gas separation factor of the mixed matrix membranes can be significantly enhanced upon decreasing the operation temperature from 308 K to 273 K, at the expenses of the gas permeabilities. Most notably, our study introduces tomographic FIB-SEM as a powerful technique to assess the spatial distribution of the MOF filler crystals, the polymer and the void space in the membrane in 3D. When combined with image analysis, this method provides a mean to quantify the filler-matrix contact, an essential feature for the performance of MMMs, that has remained notoriously difficult to assess thus far. This represents a significant step forward with respect to the classical 2D, SEM characterization of membrane cross-sections, generally after rough cryo-fracturing. Such information is envisaged particularly significant to address the impact of the MOF surface functionalization on the filler-matrix contact and to unravel the potential structural modifications undergone by the membranes during their operation. By providing precise and quantitative insight into key structural features at the nanoscale range, our approach provides feedback to the membrane casting process and therefore it represents an important advancement towards the rational design of mixed matrix membranes with enhanced structural features and separation performance.

4. Experimental Section

Synthesis of NH₂-MIL-53 (Al) MOF: NH₂-MIL-53 (Al) nanocrystals were synthesized by means of a conventional hydrothermal treatment as described elsewhere.^[14] 1.97 g of AlCl₃·6H₂O (Sigma Aldrich, 99%, 1.97 g) and 1.5 g of 2-amino terephthalic acid (Sigma Aldrich, 99%, 1.5 g), 18 mL of deionized water and 2 mL of N,N-dimethylformamide (DMF, Sigma Aldrich, >99.9%) were mixed in a Teflon-lined autoclave. The synthesis mixture was then treated at 423 K for 5 h in an oven under static conditions. The resulting powder was filtered under vacuum and washed with acetone. To efficiently eliminate remaining linker occluded in the MOF pores, the solid was consecutively re-suspended in DMF and methanol and treated at 423 K and 343 K overnight, respectively. Finally, the powder was filtered, thoroughly washed with acetone and dried at 393 K.

Preparation of Mixed Matrix Membranes: Polyimide (PI) Matrimid 5218 (kindly supplied by Huntsman Advanced Materials) was degassed at 453 K overnight under vacuum to remove the adsorbed water. To prepare the MMMs, the required amount of MOF to achieve a given weight loading (up to 25 wt%) was dispersed in 3.6 mL of chloroform under sonication for 30 min. Then 0.4 g of polymer were added to this suspension and stirred for 24 h, leading to a viscous solution. A weight proportion solvent/(filler+polymer) of 90/10 was used in all cases. For comparison purposes, a membrane based on the neat polymer was prepared following an identical procedure, but without MOF incorporation.

Before membrane casting, the mother suspension was submitted to three cycles of sonication (15 min) in order to ensure a good dispersion of the MOF crystals. Subsequently, the homogeneous suspension was poured on a flat glass surface, either a Petri dish or a Doctor Blade system and then left overnight covered by a box (30.5 length × 15.5 height × 23.0 width) cm to slow down the natural evaporation of solvent under ambient conditions at either 298 K or 273 K, followed by further degassing in a vacuum oven at 453 K overnight. This temperature is below the glass transition temperature (*T_g*) of the polymer (590 K) to prevent the transition into a rubbery-state.^[19] The thickness of the resulting membranes was evaluated using a digital micrometer (Mitutoyo, Quickmike Series). The use of the doctor blade allowed thinner membranes (35–75 μm thickness) than casting in the Petri dish (75–105 μm). Membranes were denoted as NH₂-MIL-53(Al)/PI-*x*%, where *x* corresponds to the MOF weight loading.

Characterization Methods: XRD patterns of the as-prepared MOF powder and the membranes were recorded in a Bruker D8 Advance diffractometer using Co-K_α radiation ($\lambda = 1.78897\text{\AA}$). The 2θ range of 5–50° was scanned using a step size of 0.02° and a scan speed of 0.2 s per step.

