

효과적인 CO₂ 분리를 위한 혼합 기질 분리막 충전 소재로서의 2차원 나노물질

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Two-Dimensional Nanomaterials Used as Fillers in Mixed-Matrix Membranes for Effective CO₂ Separation

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초 록

최근, 기존 분리막의 성능을 향상시켜 CO₂ 분리를 효율적으로 수행하기 위한 중요한 연구가 진행되고 있다. 이는 탄소 포집 공정에서의 활용을 확대하는 것을 목표로 하고 있다. 분리막 기술은 비용 및 에너지 효율성, 연속 운전, 작은 공정 크기 등의 장점으로 인해 탄소제로 이슈에 대처하는 유망한 탄소 포집 기술로 부상하고 있다. 연구된 여러 종류의 분리막 중 혼합기질막(mixed-matrix membrane, MMM)이 전반적인 가스 분리 공정의 효율을 향상시킬 수 있는 전통적인 분리막의 대안으로 제안되었다. 2D 나노소재는 쉬운 개질과 기능화, 다른 재료와의 결합 등 특징적인 성질로 인해 다양한 일반적인 2D 나노소재들이 가스 분리를 위한 효율적인 MMMs 제작에 사용되고 있다. 본 논문은 2D 나노소재를 사용한 MMMs 분야의 최근 발전을 검토하였다. 또한, CO₂ 분리 및 포집을 위한 2D 나노소재 기반 분리막의 현재 도전과 전망을 논의하였다.

Abstract

In recent years, significant research has been conducted to enhance the performance of existing membranes for efficient CO₂ capture, aiming to expand their application in carbon capture processes. Membrane technology has emerged as a promising carbon capture approach to addressing the net-zero challenge due to its cost and energy efficiency, continuous operation, and compact process size. Among the various types of membranes studied, mixed-matrix membranes (MMMs) have been proposed as an alternative to conventional membranes to enhance the efficiency of gas separation processes. Various common 2D nanomaterials, characterized by their ease of modification, functionalization, and compatibility with other materials, have been used to create efficient MMMs for gas separation. This article comprehensively reviews the recent developments in MMMs using 2D nanomaterials. It also discusses the current challenges and prospects of 2D nanomaterial-based membranes for CO₂ separation and capture.

Keywords: Mixed-matrix membrane, 2D nanomaterial, CO₂ capture, Inorganic filler, Gas separation

1. Introduction

Carbon dioxide (CO₂) is the primary component of greenhouse gases released into the atmosphere and is a critical global issue in modern times. The accumulation of CO₂ in the atmosphere contributes to global warming by trapping heat that would otherwise escape from the

Earth's surface[1]. This phenomenon has led to rising sea levels and intensified global warming, posing major concerns for climate change, including significant threats to global food security, human health, and economies[2-5]. Carbon dioxide is the primary driver of global warming due to its environmental accumulation[6]. According to the International Energy Agency 2023 report, global CO₂ emissions have reached an unprecedented 37.4 billion metric tons. The National Oceanic and Atmospheric Administration of the United States and the World Meteorological Organization have identified 2023 as the warmest year since global records began in 1850. Carbon capture and storage technologies have gained prominence, which efficiently reduce atmospheric CO₂ levels and substantially mitigate the greenhouse effect [4]. Various technologies are currently employed for CO₂ removal, in-

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Table 1. Comparison of MMMs with Other Conventional Membranes[54]

Properties membranes	Chemical and thermal stability	Synthesis and processability	Fabrication cost	Plasticization effect	Resistant to pressure	Mechanical strength	Gas separation performance
MMMs	High	Easy	Moderate	Partially control	High	Excellent	Above the Robeson's upper bound
Polymeric membranes	Moderate	Easy	Low	Susceptible	Moderate	Good	Below the Robeson's upper bound
Inorganic membranes	High	Difficult	High	No effect	High	Poor	Above the Robeson's upper bound

cluding oxyfuel combustion and pre- and post-combustion processes [7]. Among the prevalent CO₂ capture technologies are cryogenic distillation, chemical absorption, chemisorption, condensation, pressure and temperature swing adsorption, and membrane separation[8-14].

Among those technologies, membrane-based CO₂ capture offers cost-effectiveness, energy efficiency, continuous operation, compact size, and ease of process fabrication[15-18]. Currently, inorganic and polymeric membranes are employed for membrane-based gas separation processes[19-33]. Inorganic membranes are noted for their thermal and chemical stability, high permeability, and long life. However, their widespread use is limited by challenges such as complex membrane fabrication, higher costs, and processing difficulties[34]. On the other hand, although polymeric membranes are cost-effective, they lack sufficient mechanical and chemical durability for practical applications. Additionally, they are constrained by Robeson's upper bound, which limits the selectivity and permeability of the materials[34].

Consequently, researchers continue to explore the development of novel membranes for gas separation, aiming to overcome the limitations of inorganic and polymeric membranes. There has been a recent increase in interest in relatively facile novel membrane fabrication strategies that incorporate nanomaterials with excellent physicochemical properties into polymer matrices[35]. This results in mixed-matrix membranes (MMMs), which are heterogeneous membranes formed by interacting with polymer matrices and inorganic fillers. The excellent physicochemical properties of nanofillers and the interaction between inorganic nanofillers and polymers prevent the clumping of particles, clogging of pores, the formation of void spaces, and the hardening of the polymer during the manufacturing of MMMs, thereby enhancing gas separation efficiency[36]. As shown in Table 1, MMMs demonstrate outstanding characteristics compared to conventional membranes.

Advancements in nanotechnology have spurred significant interest and rapid development in MMMs. Based on the size of filler materials, they can be categorized into several types: 0D, 1D, 2D, and 3D materials, etc.[37]. Among these nanofillers, 2D materials have been extensively employed to develop high-performance MMMs thanks to their high aspect ratio, distinctive sub-nanoscale thickness, and slight lateral dimensions.[38]. A diverse range of 2D materials, such as graphene and its derivatives (e.g., graphene oxide (GO)), MXene, metal-organic frameworks (MOFs), graphitic carbon nitride (g-C₃N₄), layered double hydroxides (LDH), covalent organic frameworks (COFs),

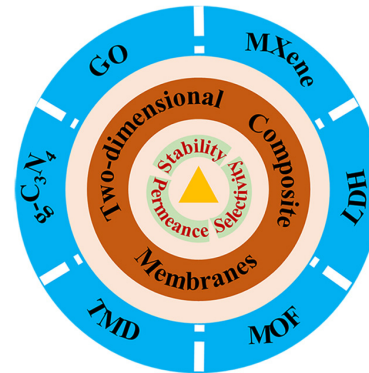


Figure 1. 2D composite membrane materials diagram. Reprint permission from reference [38], Copyright 2023, Elsevier.

hydrogen-bonded organic frameworks (HOFs), transition metal dichalcogenides (TMD), and clays have been utilized to develop high-performance MMMs (Figure 1)[39-53].

In this review, we conducted a comprehensive study of MMMs based on 2D materials for CO₂ capture. First, we discussed the 2D materials applied in MMMs for CO₂ capture. We then categorized and reviewed the research on MMMs according to the types of 2D materials used, evaluating the performance of existing 2D material-based MMMs. Finally, we discussed the current challenges and future developments in using 2D nanomaterial membranes for carbon capture.

2. Milestones in the development of 2D-material-based MMMs

Table 2 illustrates the research timeline for advancing 2D-material-based membranes[38]. The development of MMMs incorporating 2D materials for gas separation has seen significant advancements over the years. This section presents an overview of the critical milestones in developing various 2D-material-based MMMs, highlighting their unique compositions and the advancements achieved from 2014 to 2023.

In 2014, the initial efforts to incorporate 2D materials into MMMs began with the development of ZIF-8 incorporated tert-butylpolybenzimidazole (ZIF-8@PBI-BUI) MMMs and NiAl-CO₃ LDH membranes. These early studies laid the groundwork for further exploration of 2D material applications in gas separation membranes. By 2015, researchers had successfully developed polyethylene glycol and polyethyleneimine-modified GO (PEG-PEI/GO) MMMs and ZIF-8-ZnAl-NO₃ LDH MMMs.

