

## MOFs-based hybrid matrix membranes for gas separation

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### Abstract

**This paper reviews the preparation of mixed matrix membranes (MMMs) based on metal organic backbone materials (MOFs) and their applications in gas separation. The applications in gas separation such as CO<sub>2</sub> /N<sub>2</sub> , CO<sub>2</sub> /CH<sub>4</sub> and CO<sub>2</sub> /H<sub>2</sub> are mainly presented. Some modification methods are also listed to enhance the performance of MMMs, and finally, the development of MOFs-based MMMs for gas separation is proposed.**

### Keywords

**Metal-organic skeletal material; hybrid matrix membrane; gas separation.**

### 1. Introduction

The traditional energy structure overly relies on the burning of fossil fuels such as coal, oil and natural gas, leading to a sharp increase in global CO<sub>2</sub> levels, further leading to a series of climate problems such as global warming, and in high latitudes, where temperatures are rising twice as fast as the global average<sup>[1]</sup> , reducing CO<sub>2</sub> levels has become a hot issue. The mitigation of global warming and other consequent environmental problems can be started from two aspects, on the one hand, to reduce CO<sub>2</sub> emissions and use clean energy, hydrogen energy is hailed as the ideal energy source in the 21st century due to its high calorific value and non-polluting products; on the other hand, to increase CO<sub>2</sub> consumption, of which CO<sub>2</sub> capture and storage (CCS) is one of the most promising methods. CCS mainly includes absorption, adsorption and membrane separation, of which membrane separation is the most promising method because of its low energy consumption. Among them, membrane separation is widely used because of its low energy consumption, simple process, easy operation, high separation efficiency, small footprint, no pollution and easy integration with other technologies<sup>[2]</sup> . Compared with traditional polymeric gas separation membranes, MOFs-based mixed matrix membranes (MMMs) combine the advantages of different substances and are expected to break the trade-off limit between permeability coefficient and selectivity.

### 2. Introduction of metal organic skeleton material

Metal organic backbone (MOFs) materials are characterized by high porosity and specific surface area, unique structural transitions, thermally activated pore expansion and gas molecule adsorption shrinkage, and a rich variety of constituent units with different connections that can provide a higher degree of structural and functional designability<sup>[3]</sup> . MOFs are thought to provide mixed matrix membranes (MMMs) with high permeability, good interfacial compatibility, and thus improved gas selectivity. Typical MOFs materials include several families of IRMOFs, ZIFs, MIL, and UIO .<sup>[4]</sup>

### 3. Separation mechanism

Gases are separated in MMMs by two mechanisms: dissolved diffusion mechanism and facilitated transfer mechanism<sup>[5]</sup> .

### 3.1. Dissolution diffusion mechanism

The dissolution-diffusion mechanism relies on the difference in kinetic diameter and condensation properties between gas molecules, while the facilitated transfer mechanism often occurs in separation membranes where  $\text{CO}_2$  is the preferred permeable component, and relies on the difference in gas reactivity by introducing sites within the membrane that can interact with  $\text{CO}_2$  to facilitate the transfer of  $\text{CO}_2$ .

The dissolution-diffusion mechanism is usually divided into 3 steps: (i) the gas dissolves on the surface of the upstream side of the membrane, (ii) the gas diffuses from the upstream side of the membrane to the downstream side of the membrane, and (iii) the gas resolves and desorbs from the downstream side of the membrane, thus completing the transfer in the membrane, as shown in Figure 1. In MMMs, two important criteria for evaluating membrane performance are permeability coefficient and selectivity, and the dissolution process and diffusion process determine the separation performance of the membrane. Among them, the solubility and diffusivity affect the permeability coefficient, and the degree of variability between gases affects the selectivity, which, of course, is influenced by both the nature of the gas molecules themselves and the nature of the membrane itself. In other words, when the external environment and the membrane state remain constant, the separation system is certain and the separation performance of the membrane will be certain, so the permeability coefficient of the membrane reflects the intrinsic performance of the membrane material.