The texture of the as-synthesized NH₂-MIL-53(Al) MOF was assessed by means of CO₂ adsorption. The adsorption isotherm was measured in a Tristar II 3020 Micromeritics spectrometer at 273 K employing high-purity CO₂ (Linde, 99.995%). Prior to the measurements, the adsorbent was outgassed at 200 °C under vacuum for 16 h. Total micropore volume was evaluated at a relative pressure (*P/P₀*) of 0.005.

SEM was used to study the crystal size and morphology of the MOF sample. SEM micrographs were acquired in a Philips XL20 (15–30 kV) microscope after sputtering the sample with a conductive Au layer.

Diffuse-reflectance infrared fourier-transform (DRIFT) spectra of pristine MOF were recorded in a Bruker IFS66 spectrometer with CaF₂ windows using a 633 nm laser. The spectra were collected after accumulation of 264 scans with a resolution of 4 cm⁻¹. Potassium bromide was used as a background. Transmission FTIR spectra of polymer and mixed matrix membranes were recorded in a Thermo Nicolet Nexus spectrometer, equipped with a liquid N₂-cooled MCT detector and a DRIFT high-temperature cell with CaF₂ windows. The spectra were collected after accumulation of 128 scans with a resolution of 4 cm⁻¹.

TGA was employed to determine MOF loading in the MMMs. The TGA experiments were run in a Mettler Toledo TGA/SDTA851e equipment, using air flow (60 mL min⁻¹) and a heating rate of 10 K min⁻¹ up to 1123 K. The MOF loading was derived by determining the residual mass of Al₂O₃ after complete calcination.

FIB-SEM was used to assess both the spatial distribution of the MOF filler within the polymeric matrix in the MMMs and the contact

between both phases. The sample was inserted into the SEM chamber of a Zeiss Auriga field emission microscope, equipped with secondary electrons (SE) and in-lens detectors. The specimen was sputtered with a conducting layer of Pt for 120 s. A trench was milled in the specimen using an Orsay Physics “Cobra” Ga⁺ ion FIB. Thin (ca. 50 nm) slices (25 × 15 μm²) were sequentially removed from the specimen up to a depth of 20 μm and individual SEM images of the exposed cross-sections were recorded. Energy-dispersive X-ray spectroscopy (EDX) elemental analysis was applied on selected regions of the membrane cross-section using an Oxford EDX 80 mm² detector. The stack of SEM micrographs (165 images over a depth of 8.3 μm) was aligned and the corresponding 3D volume was reconstructed using Avizo(R) Fire (VSG).

Membrane thickness (μm) was determined using a digital micrometer Mitutoyo, with an accuracy of 1 μm. The measurement was performed at least at 10 different locations within each membrane and then averaged.

Gas Permeation Experiments: Membrane areas of 4.4 cm² were cut from the casted films, placed on a macroporous support and mounted in a flange between Viton O-rings. This flange fit in a permeation module that was placed inside an oven using the permeation setup described elsewhere.^[19] An equimolar mixture of CO₂ and CH₄ (100 mL min⁻¹ total flow rate) was employed as feed. Helium (67.7 mL min⁻¹) was used as sweep gas for the permeate stream, while the trans-membrane pressure was adjusted using a backpressure controller at the retentate side. The temperature in the permeation module was varied from 308 K to 273 K. Sub-ambient temperature of 273 K was achieved by immersing the separation module in a water-ice bath. An on-line gas chromatograph equipped with a packed Carboxen 1010 PLOT (30 m × 0.32 mm) column and TCD and FID detectors was used to periodically analyze the permeate stream.

Each membrane was fabricated and measured at least 3 times to ensure the reproducibility of the results.

Gas separation performance is defined by the separation factor (α) and the gas permeabilities (*P*) of the individual components.