Table 2. Timeline for the Advancement of 2D Nanomaterial-Based Membranes (Adopted from the Reference [38])

Development year	GO composite membrane	MOF composite membrane	g-C ₃ N ₄ composite membrane	COF composite membrane	MXene composite membrane	TMD composite membrane	LDH composite membrane
2023	GO-melamine composite	a) PBE/MOF-808 MMMs	g-C ₃ N ₄ -GOx/Pebax-1657 MMMs	b) TPB-DMTP-COF and IL@COF	c) MXene@CNF membranes	-	-
2022	d) ZIF-8/GO MMMs	e) ZIF-8@PAN/PEO MMMs	f) PIM-1/g-C ₃ N ₄ MMMs	g) PVAm/ZIF-8@NENP-NH ₂ MMMs	h) MXene/PEI MMMs	i) Cys-MoS ₂ /Pebax MMMs	CoNi-LDH/Pebax MMMs
2021	-	j) PVAm/ZIF-8-d-MK MMMs	GO-modified-g-C ₃ N ₄ MMMs	k) Pebax-PEG@COF MMMs	MXene hollow fiber membrane	-	-
2020	ZIF-8@GO/Pebax-1657 MMMs	PEI-ZIF-8/Pebax MMMs	g-C ₃ N ₄ /Pebax MMMs	COFs/PVAm MMMs	MXene/Pebax-1657 MMMs	-	-
2019	l) SPEEK/S-GO MMMs	m) PVA/PVAm-ZIF-L membranes	n) CS-g-C ₃ N ₄ /ZIF-8 MMMs	GO/COF MMMs	-	-	-
2018	GO/PEI MMMs	PVAm/PEI-g-ZIF-8 MMMs	-	-	Amine functionalized MXene/PEI MMMs	WS ₂ /IL SILMs	ZIF-8@LDH/Pebax MMMs
2017	o) GO-PEGDA MMMs	p) NH ₂ -ZIF-8/PA MMMs	-	-	-	-	-
2016	-	-	-	-	-	MoS ₂ /Pebax MMMs	-
2015	PEG-PEI/GO MMMs	-	-	-	-	-	ZIF-8-ZnAl-NO ₃ LDH MMMs
2014	-	q) ZIF-8@PBI-BUI MMMs	-	-	-	-	NiAl-CO ₃ LDH membrane

a) Poly(2-[3-(2H-benzotriazol-2-yl)-4-hydroxyphenyl] ethyl methacrylate)-co-poly(oxyethylene methacrylate) (PBE); b) triphenylbenzene (TPB), dimethoxyterephthaldehyde (DMTP); c) cellulose nanofiber (CNF); d) zeolitic imidazolate framework (ZIF); e) polyacrylonitrile (PAN), polyethylene oxide (PEO); f) polymers of intrinsic microporosity (PIM); g) polyvinylamine (PVAm), nitrogen-rich nanoporous polytriazine (NENP); h) polyethyleneimine (PEI); i) l-cysteine functionalized MoS₂ (Cys-MoS₂); j) metakaolin (MK); k) polyethylene glycol (PEG); l) sulfonated polyether ether ketone (SPEEK); m) poly (vinyl alcohol) (PVA); n) chitosan (CS); o) polyethylene glycol diacrylate (PEGDA); p) polyamide (PA); q) tert-butylpolybenzimidazole (PBI-BUI)

These membranes demonstrated the potential of integrating GO and LDH materials to improve gas separation performance. The year 2016 saw the development of MoS₂/Pebax MMMs, marking a significant step forward in utilizing TMDs for MMMs. This innovation showcased the potential of MoS₂ as a filler material to enhance membrane properties.

In 2017, the focus shifted towards developing GO-PEGDA MMMs and NH₂-ZIF-8/PA MMMs. These membranes further highlighted the versatility of GO and MOFs in creating efficient gas separation membranes. The advancements continued in 2018 with the creation of GO/PEI MMMs, PVAm/PEI-g-ZIF-8 MMMs, and amine-functionalized MXene/PEI MMMs. This year also saw the introduction of WS₂/IL supported ionic liquid membranes (SILMs) and ZIF-8@LDH/Pebax MMMs, expanding the range of 2D materials used in MMMs. By 2019, researchers had developed sulfonated poly(ether ether ketone)/sulfonated polymer brush functionalized graphene oxide (SPEEK/S-GO)

MMM, polyvinyl alcohol/polyvinyl amin-zeolitic imidazolate framework-L (PVA/PVAm-ZIF-L) membranes, Chitosan-g-C₃N₄/zeolitic imidazolate framework-8 (CS-g-C₃N₄/ZIF-8) MMMs, and GO/COF MMMs. These innovations demonstrated the continued interest in exploring 2D materials for MMM applications.

In 2020, significant progress was made with the development of ZIF-8@GO/Pebax-1657 MMMs, PEI-ZIF-8/Pebax MMMs, g-C₃N₄/Pebax MMMs, COFs/PVAm MMMs, and MXene/Pebax-1657 MMMs. These membranes showcased the potential of combining different 2D materials to enhance gas separation efficiency. The year 2021 saw the introduction of PVAm/ZIF-8-decorated metakaolin (PVAm/ZIF-8-d-MK) MMMs, GO-modified-g-C₃N₄ MMMs, Pebax-PEG@COF MMMs, and MXene hollow fiber membranes. These developments highlighted ongoing innovation in creating more efficient gas separation membranes. In 2022, researchers developed ZIF-8/GO MMMs, ZIF-8@polyacrylonitrile/poly ethylene oxide (ZIF-8@PAN/PEO) MMMs, intrinsi-

Table 3. Advantages of 2D Materials in Terms of Fillers for Gas Separation MMMs

2D material	Merits as filler	Ref.
GO	<ul style="list-style-type: none"> • 2D nanostructures possessing functional groups that are capable of being modified and combined with other substances • Optimal separation of CO₂ 	[55]
MOFs	<ul style="list-style-type: none"> • Ligand compounds with functionalized, designable, and tunable nanospaces • Preparation of high selectivity and high permeability separation membranes 	[56]
COFs	<ul style="list-style-type: none"> • COF-5/Pebax membrane was uniform, which is beneficial to the CO₂ capture • COF-5/Pebax shows high CO₂ uptake capacity. 	[57]
MXene	<ul style="list-style-type: none"> • Excellent chemical stability, high specific surface area, and environmental compatibility • Composites could be used for air purification 	[58]
g-C ₃ N ₄	<ul style="list-style-type: none"> • 2D layered material, capable of synthesizing ultra-thin layered nanochannels with selective loading • Gas separation membranes with high permeability and different selectivity can be prepared fabrication of ultra-high permeability gas separation membranes 	[59]
LDH	<ul style="list-style-type: none"> • LDHs into single-layer nanosheets enabled to maximize the surface area, which was favorable for their utilization as high-performance separation membranes • LDHs, a representative of anionic clays, have attracted extensive interest and exhibited promising prospects for membrane applications 	[60]

cally microporous polymer/g-C₃N₄ (PIM-1/g-C₃N₄) MMMs, PVAm/ZIF-8 @nitrogen-enriched nanoporous polytriazine (PVAm/ZIF-8@ NENP-NH₂) MMMs, MXene/PEI MMMs, L-cysteine-functionalized MoS₂/Pebax (Cys-MoS₂/Pebax) MMMs, and CoNi-LDH/Pebax MMMs. These membranes further underscored the diverse applications of 2D materials in MMMs.

Finally, in 2023, several cutting-edge MMMs were introduced, including GO-melamine composites, poly(2-[3-(2H-benzotriazol-2-yl)-4-hydroxyphenyl] ethyl methacrylate)-co-poly(oxyethylene methacrylate)/MOF-808 (PBE/MOF-808) MMMs, g-C₃N₄-GOx/Pabax-1657 MMMs, triphenylbenzene-dimethoxyterephthaldehyde-COF (TPB-DMTP-COF) and ionic liquid@COF (IL@COF) MMMs, and MXene@cellulose nanofiber (MXene@CNF) membranes. These innovations represent the latest advancements in the field, showcasing the ongoing evolution and potential of 2D-material-based MMMs for gas separation.

3. 2D nanomaterials employed as fillers for gas separation MMMs

3.1. Properties of 2D materials as fillers for gas separation MMMs

Table 3 demonstrates the merits of various 2D materials used as fillers in MMMs for gas separation. The merits of 2D materials in MMMs originate from the following properties. Various 2D nanomaterials are categorized into porous and non-porous types based on their void structure. Common 2D non-porous materials include TMDs, LDHs, MXenes, and GO[9,23,39,52,55]. These materials are frequently utilized in gas separation membranes due to their atomic-layer thickness, facile fabrication process, and significant specific surface area[23, 38]. However, the primary characteristic of most 2D non-porous materials is their impervious surface, which complicates gas transport[38]. Molecular structures such as TMD, MXene, and GO are employed as single-atomic layer-thickness basic nanosheets, which obstruct the flow of gas molecules due to their large lateral dimensions[9,23,39,52]. Consequently, smaller gas molecules can permeate through the interlayers or flaws in the nanosheets[38].