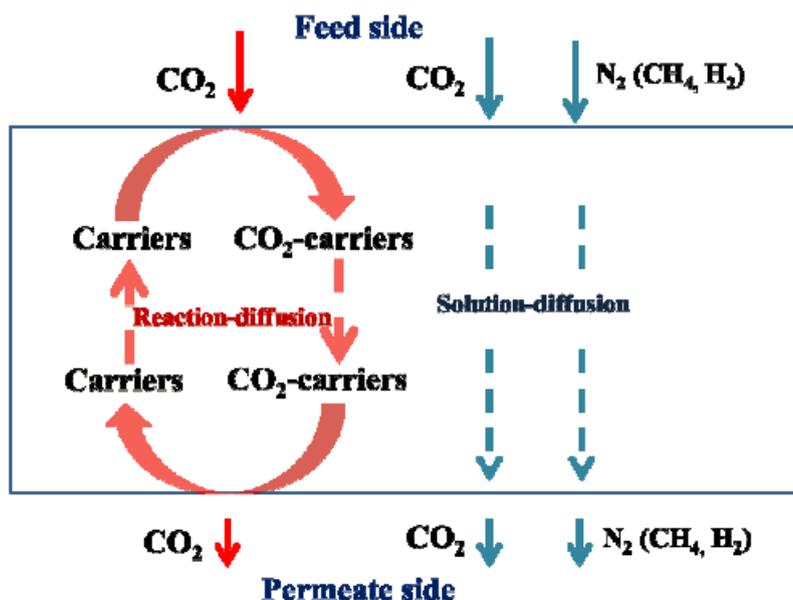


Figure 1 Dissolution diffusion mechanism[5]

### 3.2. Facilitating delivery mechanisms

The facilitated transfer mechanism usually occurs in the facilitated transfer membrane with  $\text{CO}_2$  as the preferred permeable component, and there are sites within the membrane that can react with  $\text{CO}_2$ . During the facilitated transfer process,  $\text{CO}_2$  reacts with the sites within the membrane on the upstream side to produce intermediates, which diffuse within the membrane driven by the concentration difference, and finally resolve and desorb on the downstream side of the membrane to complete the transfer, as shown in Figure 2<sup>[6-7]</sup>. The sites within the membrane that can react with  $\text{CO}_2$  are called carriers, and common carriers of  $\text{CO}_2$  are amine groups, carboxyl groups, etc. In the dissolution-diffusion mechanism, the pressure difference between the front and back of the membrane is the driving force, and as the pressure difference increases, the volumetric flow rate increases, but the permeability coefficient remains the same; the facilitated transfer mechanism uses the difference in reactivity between  $\text{CO}_2$  and other gases

for separation, and the number of carriers inside the membrane determines the volumetric flow rate. When the number of carriers is uniform, increasing the driving force (component pressure difference) does not result in an increase in the bulk flow rate after the carriers are fully utilized, and thus the permeability coefficient of the membrane is inversely proportional to the pressure difference; increasing the pressure difference causes a decrease in the membrane permeability coefficient, i.e., carrier saturation. In fact, for facilitated transfer membranes, the matrix is still a polymer and the dissolution-diffusion mechanism and facilitated transfer mechanism usually coexist in the membrane during separation<sup>[8]</sup>.

#### 4. Preparation method of MMMs

MOFs hybrid matrix membrane preparation is mainly composed of dispersed phase MOFs particles combined with continuous phase polymer matrix. MOFs combined with polymer can interact with polymer matrix to avoid the formation of significant defective pores.

One of the common methods to prepare MOFs hybrid substrate films is the co-blending method, as shown in Figure 2. Meng et al.<sup>[9]</sup> prepared hybrid substrate films by homogeneously mixing BUT-8 with polyethyleneimine solution and drop coating on HPAN substrates using a rotational coating method, and the finished products were produced with high MOFs loading (50% mass fraction) and exhibited fairly high permeability ((396~683 L/(m<sup>2</sup> · h · MPa)). However, the preparation of hybrid matrix membranes by this method suffers from agglomeration of MOFs particles, high raw material consumption, and severe contamination with organic solvents<sup>[10]</sup>.