The permeability for the *j*-component (*P_j*) was calculated as follows (Equation 1):

$$P_j = \frac{\phi_{n,j}}{\Delta P_j} \quad (1)$$

where $\phi_{n,j}$ denotes the molar flow rate of *j*-compound, δ is the thickness of the membrane, ΔP_j is the partial pressure difference of the *j*-component across the membrane and *A* is the membrane area.

The SI unit for the permeability is mol s⁻¹ m⁻¹ Pa⁻¹. However, here gas permeabilities are reported in the widely used non-SI unit Barrer, where 1 Barrer = 3.35 10⁻¹⁶ mol m⁻¹ Pa⁻¹ s⁻¹. The separation factor or mixed gas selectivity (α) was calculated as the ratio of the permeability of the more permeable compound (CO₂) to the permeability of the less permeable compound (CH₄) (Equation 2).

$$\alpha = \frac{P_{\text{CO}_2}}{P_{\text{CH}_4}} \quad (2)$$

In all cases, gas separation performance was evaluated after ensuring steady operation (vide infra, Section 2.3.1.).

Supporting Information

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

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- [1] a) E. Favre, R. Bounaceur, D. Roizard, *J. Membr. Sci.* **2009**, 328, 11; b) S. A. Stern, B. Krishnakumar, S. G. Charati, W. S. Amato, A. A. Friedman, D. J. Fuess, *J. Membr. Sci.* **1998**, 151, 63.
- [2] B. Zornoza, J. Coronas, J. Gascon, F. Kapteijn, *Microporous Mesoporous Mater.* **2013**, 166, 67.
- [3] a) L. M. Robeson, *J. Membr. Sci.* **2008**, 320, 390; b) L. M. Robeson, *J. Membr. Sci.* **1991**, 62, 165.
- [4] a) T. Visser, N. Masetto, M. Wessling, *J. Membr. Sci.* **2007**, 306, 16; b) W. J. Koros, G. K. Fleming, *J. Membr. Sci.* **1993**, 83, 1; c) W. J. Koros, R. Mahajan, *J. Membr. Sci.* **2000**, 175, 181; d) H. Q. Lin, B. D. Freeman, *J. Mol. Struct.* **2005**, 739, 57; e) M. Ulbricht, *Polymer* **2006**, 47, 2217; f) T. Matsuura, *Synthetic membranes and membrane separation processes*, CRC Press, Boca Raton, FL **1994**.
- [5] a) C. M. Zimmerman, A. Singh, W. J. Koros, *J. Membr. Sci.* **1997**, 137, 145; b) I. F. J. Vankelecom, E. Merckx, M. Luts, J. B. Uytterhoeven, *J. Phys. Chem.* **1995**, 99, 13187.
- [6] S. Basu, A. L. Khan, A. Cano-Odena, C. Liu, I. F. J. Vankelecom, *Chem. Soc. Rev.* **2010**, 39, 750.
- [7] K. F. R. R. Zoland, *Membrane Handbook*, Van Nostrand Reinhold, New York **1992**.
- [8] P. S. Goh, A. F. Ismail, S. M. Sanip, B. C. Ng, M. Aziz, *Sep. Purif. Technol.* **2011**, 81, 243.
- [9] a) Y. Li, H. M. Guan, T. S. Chung, S. Kulprathipanja, *J. Membr. Sci.* **2006**, 275, 17; b) R. Mahajan, W. J. Koros, *Ind. Eng. Chem. Res.* **2000**, 39, 2692; c) O. G. Nik, X. Y. Chen, S. Kaliaguine, *J. Membr. Sci.* **2011**, 379, 468; d) T. W. Pechar, S. Kim, B. Vaughan, E. Marand, V. Baranauskas, J. Riffle, H. K. Jeong, M. Tsapatsis, *J. Membr. Sci.* **2006**, 277, 210.