When using materials like these as fillers, it is crucial to consider both the dimensions of the interlayer channels and the obstructive impact of the substance. On the other hand, 2D porous materials such as g-C₃N₄, COFs, and MOFs show higher potential for use in composite membranes as fillers[46,49,41,56]. Modifying the size of the micropores in the 2D porous materials can serve as efficient pathways for small gas molecules while maintaining gas selectivity[38]. After membrane development, gas molecules can flow through the 2D nanochannels and natural holes on the membrane, which can also function as mechanisms for gas transport[46,49,51].

With their numerous surface functional groups, MOFs can facilitate gas diffusion by leveraging interaction forces[49,56]. Gas separation membranes benefit from COFs due to their remarkable crystallinity, substantial specific surface area, enduring porosity, and exceptional thermal resistance[46,57].

3.2. Synthesis of 2D materials

There are two primary approaches for synthesizing 2D materials: top-down and bottom-up. The top-down approach involves removing layers from more extensive materials through mechanical or chemical processes, while the bottom-up approach constructs materials from molecular or atomic precursors. The bottom-up method directly creates 2D materials using techniques such as templating, interfacial growth, chemical vapor deposition (CVD), physical vapor deposition (PVD), and topochemical transformations. In contrast, the top-down approach produces 2D nanosheets through exfoliation methods, including electrochemical exfoliation, freeze-thaw exfoliation, sonication exfoliation, mechanical exfoliation, ion-exchange exfoliation, and solvent-assisted exfoliation[61-69].

2D nanosheets can be fabricated into membranes using solution casting, hot dropping, or filtration[70,71]. Both top-down and bottom-up approaches offer significant advantages over other methods and have been the focus of extensive research due to their effectiveness and versatility.

Recent advances in the synthesis of 2D materials for gas separation

membranes have been widely reviewed, highlighting the emergence of new materials such as graphene derivatives, MOFs, COFs, HOFs, MXenes, g-C₃N₄, TMDs, and LDHs. These materials are proving increasingly attractive for enhancing gas separation, presenting promising avenues for future research.

3.3. Working principles of 2D materials as fillers in MMMs

The working mechanisms of 2D materials as fillers in MMMs can differ based on their distinct characteristics and interactions within the polymer matrices. Here are several fundamental principles. To begin with, numerous 2D materials feature an atomic-layer thickness, enabling precise manipulation of the membrane's structure and attributes. This thinness facilitates gas diffusion across the membrane while preserving its selectivity[41].

Next, many 2D materials possess a substantial specific surface area, offering abundant active sites for gas adsorption and streamlining gas separation processes. In addition, certain 2D materials, particularly porous ones like MOFs and COFs, exhibit well-defined pore structures. These pores act as conduits for gas molecules, facilitating efficient gas transfer and segregation[49,50].

Also, functionalized 2D materials may carry specific chemical groups on their surfaces, capable of interacting with gas molecules through adsorption or chemical reactions. These interactions can enhance gas separation efficiency by selectively capturing target molecules[38]. Furthermore, 2D materials feature adjustable tortuous interlayer galleries between 2D materials in polymer matrices. These interlayer networks influence the permeability of gas molecules through the membrane, with shorter interlayer networks promoting faster diffusion[41].

Finally, certain 2D materials like graphene and MXenes demonstrate exceptional mechanical strength. When integrated into MMMs, these materials can bolster the membrane's structural integrity while preserving its gas separation efficiency[38].

4. Performance assessment of 2D materials-based MMMs in CO₂ capture

4.1. Graphene-based MMMs

Graphene is a single-atom-thick graphite consisting of a monolayer of carbon atoms organized in a 2D configuration. The structure comprises a hexagonal carbon network, with every atom forming covalent interactions with three adjacent atoms by the sigma bond[72]. Graphene and its derivatives have recently gained significant attention in gas separation using membrane technology[73-76]. These materials are known for their exceptional thermal stability, impressive mechanical strength, chemical inertness, high aspect ratio, large specific surface area, unique 2D structure, and ultra-thin mono-atomic thickness [77-81]. Graphene can be synthesized using different methods, like top-down and bottom-up directions[82,83]. Graphene is commonly utilized in various forms, such as graphene-based composites, graphene laminates, and nano-porous graphene, to separate mixtures of gas and individual gas components[77].

Table 4 concisely overviews graphene-based MMMs fabricated using

various polymers and supplements for gas separation. In a study conducted by Lee and coworkers[84], it was found that a membrane made of nano-porous graphene can effectively separate CO₂ from various gas mixtures like CO₂/O₂, CO₂/N₂, CO₂/CH₄, and CO₂/H₂. Its single-atom thickness offers exceptional permeability and selectivity for gas molecules, surpassing other carbon materials. Koenig *et al.* utilized graphene nanosheets that had carefully engineered nanopores to facilitate the permeation of CO₂ gas and other gas molecules[85]. He *et al.* created a hybrid membrane by altering a single-layer graphene with polyethylenimine. This membrane has a CO₂/N₂ selectivity of 22.5 and a CO₂ permeance of 6180 GPU[86].

Tian *et al.* found that when porous graphene was coated with 1-ethyl-3-methyl imidazolium tetrafluoroborate ([emim][BF₄]) IL, it showed a CO₂/CH₄ selectivity of 40 and CO₂ permeance of 105 GPU[87]. Guo *et al.* created a nanoporous graphene membrane modified with 1-butyl-3-methyl imidazolium tetrafluoroborate ([Bmim][BF₄]) IL to separate CO₂ and N₂ gases[88]. The CO₂ permeance was enhanced to 4000 GPU, and the CO₂/N₂ selectivity was improved to 32 by using a loaded IL that allowed for adjustment of the chemical affinity and nanopore size.

GO composites and functional derivatives of graphene are superior materials for CO₂ separation. GO may be readily manufactured in huge quantities and can be processed into laminates. Researchers have extensively examined GO-composite membranes in recent studies due to their enhanced permeability and selectivity for CO₂ compared to pristine GO laminates. These membranes have a strong conjugated π system, which enhances their selectivity for CO₂[89]. Wu *et al.* created MMMs using graphene oxide as a foundation material. The GO was modified with PEI and PEG and added to a Pebax material[90]. The authors have observed that by implementing this technique, the permeability of CO₂ has been measured to be an impressive 1330 Barrer while maintaining a selectivity of 120 for CO₂/N₂ and 45 for CO₂/CH₄. The results indicate that the effectiveness of separating CO₂ can be improved by integrating appropriate interconnections of functional groups within GO layers.

Wang *et al.* fabricated a GO membrane for CO₂ separation using the vacuum filtration method. The membrane was crosslinked with borate, resulting in a CO₂ permeability of 650 GPU and CO₂/N₂ selectivity of 75[91]. Shen *et al.* demonstrated the creation of a specialized CO₂ transport Pebax/GO MMM that possesses CO₂ transport routes with a molecular-sieving structure[75]. This GO membrane achieved a CO₂ permeability of 100 Barrer and CO₂/N₂ selectivity of 91. Li *et al.* developed 0.05 wt% graphene-containing MMMs, which exhibited a 21% CO₂ permeability increase and a CO₂/N₂ selectivity increase of 20.8%[92]. Wang *et al.* created polyetheramine-grafted graphene oxide and utilized it to fabricate Pebax MMMs to separate N₂ and CO₂ gases[93]. MMMs containing 15 wt% of PEI-grafted graphene oxide had the most superior achievement of all the compositions analyzed. Specifically, it exhibited a CO₂ permeability of 242 and CO₂/N₂ selectivity of 56.