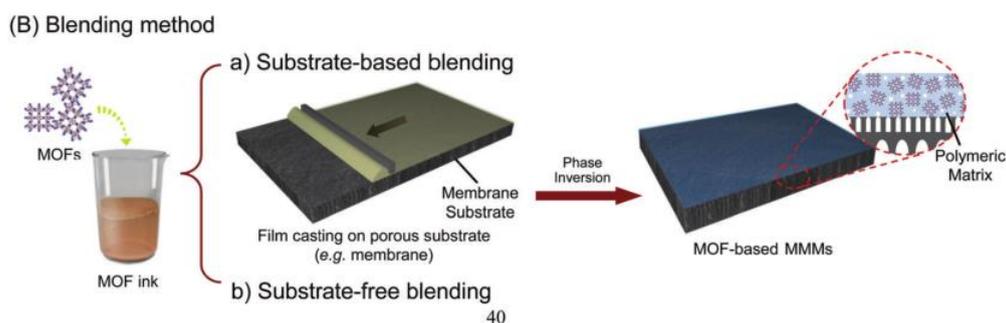


Fig. 2 Co-mingling method<sup>[11]</sup>

A new co-hybrid method is now proposed in combination with self-assembly techniques. The substrate is a hydrolyzed polymer film and the MOFs precursors are immobilized by electrostatic attraction; after contacting a mixture of organic ligands and polymers, the MOFs are formed in situ in the polymer matrix on the surface of the modified substrate. This method is accomplished by integrating the preparation of both MOFs and hybrid matrix membranes into a multicomponent system, resulting in improved interfacial compatibility between MOFs and polymer matrix. Yang et al.<sup>[12]</sup> first hydrolyzed polyacrylonitrile to prepare negatively charged ultrafiltration membrane substrates, followed by electrostatic attraction to deposit Zn<sup>2+</sup> and positively charged polyethyleneimine on the substrates to produce ZIF-8 in the polyethyleneimine layer to prepare thin and homogeneous mixed matrix membrane, which reduces particle agglomeration to some extent and particles are uniformly distributed in the polymer matrix<sup>[10]</sup>.

Compared with pure MOFs membranes, hybrid matrix membranes combine the excellent separation performance of MOFs particles with porosity and the advantages of polymer matrix such as low price and easy preparation, and the encapsulated MOFs particles are more stable than pure MOFs for long-term stable operation

## 5. Application

The application of MOFs-based hybrid matrix membranes for gas separation can be divided into CO<sub>2</sub> and N<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub>, and CO<sub>2</sub> and H<sub>2</sub> depending on the gas to be separated, with CO<sub>2</sub> and N<sub>2</sub> being the more common applications.

### 5.1. Separation of CO<sub>2</sub> and N<sub>2</sub>

CO<sub>2</sub> capture and storage (CCS) technology can effectively reduce atmospheric CO<sub>2</sub> levels, while CO<sub>2</sub> is also an important carbon resource that can be used to make chemical products such as urea, soda ash, and dry ice.

Open metal sites can serve as preferential adsorption sites for CO<sub>2</sub> [15-16]. MOFs with open metal sites drive selective sequestration of CO<sub>2</sub> and separation from other gas molecules (e.g., N<sub>2</sub>) such as HKUST-1 and MOF-74 (CPO-27)<sup>[13-14]</sup> through electrostatic interactions with CO<sub>2</sub> molecules. Among them, Mg-MOF-74 exhibits the highest CO<sub>2</sub> capacity in the MOF-74 series. Jung et al. suggested that the binding affinity of MOF-74 for CO<sub>2</sub> can be adjusted by metal substitution, and they calculated by using density functional theory (DFT) that for V and Ti-MOF-74 the binding energy to CO<sub>2</sub> is 6-9 kJ/mol higher compared to Mg-MOF-74 -9 kJ/mol<sup>[15]</sup>.

Organic ligands with nucleophilic groups (e.g., amine groups, hydroxyl groups, etc.) can provide sites for CO<sub>2</sub> adsorption via Lewis acid-base interactions and can exhibit successful CO<sub>2</sub> adsorption behavior both under dry and wet conditions. This is a major advantage over MOFs with only open metal sites for CO<sub>2</sub> adsorption, since open metal sites can be occupied by water molecules resulting in reduced adsorption performance. Also these organic groups can form hydrogen bonds, van der Waals forces and other interactions with the polymer matrix, for example, amino groups can construct hydrogen bonds between Pebax, PSF<sup>[16-17]</sup>, and improve the interfacial compatibility of the mixed matrix membrane. Modification of UiO-66-NH<sub>2</sub> with phenylacetyl, the modified UiO-66-NH<sub>2</sub> will have  $\pi$ - $\pi$  stacking interaction with the polymer at the same time the amino group of UiO-66-NH<sub>2</sub> will have hydrogen bonding interaction with the amide group of Matrimid as shown in Figure 3. Guo Ruiqian et al.<sup>[18]</sup> added NH<sub>2</sub>-mil-53 with 10% mass fraction to brominated PESF, and the results showed that the permeability coefficient reached 113.0 bar, the CO<sub>2</sub>/N<sub>2</sub> selectivity was 29.2, and the CO<sub>2</sub> separation was good. The pore size and shape of MOFs play an important role in CO<sub>2</sub> adsorption, and their microporous structure can well adsorb CO<sub>2</sub>. ZIF as a typical cage-like 3D framework of MOFs are an ideal trap for CO<sub>2</sub>. Yang et al. tailored the effective cage size of ZIF-8 to be between CO<sub>2</sub> and N<sub>2</sub> by confining the ionic liquid to the cage of ZIF-8, resulting in a significant increase in CO<sub>2</sub>/N<sub>2</sub> adsorption selectivity from 19% for ZIF-8 to 100% for ZIF-8 after ionic liquid modification with better separation<sup>[19]</sup>. As shown in Figure 4.