- [10] a) T.-S. Chung, L. Y. Jiang, Y. Li, S. Kulprathipanja, *Prog. Polym. Sci.* **2007**, 32, 483; b) P. Bernardo, E. Drioli, G. Golemme, *Ind. Eng. Chem. Res.* **2009**, 48, 4638.
- [11] a) M. Anson, J. Marchese, E. Garis, N. Ochoa, C. Pagliero, *J. Membr. Sci.* **2004**, 243, 19; b) D. Vu, W. J. Koros, S. J. Miller, *J. Membr. Sci.* **2003**, 221, 233; c) D. Q. Vu, W. J. Koros, S. J. Miller, *J. Membr. Sci.* **2003**, 211, 311.
- [12] H. Yehia, T. J. Pisklak, J. P. Ferraris, K. J. Balkus, I. H. Musselman, *Abstr. Pap. Am. Chem. Soc.* **2004**, 227, U351.
- [13] T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, G. Ferey, *Chem. Eur. J.* **2004**, 10, 1373.
- [14] a) J. Gascon, U. Aktay, M. D. Hernandez-Alonso, G. P. M. van Klink, F. Kapteijn, *J. Catal.* **2009**, 261, 75; b) J. L. C. Rowsell, O. M. Yaghi, *J. Am. Chem. Soc.* **2006**, 128, 1304.
- [15] a) Z. Wang, S. M. Cohen, *Chem. Soc. Rev.* **2009**, 38, 1315; b) F. X. Llabres i Xamena, A. Abad, A. Corma, H. Garcia, *J. Catal.* **2007**, 250, 294; c) X. Zhang, F. X. Llabres i Xamena, A. Corma, *J. Catal.* **2009**, 265, 155.
- [16] a) H. Hayashi, A. P. Cote, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Nat. Mater.* **2007**, 6, 501; b) R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Science* **2008**, 319, 939.
- [17] a) S. Couck, J. F. M. Denayer, G. V. Baron, T. Remy, J. Gascon, F. Kapteijn, *J. Am. Chem. Soc.* **2009**, 131, 6326; b) P. L. Llewellyn, S. Bourrelly, C. Serre, A. Vimont, M. Daturi, L. Hamon, G. De Weireld, J.-S. Chang, D.-Y. Hong, Y. K. Hwang, S. H. Jhung, G. Ferey, *Langmuir* **2008**, 24, 7245.
- [18] S. Couck, E. Gobechiya, C. E. A. Kirschhock, P. Serra-Crespo, J. Juan-Alcaniz, A. M. Joaristi, E. Stavitski, J. Gascon, F. Kapteijn, G. V. Baron, J. F. M. Denayer, *ChemSusChem* **2012**, 5, 740.
- [19] B. Zornoza, A. Martinez-Joaristi, P. Serra-Crespo, C. Tellez, J. Coronas, J. Gascon, F. Kapteijn, *Chem. Commun.* **2011**, 47, 9522.
- [20] E. Stavitski, E. A. Pidko, S. Couck, T. Remy, E. J. M. Hensen, B. M. Weckhuysen, J. Denayer, J. Gascon, F. Kapteijn, *Langmuir* **2011**, 27, 3970.
- [21] S. Mitchell, N.-L. Michels, K. Kunze, J. Perez-Ramirez, *Nat. Chem.* **2012**, 4, 825.
- [22] R. F. Boyer, R. L. Miller, *Macromolecules* **1977**, 10, 1167.
- [23] X. Y. Chen, H. Vinh-Thang, D. Rodrigue, S. Kaliaguine, *Ind. Eng. Chem. Res.* **2012**, 51, 6895.
- [24] a) A. Bos, I. G. M. Punt, M. Wessling, H. Strathmann, *J. Membr. Sci.* **1999**, 155, 67; b) N. Du, H. B. Park, M. M. Dal-Cin, M. D. Guiver, *Energy Environ. Sci.* **2012**, 5, 7306.
- [25] W. Lu, J. P. Sculley, D. Yuan, R. Krishna, Z. Wei, H.-C. Zhou, *Angew. Chem. Int. Ed.* **2012**, 51, 7480.