Based on the previous discussions, graphene materials are a promising option for creating MMMs with appropriate polymer matrices. This

Table 4. An Overview of the CO₂ Separation Performances of Graphene-Based MMMs

Polymers	Filler	Loading (wt%)	Pressure (bar)	Temperature (°C)	CO ₂ /N ₂ gas pair		CO ₂ /CH ₄ gas pair		Ref.
					Permeability (Barrer)	Selectivity	Permeability (Barrer)	Selectivity	
Pebax	Graphene	4.0	1.0-2.0	25	239.8	95.5	-	-	[37, 94]
Matrimid	Nitrogen-doped Graphene	0.07	1.0	35	10.3	41.1	-	-	[95]
PIM-1	Few-layer graphene	0.001	1.0	25	12700	14.6	12700.0	8.76	[96]
^{a)} PDMS	Graphene flakes	0.5	2.0	37	4460	8.1	4460.0	4.20	[97]
PVA	Graphene nanoplate	1.5	1.0	25	-	-	81.4	41.90	[98]
^{b)} PPO	Graphene	0.3	1.4	35	62	17.7	-	-	[99]
Pebax	Graphene	0.7	4.0	25	44.78	111.95	-	-	[100]
Pebax	GO	1.0	4.0	25	55.87	120.72	-	-	[100]
PIM-1	^{c)} APTS-GO	-	1.5	25	-	-	4850.0	11.00	[101]
Cellulose	GO-PEI- Zn ²⁺	17.0	1.0	25	267	48.9	268.9	57.04	[102]
Pebax	^{d)} GO-DA-Zn ²⁺	1.0	2.0	30	-	-	138.0	28.81	[103]
Pebax	GO	1.0	3.0	25	94.7	84.37	-	-	[104]
^{e)} PVDF	GO	0.5	5.0	27	0.897	40.63	-	-	[105]
PEO	GO	1.0	10.0	35	280	46.58	-	-	[106]
Pebax	GO	0.8	5.0	25	28.08 GPU	42.55	28.08 GPU	52.57	[107]
Pebax	GO	1.0	2.0	30	114.17	69.13	-	-	[108]
Pebax	^{f)} GO-mPD	0.7	4.0	25	29.60	142.9	-	-	[109]
Pebax	^{g)} A-prGO	0.05	4.0	25	49.30	98.60	49.3	22.41	[110]
^{h)} PI	GO-NH ₂	3.0	1.0	25	12.34	38.56	-	-	[111]
Pebax	GO-Silane	0.5	2.0	35	174.00	14.5	174.0	43.50	[112]
Pebax	ⁱ⁾ GO-Im	0.5	4.0	25	66.40	74.33	66.4	24.43	[113]
SPEEK	^{j)} S-GO	8.0	1.0	25	1326.55	86.44	1326.6	72.25	[114]
PIM-1	^{k)} rGO-OA	0.25	2.0	25	-	-	6300.0	17.60	[115]

a) Polydimethylsiloxane (PDMS); b) poly(p-phenylene oxide) (PPO); c) (3-aminopropyl)triethoxysilane (APTS); d) dopamine (DA); e) polyvinylidene fluoride (PVDF); f) m-phenylenediamine (mPD); g) aminated partially reduced graphene oxide (A-prGO); h) polyimide (PI); i) imidazole functionalized graphene oxide (ImGO); j) sulfonated polymer brush functionalized graphene oxide nanosheets (S-GO); k) octylamine (OA)

is due to their extremely thin structure at the atomic level, impressive mechanical strength, ability to disperse nicely in polymers, and potential for selectively transporting molecules of specific sizes through nanopores.

4.2. MOF-based MMMs

MOFs are a structured material comprised of metallic ions and organic ligands that form a crystalline and porous solid. Research on MOFs has explored its potential applications in several fields, such as gas storage, sensors, separation, adsorption, catalysis, solar fuel production, drug delivery, molecular identification, and anticorrosion coating on metal surfaces[116,117]. Several synthesis strategies have been assessed for the synthesis of MOFs, including sonochemical, mechanochemical, solvothermal, electrochemical, ultrasonic, and microwave-assisted heating[118-121].

The researchers were driven to create MOF-based MMMs to en-

hance the characteristics of membranes by integrating materials into a polymer matrix. Recently, MOF-based membranes have been widely acknowledged as the most efficient materials for gas separation. The unique characteristics of this material, such as its rich porosity, low density, extensive surface area with a range of 1000 to 10000 m²/g, particle size, chemical functionality, dimensions and flexibility in topology, as well as its tiny aperture size, wide range of pore size, and chemical and physical properties, make it a preferred choice for various gas separation applications compared to alternative porous materials like zeolites, activated carbons and silica[122-127].

Porous MOFs can increase the capacity of gas to pass through a dense polymeric matrix[120]. Theoretically, the primary focus is on the size of the particles' aperture. By molecular sieving, MOFs can separate the molecules in gas. Meanwhile, the filler dimensions are paramount in establishing the polymer's available space. Concurrently, the nanoparticle structure influences the configuration and dimensions of

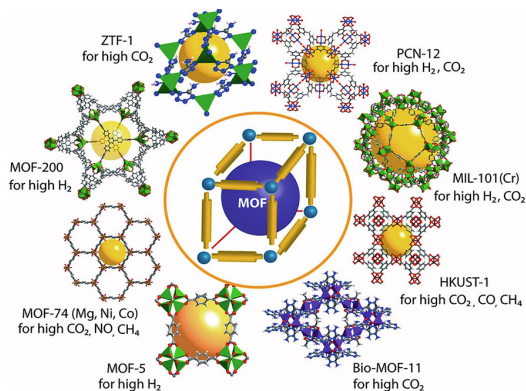


Figure 2. 3D structures of various MOFs. Reprint permission from reference [54], Copyright 2021, Elsevier.

the pore, impacting the system's separation process[129]. The critical distinction is in the sheet-shaped MOF's surface area, which enhances the interaction between gases and fillers that flow through. These characteristics allow for the obstruction of the flow of unwanted gases through MMMs. Various varieties of MOFs have been introduced, and their number continues to increase. Recent research has demonstrated the successful utilization of well-known MOF structures, including ZIF-series, Material of Institute Lavoisier (MIL)-series, University of Oslo (UiO)-series, and Hong Kong University of Science and Technology (HKUST), in creating MMMs for applications of different gas separations (Table 5). The exceptional membrane properties of MOFs have been verified through over both computational and experimental investigations. MOFs may be utilized for membrane separation in two ways: either as fillers or as pure films in polymer matrices to create MMMs[130]. Figure 2 shows the 3D structure of various MOFs.

4.2.1. ZIF-based MMMs

ZIFs are a kind of MOFs that have a zeolite-like structure with different pore sizes. ZIFs provide several benefits, including easy synthesis, scalability, affordability, efficient dispersion, eco-friendliness, and excellent resistance to hydrothermal conditions[131-133]. ZIFs comprise metal nodes linked to imidazole linkers by substituting Si/Al atoms with imidazolates and transition metals. The bond angle between the linker and metal in ZIFs is also comparable to the zeolites Si/Al-O-Al/Si repeating unit[134]. The range of ZIF materials is synthesized by altering the imidazole linkers and transition metal ions (Zn and Co). Some examples of these materials are ZIF-302, ZIF-108, ZIF-78, ZIF-71, ZIF-11, ZIF-8 and ZIF-7. ZIFs often include spacious internal voids with narrow pore apertures closely matching the size of CO₂ molecules. This characteristic makes ZIFs appropriate for separating CO₂ as a filler material in MMMs.

Li *et al.* successfully produced ZIF-7/Pebax composites without defects and obtained a high permeability when the filler loading was 22 wt%. Furthermore, the selectivity was further enhanced by raising the filler proportion to 34%. However, the permeability dropped from 145 to 41 Barrer due to the increased rigidity of the Pebax chain caused by more filler[11]. ZIF-8 fillers have a strong bond with the soft Pebax

domain, resulting in a 4.32-fold increase in CO₂ permeability compared to Pebax alone. A permeability of up to 994 Barrer was reached using a mixture of 35 wt% ZIF-8 and Pebax. The selectivity of CO₂/CH₄ and CO₂/N₂ was 9 and 32, respectively[135]. Nordin *et al.* created MMMs by evenly distributing ZIF-8 (0.5%) in a polysulfone (PSf) matrix with abundant free space. This led to CO₂ penetration and selectivity that were 1.37 and 1.19 times higher, respectively, compared to previous results[136].

Tanh Jeazet *et al.* did a study on the separation of CO₂ using a combination of ZIF-8 and PSf. They found that the selectivity and permeability of gas separation rose by 1.52 and 2.0 times, respectively, after increasing the ZIF-8 loading to 8 wt% compared to a PSf membrane with a lower ZIF-8 content. Furthermore, the highest level of permeability, about 4.8 times greater, was attained at a concentration of 24 wt%. The loading and selectivity of ZIF-8 fell to 1.04 due to the trade-off in membrane characteristics[137]. Thompson *et al.* created MMMs by modifying the surface of ZIF-8 by combining Matrimid, 2-aminobenzimidazole, and 2-benzimidazole. The findings demonstrated that ZIF-8 samples treated with 2-benzimidazole had the highest CO₂ permeability value of 10 Barrer, with a 4% decrease in CO₂/CH₄ selectivity compared to thin polymers[138].