### 5.2. Separation of CO<sub>2</sub> and CH<sub>4</sub>

Natural gas has an important position in the current energy transition in China, and it is used in large quantities as a clean energy source. However, natural gas is often mixed with CO<sub>2</sub> impurities, which inevitably reduces the energy density of natural gas and even causes corrosion of pipelines in wet conditions. CO<sub>2</sub> needs to be removed before transmission, so the industrial treatment of natural gas has been faced with the challenge of how to separate CO<sub>2</sub> and CH<sub>4</sub>.

Waqas et al.<sup>[21]</sup> made hybrid matrix membranes by adding UiO-66 (30%) to the matrix membrane as PI, which showed a significant improvement in the permeability of CO<sub>2</sub> and selectivity of CO<sub>2</sub>/CH<sub>4</sub> over the pure PI membrane, with CO<sub>2</sub> permeability of 19.4 bar, an increase of 50%, and CO<sub>2</sub>/CH<sub>4</sub> selectivity of 47.7, an increase of 540%<sup>[22]</sup>. However, mixed matrix membranes also have problems with interfacial defects and often require modification of MOFs. In the separation of CH<sub>4</sub> can be analogous to the separation of N<sub>2</sub> by introducing

organic functional groups such as amino, nitro, and hydroxyl groups to enhance the affinity of the two phases while improving the preferential selectivity for CO<sub>2</sub> adsorption<sup>[23]</sup>. Khdayyer et al.<sup>[24]</sup> made hybrid matrix membranes by embedding three MOFs, UiO-66, UiO-66-NH<sub>2</sub>, and UiO-66-(COOH)<sub>2</sub> into PIM-1 and comparing the three membranes for CO<sub>2</sub>/CH<sub>4</sub> separation. It was concluded that UiO-66-NH<sub>2</sub> kept the selectivity constant while improving the permeability, and the permeability coefficients of both UiO-66 and UiO-66-(COOH)<sub>2</sub> increased with the number of MOFs loaded and the gas selectivity decreased only slightly. It has also been pointed out that achieving two-phase interfacial crosslinking can also improve the two-phase interfacial compatibility<sup>[23]</sup>. Shao Lu's group at Harbin Institute of Technology<sup>[25]</sup> introduced an isopropene group on the surface of UiO-66-NH<sub>2</sub> and cross-linked the group with poly(ethylene oxide) capped by methyl acrylate under UV irradiation, resulting in improved interfacial morphology.

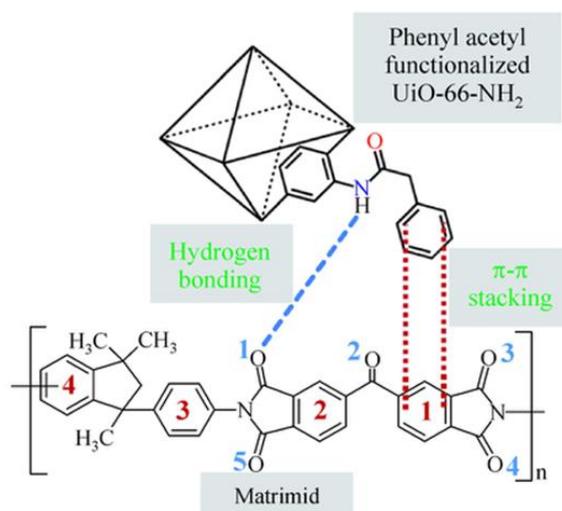


Fig. 3 Good interaction between phenylacetyl-modified UiO-66-NH<sub>2</sub> and polymers<sup>[19]</sup>