Chi *et al.* examined the properties of styrene-based MMMs by evenly distributing ZIF-8 particles of various sizes inside a copolymer matrix of polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SEBS) while preserving the distinct structure of the polymer matrix. The findings demonstrated that the CO₂ permeability of ZIF-8 with a medium size of 240 nm was 2.66 times. Additionally, the selectivity of CO₂/N₂ and CO₂/CH₄ were 12 and 5.4, correspondingly[139]. Nevertheless, IL@ZIF-8 exhibited better gas separation capabilities than the highest limit of polymeric membrane performance set by Robeson in 2008. The IL@ZIF-8 material has shown exceptional durability over time and improved CO₂ selectivity and permeability over standard ZIF-8. Specifically, the CO₂ selectivity and permeability values for CO₂/N₂ and CO₂/CH₄ were 64.9, 15.1, and 292 Barrer, correspondingly, which were higher than those of plain ZIF-8[140]. Ban *et al.* created a composite material by incorporating Co-metal into the PSf matrix and ZIF 108. ZIF-108 possesses many active sites that can accommodate other metals instead of its own. The Co-doped ZIF-108/PSf secondary metal exhibited a CO₂ permeability approximately seven times greater than the value of ZIF-108/PSf and 17 times greater than pure PSf.

The pore size of the ZIF-108 framework increased with the addition of Co metal. As a result, the compatibility between the PSf membrane and the fillers was enhanced, leading to increased separation factors and CO₂ permeability[141]. In the study conducted by Nafisi and H'agg[135], ZIF-8 was permeated into 2,2'-bis(3,4'-dicarboxyphenyl) hexafluoropropane diandrydride (6FDA)-durene polyimide (PI) that was produced. The resulting membrane greatly enhanced the transport channels for four gases: N₂, O₂, CH₄, and CO₂. Nevertheless, the selectivity of the CO₂/CH₂ and CO₂/N₂ gases was reduced. The rise in gas transport may be primarily attributed to the inclusion of ZIF-8, which increased free space and disrupted the polymer chain in the membrane.

Table 5. Evaluation of MMMs Created with Different Combinations of Polymer and MOFs, Including Their Performance, Optimal and Operating Conditions, and Modifications to the MOFs

Membrane material	MOF type	Filler loading (wt%)	Pressure (bar)	Temperature (°C)	CO ₂ /N ₂ gas pair		CO ₂ /CH ₄ gas pair		Ref.
					Permeability (Barrer)	Selectivity	Permeability (Barrer)	Selectivity	
PEI	MOF-5	25.0	6.00	25	-	-	5.4	23.4	[176]
Matrimid- 5218	MOF-5	30.0	2.00	35	-	-	20.2	44.7	[177]
PIM-1	MOF-801	5.0	0.40	35	9686.00	27.0	-	-	[178]
Pebax-1657	ZIF-7	22.0	3.75	25	111.00	97.0	-	-	[11]
Pebax-1074	ZIF-7	25.0	3.00	30	95.00	28.1	-	-	[179]
Pebax-2533	ZIF-7-OH	14.0	4.50	25	273.00	38.1	-	-	[180]
PIM-1	NH ₂ -ZIF-7	20.0	2.00	30	2953.00	20.6	-	-	[181]
Pebax-1657 PVAm	ZIF-8	5.0	11.00	35	162.00	81.0	-	-	[182]
PVAm	ZIF-8	-	1.65	22	297.00	83.0	-	-	[183]
^{a)} PVA/PG	ZIF-8	5.0		95	328.00	370.0	-	-	[184]
^{b)} PBI/ Matrimid [®] 5218	ZIF-8	10.0	7.00	150	107.00	16.1	-	-	[185]
^{c)} PTMSP	ZIF-L	20.0	2.00	-	1489.00	13.5	-	-	[186]
Pebax-1657	ZIF-C 85-124 (20)	20.0	2.00	24	387.00	47.1	-	-	[187]
PIM-1	ZIF-67	20.0	2.00	30	3542.00	24.2	-	-	[188]
Pebax-2533	ZIF-11	70.0	2.00	20	-	-	402.9	12.5	[189]
6FDA-DAM	ZIF-11	20.0	4.00	30	-	-	257.0	31.0	[190]
^{d)} 6FDA-TP PI	ZIF-90	50.0	9.80	35	-	-	63.0	36.0	[191]
PIM-1	^{e)} BCoC-ZIF	10.0	3.00	25	7326.00	32.5	-	-	[192]
Matrimid 5218	MIL-101	10.0	10.00	35	6.95	52.0	-	-	[155]
Matrimid 9725	NH ₂ -MIL-125	30.0	9.00	35	-	-	50.0	37.0	[161]
Matrimid 5218/PVDF	MIL-101	10.0	7.00	35	-	-	14.9	62.0	[193]
Matrimid 5218	MIL-101-IL	20.0	0.70	30	9.90	26.9	-	-	[194]
Pebax-1657	NH ₂ -MIL-53	5.0	10.00	35	134.60	59.3	-	-	[195]
^{f)} 6FDA-ODA PI	UiO-67		10.34	35	-	-	20.8	15.0	[148]
^{g)} ODPa-TMPDA PI	UiO-66-(OH) ₂	20.0	1.00	35	125.00	38.9	-	-	[170]
6FDA-DAM PI	UiO-66	14.0	2.00	35	-	-	1912.0	31.0	[196]
Matrimid [®] 5218	^{h)} UiO-66-NH ₂ @ICA	10.0	3.00	25	-	-	40.1	64.7	[197]
Polymide-11	UiO-66-NH ₂	-	0.49	34	-	-	7.6	95.1	[198]
Matrimid [®] 5218	UiO-67	10.0	5.00	30	-	-	27	75.0	[199]
Matrimid [®] 5218	HKUST-1-NH ₂	20.0	1.00	35	13 GPU	42.7	-	-	[174]
6FDA-durene	HKUST-1	10.0	1.00	25	1.41	1.2	1.4	1.3	[200]
PSf	ⁱ⁾ HKUST-1/S1C	16.0	2.75	35	2.00	1.5	2.0	0.9	[201]
Pebax-1657	^{j)} CuBDC-ns@MoS ₂	2.5	4.00	35	123.00	69.0	123.0	18.0	[202]
PIM-1	^{k)} NUS-8-COOH	2.0	2.00	25	10400.00	31.0	-	-	[203]
^{l)} PEGMEA	^{m)} Cu-TCPP	0.1	1.50	25	1183.00	75.6	-	-	[204]
Pebax	ⁿ⁾ SUM-9	1	2	25	539	24.7	-	-	[205]
Polyvinyl acetate	Mg-MOF-74	20	6	-	-	-	4.7 GPU	24.8	[206]
PDMS	Mn-MOF-74	2.5	4	30	1466	18.0	-	-	[207]

a) Piperazine glycinate (PG); b) polybenzimidazole (PBI); c) poly(1-trimethylsilyl-1-propyne) (PTMSP); d) thermoplastic (TP); e) basic cobalt carbonate supported zeolitic imidazolate framework-67 (BCoC-ZIF); f) oxydianiline (ODA); g) 4,4'-oxydiphthalic anhydride (ODPA), 2,4,6-trimethyl-m-phenylenediamine (TMPDA); h) imidazole-2-carbaldehyde (ICA); i) Silicalite-1 (S1C); j) nanosheet (ns); k) National University of Singapore (NUS); l) poly(ethylene glycol) methyl ether acrylate (PEGMEA); m) tetrakis(4-carboxyphenyl)porphyrin (TCPP); n) Sichuan University Materials (SUM)

Conversely, the decline in selectivity can be attributed to the excessively higher transportation rates for CH₄ and N₂ than CO₂. Bae *et al.*[142] incorporated ZIF-90 into 6FDA-diamino-mesitylene (DAM) PI using the non-solvent-induced crystallization process, producing 6FDA-DAM/ZIF-90 MMMs and adding ZIF-90 to the 6FDA-DAM PI significantly enhanced gas permeability and membrane selectivity. Specifically, CO₂/CH₄ selectivity increased from 24 to 37, while CO₂ permeability rose from 390 to 720 Barrer.

Japip *et al.* examined how the gas transportation capabilities of 6FDA-Durene were affected by three distinct diameters (600 nm, 200 nm, and 30 nm) of ZIF-71[143]. The gas separation efficiency achieved with membranes containing ZIF-71 particles smaller than 200 nm was superior to that of membranes containing ZIF-71 particles larger than 200 nm. Remarkably, the MMMs containing ZIF-71 particles of 200 nm in diameter demonstrated superior gas separation ability. Yahia *et al.* conducted a study that produced MMMs by incorporating ZIF-8 particles of varied sizes (ranging from 45 nm to 450 nm) into a PIM-1 matrix[144]. These membranes were explicitly designed for the isolation of CH₄ and CO₂ gases. The result suggested that the gas transport capabilities of MMMs were most significantly enhanced when they incorporated ZIF-8 particles measuring 120 nm, which were uniformly distributed throughout the material. The membranes demonstrated a remarkable selectivity of 11.4 for CO₂/CH₄ and a CO₂ permeability of 9700 Barrer.

Suhaimi *et al.* examined MMMs that included ZIF-8 particles modified with three distinct amino-functional groups (mono, di, and tri-amine)[145]. These particles were incorporated into a polymer matrix made of 6FDA-durene to separate CH₄ and CO₂ gases. Both investigations demonstrated that the amine-functionalized MOFs displayed flawless and consistent particle circulation, resulting in enhanced permeability and selectivity. Zhang *et al.* synthesized ZIF-8@CNTs by combining acidified carbon nanotubes (CNTs) with ZIF-8 nanoparticles[146]. These were subsequently incorporated into Pebax MMMs. Adding oxygen groups and carboxyl groups to ZIF-8@CNTs resulted in excellent filler dispersion inside the MMMs. As a result, there was a rise in the available space, which enhanced the adsorption of CO₂ and the separation performance of CO₂/N₂.

Yuan *et al.*[147] were the first to create a ZIF-300/polyether block amide (PEBA) MMM by combining ZIF-300 crystals with the PEBA matrix. This MMM was then used to capture CO₂. The ZIF-300 crystals that were obtained were evenly distributed throughout the PEBA matrix, maintaining the pore structure intact. This resulted in a remarkable ability to absorb CO₂ and a high selectivity for CO₂/N₂. Consequently, the pure PEBA membrane's CO₂/N₂ selectivity and permeability were enhanced by adding ZIF-300 crystals, reaching a maximum improvement of 30 wt%. The Zn atoms in the tetrahedral structure are surrounded by four imidazolate linkages, each of which may bind to two other molecules. These links connect the Zn atoms, forming a 3D network with the stated topology. The hypothesis posited that ZIFs synthesized with a secondary linker would have a notably greater capacity for sorption and a stronger affinity for CO₂ than N₂. These ZIFs also showed exceptional performance despite having a limited

surface area. The disparity in structure ultimately led to distinct interactions with CO₂ gas molecules.

4.2.2. MIL-based MMMs

MIL is a series of MOFs composed of trivalent metal ions (Al, Cr, Ti) coupled to oxygen-anion-terminated linkers. MILs showcase desirable traits like a significant pore volume, exceptional resistance to chemicals, a high surface area, an impressive capacity for gas adsorption, and distinctive qualities related to structural breathing. Due to the presence of hydroxyl groups, it exhibits strong interaction with CO₂ and consists of a single-direction diamond-shaped pore channel. Contemporary scholarly works suggest that MILs are effective fillers in membrane development due to their strong compatibility and uniform dispersion with polymers, resulting in superior gas separation. MOFs are commonly employed in MMMs as fillers, with several MOFs, such as MIL-125, MIL-101, MIL-68, and MIL-53, described and utilized.

Interestingly, the diameter of the apertures of MILs is more significant than the kinetic diameter of gas molecules, like CH₄ (3.8 Å), CO₂ (3.3 Å), N₂ (3.6 Å), and H₂ (2.9 Å)[128]. MILs are composed of the benzene ring. Fillers with a broad aperture increase permeability but have a detrimental impact on selectivity. Considerable focus has been directed on altering these sorts of fillers to impede the permeability of the larger gas molecules. Amine functionalization is commonly employed for this purpose[148,148]. MIL-53 comprises interconnected dicarboxylate anions and hexagonal chains, creating a 3D network[150]. Every dicarboxylate function joins two metal centers. Subsequently, it connects with another set of metals, where the second dicarboxylate bonds similarly. This method results in the formation of octahedral coordination around the metal. MIL-53 has a distinctive attribute referred to as the breathing effect, which arises from the adjustable connection between the carboxylate groups and the metal centers. Breathing refers to the reversible change in the volume of the unit cell when guest molecules are absorbed or released[151]. The CO₂ quadrupole moment enhances its adsorption and reduces the size of particles' pores, resulting in beneficial effects for purification purposes[152]. Also, MIL-101 is created by combining terephthalate linkers with carboxylate trimers connected to octahedrally bonded chromium ions[153].

Abedini *et al.* created MMMs by spreading NH₂-MIL-53 within a poly(4-methyl-1-pentyne) (PMP) matrix. They discovered that the selectivity of CO₂/CH₄ in these MMMs was 15, and the CO₂ permeability was 259 Barrer when the MMMs had a 30 wt% filler load. These values were higher compared to a pure PMP membrane. The NH₂-MIL-53/PMP material exhibited superior separation performance compared to the Robeson upper bound at a temperature of 30 °C[154]. Naseri *et al.* used micron-sized MIL-101 crystals with a loading capacity of up to 30 wt% as the inorganic constituent and merged them with Matrimid to produce MIL-101/Matrimid MMMs[155]. The developed membranes were subsequently assessed for their ability to separate CO₂ from N₂ and CO₂ from CH₄. The MIL-101 particles exhibited more attraction to CO₂ than N₂ and CH₄ gases. The optimal performance was achieved with a 10 wt% loading of MIL-101, resulting in an

improved CO₂ permeability of 6.95 Barrer and CO₂/CH₄ selectivity of 56 compared to the initial values of 4.44 Barrer and 35, respectively.

Sabetghadam *et al.* examined the impact of MOF shape on the gas separation efficiency of MMM[156]. The NH₂-MIL-53(Al) material, which exists in three distinct forms: microneedles, nanorods, and nanoparticles- was incorporated into a Matrimid polymer matrix to separate CH₄ and CO₂ gases. The researchers found that NH₂-MIL-53(Al) with a nanoparticle structure exhibited a notable enhancement in CO₂ permeability compared to other structures. However, there was no increase in CO₂/CH₄ selectivity when the MMM supplied an equal amount of CH₄ and CO₂. The NH₂-MIL-53(Al) nanoparticle disrupted the Matrimid polymer chain, resulting in a rise in the polymer's free fraction volume. The enhanced gas permeability in the MMM resulted from the combined effect of the increased volume of polymer with a higher free fraction and the presence of porous MOF. However, when the filler content of NH₂-MIL-53(Al) was increased to 16 wt%, a decrease in gas permeability was detected. This decrease was linked to the stiffening of the polymer chain. The gas permeability of the MMM containing NH₂-MIL-53(Al) nanoparticles was excessively attenuated compared to the nanorods, indicating that the nanoparticle shape allows for improved interaction with the Matrimid polymer matrix. Subsequently, they introduced NH₂-MIL-53(Al) nanoparticles comprising 20 wt% of the mixture into a highly permeable 6FDA-DAM PI. This enhanced 88% CO₂ permeability while maintaining a somewhat steady CO₂/CH₄ selectivity compared to the original 6FDA-DAM material.

Rodenas *et al.* studied the impact of filler and polymer on MMMs. The NH₂ MIL-53(Al) and MIL-101(Al) were individually distributed in PSf matrices and PI. The gas transport efficiency of MIL-53(Al)/PI and MIL-101(Al)/PSf is 60% higher than that of the pure matrix while maintaining selectivity[157]. Feijani *et al.* studied PVDF MMMs produced with MIL-53(Al), which showed better CO₂/CH₄ permeability but lower CO₂/CH₄ selectivity than pure PVDF membrane[158]. As a result, they proposed the existence of indiscriminate gaps between the fillers and polymer matrix, which caused a decrease in gas selectivity. Furthermore, MIL-53(Al) exhibits a large pore size (7-8Å) compared to the gas kinetic diameter, potentially enhancing the reduction in gas selectivity. Nevertheless, including an amine group in NH₂-MIL-53(Al) resulted in a simultaneous increase in gas permeability and selectivity. This suggests a strong competence between the polymer matrix and filler and indicates that the formation of nanovoids was eliminated through the functionalization of the filler. Dong *et al.* examined the impact of MIL-68(Al)/PI MMMs on the separation of CO₂. The results demonstrated that the selectivity and permeability of CO₂ were 2.25 times greater than those of the original polymer. This may be linked to the strong contact between the polymer and the surface hydroxyl groups of MIL-68(Al) and the enhanced affinity of CO₂ adsorption[159].