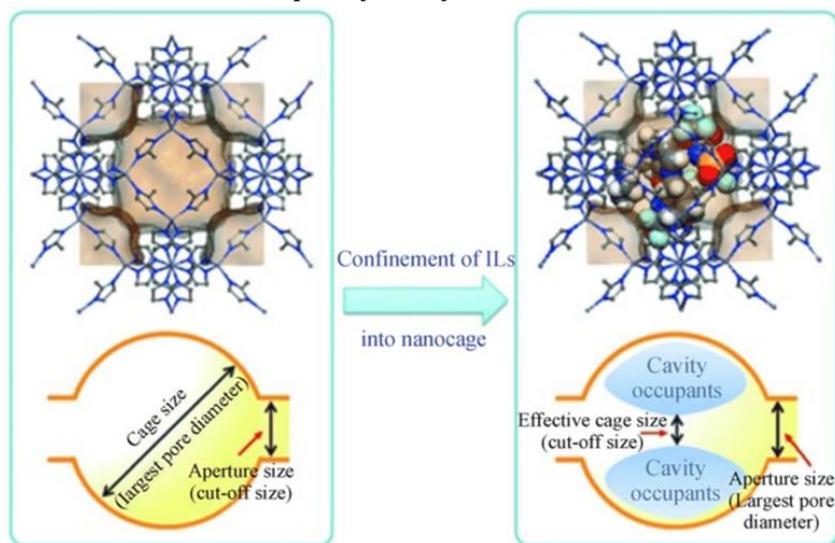


Figure 4 Ionic liquid modified ZIF-8<sup>[20]</sup>

### 5.3. Separation of CO<sub>2</sub> and H<sub>2</sub>

H<sub>2</sub> is a green energy source and is expected to replace fossil fuels as the most promising energy source in the future. It can be used as a chemical feedstock to synthesize ammonia and hydrochloric acid, as well as a substitute for carbon in metal smelting, and liquid hydrogen is

also an excellent rocket launch fuel. However, the separation of H<sub>2</sub> severely limits its commercial application. MOFs mixed matrix membrane as an efficient and clean means can effectively achieve the separation of H<sub>2</sub>.

Sánchez-Laínez et al.<sup>[26]</sup> prepared a hybrid matrix membrane for the purification of H<sub>2</sub> by mixing ZIF-8 nanoparticles of different sizes as fillers into polybenzimidazole (PBI). It was found that the H<sub>2</sub> /CO<sub>2</sub> separation factor of the hybrid matrix membrane was 7.2 at 1.33 MPa and 3.5 °C, and the permeability at 180 °C exceeded the Robeson upper limit, which has great application prospects. Lujie Cao<sup>[27]</sup> et al. prepared a thin MMM with a thickness of about 10 μm by mixing the aminated MOFs (CAU-1-NH<sub>2</sub>) into polymethyl methacrylate (PMMA), and the 3D framework of CAU-1-NH<sub>2</sub> has micropores with a pore size of 0.3-0.4 nm, which can separate the small gas molecule H<sub>2</sub> from the large gas molecule CO<sub>2</sub>. Meanwhile, the amino group of CAU-1-NH<sub>2</sub> can form a large number of hydrogen bonds with the PMMA carbonyl group, which is conducive to the interfacial compatibility between MOFs and polymers.

## 6. Outlook

MOFs-based hybrid matrix membranes have made great progress as a promising technology for CO<sub>2</sub> separation and purification. However, there are still some problems to be solved in its preparation and application. At present, there are mainly the following problems: (1) the defects of MOFs membranes and their mechanical properties deteriorate due to the compatibility problem between MOFs and polymers and the easy agglomeration of MOFs themselves, which are challenging in the preparation of large-area industrial MOFs membranes; (2) because MOFs-based MMMs are connected by metal ions or metal clusters with organic ligands through coordination bonding, MOFs have poor water stability and short service life of MMMs; (3) the high cost of MOFs materials makes it difficult to achieve industrial-scale applications. Although, membrane technology consumes less energy than MOFs adsorbent, MOFs adsorbent can fill the gap between laboratory research and industrial practice in a short period of time. Meanwhile, the problems about MMMs will eventually be solved with the depth of research, and the application of MMMs in gas separation will be more extensive.

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