MIL-101 is commonly selected for gas separation in MMM due to its greater specific surface area and high affinity for CO₂. MIL-101 has a higher CO₂ adsorption capacity than CH₄ due to its significant quadrupole moment and polarity[160]. This characteristic makes it well-suited for the separation of CO₂ and CH₄. Waqas Anjum conducted a

study on the impact of the NH₂ group on gas transportation. The results revealed that when NH₂-MIL-125(Al) fillers and MIL-125(Al) were included in a PI matrix, the permeability increased to 21 and 44 Barrer, respectively, compared to the pure polymer. The CO₂/CH₄ selectivity increased up to 23%. But, NH₂-MIL-125(Al)/PSf demonstrated enhanced permeability and selectivity compared to a pure PSf membrane, with a permeability of 13.3 barrer and a selectivity of 10%[161].

4.2.3. UiO-66-based MMMs

UiO-66 belongs to the subfamily of zirconium-based MOFs. The structure consists of zirconium oxide (Zr₆O₄(OH)₄) nodes that are linked with 1,4-benzenedicarboxylate (BDC) ligands. The structure consists of tetrahedral and octahedral cages in a ratio of 2:1, connected by triangular pore windows[162]. Additionally, it possesses a notable adjustable pore structure, level of porosity, and substantial surface area, rendering it highly attractive for gas separation purposes. The UiO-66 material has been altered on its surface to possess polar and essential characteristics, including methoxy (-OMe), nitro (-NO₂), amino (-NH₂), and hydroxylated (-OH) groups. Specifically, studies have shown that UiO-66 treated with polar groups may increase the selectivity of CO₂/CH₄ and CO₂/N₂ and improve CO₂ adsorption[163-165].

The study conducted by Nik *et al.* utilized five distinct UiO-67, UiO-66, NH₂-UiO-66, MOF-199 (Cu-benzene-1,3,5-tricarboxylate (BTC)), and NH₂-MOF-199 in the production of Matrimid-based MMMs[148]. Among the several membranes assessed, those made using UiO-66 demonstrated exceptional gas permeability for CO₂. In contrast, the introduction of amine groups to the MOF-MMM (NH₂-MOF-199) enhanced CO₂ permeability and selectivity over CH₄. It was determined that the H-bonding between the -COOH groups in the polymer chain and the -NH₂ groups in the filler was responsible for the improved selectivity. This interaction promotes the polymer chain process's stiffening at the interface. As a result, the permeability was reduced while the selectivity was enhanced. Liu's group produced UiO-66 membranes with exceptional CO₂/N₂ separation capabilities using a novel method, including a simultaneous Zr source[166]. The membrane has excellent gas separation capabilities and exhibits outstanding chemical stability.

In addition, it has been demonstrated that UiO-66/PEBA MMMs exhibit a significant attraction to CO₂, resulting in an increased CO₂/N₂ selectivity and CO₂ permeability of approximately 40-65% and 80-90%, respectively, compared to PEBA membranes[167]. Qian *et al.* produced MMMs by integrating a 6FDA-Durene polymer matrix with imide-functionalized UiO-66-NH₂ nanoparticles[168]. The purpose was to improve the selectivity and permeability of CO₂/CH₄. Jin *et al.* utilized a novel technique to attach UiO-66-NH₂ to PI by modifying the PI matrix with a carboxylic acid[169]. This modification removes the indiscriminate space between the fillers and the polymer matrix. These membranes also exhibit an elevated CO₂ plasticization pressure, ranging from 10 to 30 bar, and demonstrate exceptional resistance to aging, with a minor drop in CO₂ permeability. Chuah *et al.* examined several ligands containing diverse functional groups, including hydroxyl groups, bromine, and amine, which were attached to UiO-66 particles

to create UiO-66-(OH)₂, UiO-66-Br and UiO-66-NH₂ respectively[170]. Including UiO-66 derivatives improved the rate at which CO₂ molecules spread and decreased the ability of N₂ molecules to dissolve, leading to a greater preference for CO₂ over N₂. The selectivity of CO₂/N₂ was increased by 12%, 4% and 17% with the use of UiO-66-(OH)₂, UiO-66-Br and UiO-66-NH₂ respectively. The results indicate that including diverse functional groups is a useful strategy for improving the separation efficiency of MMM. Anjum and colleagues created MMMs by forming a strong chemical bond between Zr terephthalate UiO-66 fillers and a PI matrix functionalized with amine groups. The gas transportation was improved by incorporating amino-benzoic acid (ABA) and benzoic acid (BA) into NH₂-UiO-66. The resulting NH₂-UiO-66-ABA-filled MMMs demonstrated great permeability and selectivity, making them excellent candidates for CO₂/CH₄ separations[171].

4.2.4. HKUST-1-base MMMs

HKUST-1, also referred to as MOF-199 and Cu-BTC, is composed of a benzene-1,3,5-tricarboxylate ligand that serves as a connector, linking dicopper tetracarboxylic paddlewheel secondary building units. Another possible candidate for synthesizing MMMs for gas separation is being considered because of their significant accessible surface area and high porosity[172]. Casado-Coterillo *et al.* created CS-based MMMs and performed gas permeation tests with pure N₂ and CO₂ and gases[173]. The CS membrane holding 5 wt% of HKUST particles demonstrated the highest CO₂ permeation rate of 4754 ± 1388 Barrer, along with the highest CO₂/N₂ selectivity of 19.3. This effect may arise from the compatibility and robust adhesion between the HKUST and CS polymer matrix.

Chuah *et al.* synthesized Amine-functionalized HKUST-1 nanocrystals using a post-synthetic approach. Subsequently, these nanocrystals were employed to fabricate MMMs designed to separate CO₂/N₂[174]. On the other hand, the HKUST-1 nanocrystals that were functionalized with amines significantly increased the selectivity of CO₂/N₂ (by up to 38%) and improved the permeability of gases. This elevation in performance is highly desirable. Nevertheless, the HKUST-1 compound with amine functionality successfully reduced the rate of diffusion and solubility of N₂ while significantly enhancing the rate of diffusion of CO₂ by a factor of 100. Wang *et al.* fabricated HKUST-1@pyrrole (Pyr) composites and the original material using a rapid synthesis process at room temperature. HKUST-1@Pyr0.3 shows an exceptional ability to adsorb CO₂, having a 3.19 mmol/g capacity at 298 K temperature and 100 kPa pressure. Furthermore, this composite exhibited a significant preference for CO₂/N₂ bicomponent gas (with a ratio of 15:85), surpassing the selectivity of HKUST-1 by 150%[175].

Functionalizing the HKUST-1 nanofiller with amine groups decreased the effective pore diameter[174]. The gas selectivity of the resulting MMMs can be improved by limiting the diffusion of more giant gas molecules, like N₂, into a more constricted channel. 20 wt% pure HKUST-1 nanofiller increased the gas permeability, while gas selectivity remained unchanged. Including the HKUST-1 filler, we have

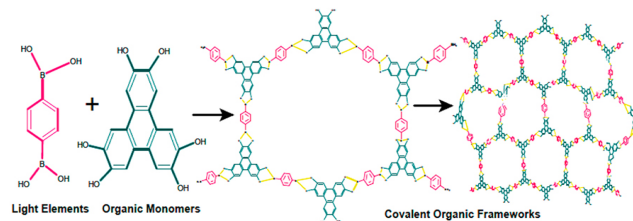


Figure 3. COFs structure diagram. Reprint permission from reference [219], Copyright 2024, Elsevier.

greatly enhanced the permeation and dissolvability of both CO₂ and N₂ without exhibiting any selectivity. The addition of amine-functionalized HKUST-1 nanofiller increased the CO₂ selectivity over N₂, increasing it from 33.8 to 42.7. This improvement was accomplished by significantly enhancing the ability of CO₂ to spread out while at the same time reducing the ability of N₂ to diffusivity and solubility.

Overall, MOFs have been extensively applied in gas separation studies because of their adjustable pore size, significant specific surface area, and exceptional porosity. Nevertheless, defects at the interface between the polymer and filler pose a significant challenge in enhancing the efficacy of MOF-based membrane separation. The ongoing research primarily focuses on improving the interface compatibility between polymers and fillers.

4.3. COF-based MMMs

The growing acceptance of incorporating COFs as additives in the fabrication of MMMs comes from their unique two-dimensional (2D) porous crystalline structures coupled with strong covalent bonds. Due to its high crystallinity structure, low densities, acceptable features, outstanding heat resistance, tunable organic groups, permanent porosity, and large specific surface area, it is commonly employed as an optimal material for gas separation membranes[208-210]. COFs provide notable advantages due to their exceptional chemical and thermal stability, which may be attributed to their covalent linkages[211]. Additional investigation and progress are anticipated to result in more sophisticated MMMs with improved stability, selectivity and permeability, making them suitable for environmental and industrial operations. Although several structures of COFs have been synthesized, only a limited number of COFs have been utilized in the field of membrane gas separation, mainly mixed COF-polymer membranes[212-214]. Figure 3 shows the general structure of COFs.

Table 6 concisely overviews COFs-based MMMs fabricated using various polymers and supplements for CO₂ separation. Biswal *et al.* generated ultrathin TpBD synthesized with 1, 3, 5-triformylphloroglucinol (Tp) and benzidine (BD) and TpPa-1 constructed by Tp with p-phenylenediamine (Pa-1) sheets using the mechanical grinding of their bulk phases[215]. The formation of the MMMs involved the reaction between two COF nanosheets and polybenzimidazole (PBI-Bul). The MMMs developed with a 50% loading of COF exhibited reduced selectivity of CO₂/CH₄ and CO₂/N₂ compared to the neat polybenzimidazole membrane. The permeability of CO₂ in the MMMs was approximately seven times higher compared to the original PBI-Bul

Table 6. Evaluation of MMMs Created with Different Combinations of Polymer and COFs, Including Their Performance, Optimal and Operating Conditions, and Modifications to the COFs

Membrane material	COF	Filler loading (wt%)	Pressure (bar)	Temperature (°C)	CO ₂ /N ₂ gas pair		CO ₂ /CH ₄ gas pair		Ref.
					Permeability (Barrer)	Selectivity	Permeability (Barrer)	Selectivity	
Matrimid-5218	^{a)} ACOF-1	16.00	4.0	35	-	-	15.3	32.4	[50]
Pebax-1657	COF-5	0.40	1.0	30	493.0	49.3	-	-	[57]
Pebax-1657	PEG@COF	3.00	1.0	25	-	-	944.0	33.0	[211]
PEBA	TpPa-1-nc	1.00	3.0	25	7.5 GPU	72.0	-	-	[213]
PBI	NUS-2	20.00	3.5	35	-	-	4.4	33.9	[214]
PBI-BuI	TpBD	50.00	20.0	35	-	-	14.8	48.7	[215]
Pebax-1657	Covalent triazine piperazine polymer	0.025	3.0	25	73.0	79.0	-	-	[216]
Matrimid	^{b)} HHU-COF-2	24.00	1.0	25	-	-	7.1	51.0	[217]
6FDA-DAM	3D-COF	10.00	1.0	25	-	-	850.0	29.0	[220]
PI	^{c)} SNW-1	5.00	4.0	25	-	-	12.4	13.3	[221]
PIM-1	SNW-1	28.00	2.0	30	4270.0	21.9	-	-	[222]
6FDA-DAM	COF-300	-	1.0	25	-	-	9830.0	75.0	[223]
PSf	UiO-66-NH ₂ @ TpPa-1	5.00	1.0	25	-	-	48.0	79.0	[224]
Pebax	^{d)} [bmim][Tf ₂ N] @ COF-300	7.00	1.0	30	-	-	1601.0	39.0	[225]
^{e)} XLPEO	2D-COF	1.23	5.0	30	803.9	61.4	-	-	[226]
PIM-1	^{f)} FCTF-1	2.00	1.0	30	-	-	4383.0	22.0	[227]
Pebax-1657/ PVDF	^{g)} TpDT	1.00	1.0	25	-	-	142.3	36.0	[228]
PDA	^{h)} TD-COF	3.00	1.0	30	9750.6	26.4	-	-	[229]

a) Pazine-linked covalent organic frameworks (ACOF-1); b) Heinrich-Heine University (HHU); c) Schiff base network (SNW); d) 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf₂N]); e) Crosslinked poly(ethylene oxide) (XLPEO); f) fluorinated covalent triazine frameworks (FCTF-1); g) TpDT synthesized with 1,3,5-tri-formyl-phloroglucinol (Tp) and 3,5-diamino-1,2,4-triazole (DT); h) transverse direction COF (TD-COF)

membrane. This can be attributed to the presence of porous features in the embedded COF nanosheets.

Duan *et al.* synthesized a combination of Pebax-1657 matrix and COF-5 nanosheets to create MMMs for CO₂ separation. These MMMs exhibited a significant increase in the permeability of CO₂ compared with unmodified membranes. Two potential theories were put forward to account for this tendency. 1) COF-5 and Pebax-1657 exhibit strong compatibility, allowing for the formation of H-bonds in the membrane and facilitating the transport of CO₂. 2) The COF-5 possesses a porous structure with a pore diameter of 2.7 nm, which reduces the barrier to gas transportation across MMMs[57]. Furthermore, when filler loading ranged from 0.1 ~ 1 wt%, the selectivity of CO₂/N₂ increased compared with the unmodified membrane, and there was an increase in permeability. The observed performance may be attributed to the uniform distribution of fillers within the specified range, resulting in the selective penetration of CO₂ over N₂ across the membrane. To provide more elucidation, Figure 4 presents a structure diagram of the behavior of the COF-based MMMs in the process of separating CO₂ from N₂. During a 120-hour testing period, the membranes consistently demonstrated steady function, indicating long-term stability.

Kang *et al.* established the initial application of COF-based MMMs

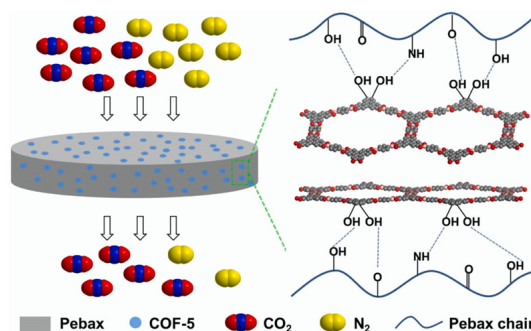


Figure 4. Gas transport schematic diagram of the COF-5/Pebax MMMs. Reprint permission from reference [57], Copyright 2019, Elsevier.

for gas separation by implementing NUS-2 and NUS-3[214]. The preparation of MMMs involved blending 2D COF nanosheets with PBI and poly (ether imide). These MMMs exhibited exceptional water stability, improved mechanical strength, enhanced gas permeability, and selectivity between the COFs and polymer matrices. The NUS-2@PBI MMMs exhibited an H₂/CO₂ selectivity of 31.4 when loaded with 20 wt% COFs, above the top limit set by Robeson in 2008. Nevertheless,

the flow (4.08 ± 0.03 Barrer) remained insufficient for commercial use.

The MMMs were created by Thankamony *et al.* for gas separation of CO₂/CH₄ and CO₂/N₂ utilizing covalent triazine piperazine (CTPP) in polyether-block-amide (Pebax-1657)[216]. The CTPP system, when combined with Pebax-1657, demonstrated robust interaction due to a substantial hydrogen bonding density. This resulted in the stiffening of the Pebax chain, even when the loading rates were modest. Imine-based COFs incorporating a biphenyl linker and triazine node were employed by Bügel *et al.*[217]. Additionally, they serve Matrimid-based MMMs as fillers along with their fluorinated derivative to separate CO₂ and CH₄. This choice was made based on the proper porosity and crystalline structure of the COFs, which resulted in enhanced membrane performance. When the COF filler loaded 24 wt%, the permeability of CO₂ increased from 6.8 to 13 Barrer. Nevertheless, a notable issue emerged regarding the enduring strength of the MMMs since they underwent shut-off within one year.

Guoliu *et al.* produced a set of MMMs by dispersing β -ketamine-linked TpTta-COF constructed by Tp and 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline (Tta) into PIM-1. To prevent the production of interface defects, it is essential to consider the separation selectivity and permeability of MMMs in the CO₂ transmission channel. The TpTta-COF and PIM-1 MMM exhibited a robust interaction, resulting in the most efficient separation of CO₂/N₂ with a selectivity of 26.3 and permeability of 9672 Barrer. The observed favorable pairing performance can be attributed to the allocation of TpTta-COF particles, which strongly attract CO₂ and play a crucial role in gas membrane separation[218].

The aforementioned studies emphasize the potential of COFs to play role in gas membrane separation. This is attributed to their adjustable chemical properties, distinct nano-channels, and organic structure. Incorporating COFs into polymer matrices has been shown to have long-term performance, stability, selectivity, and enhanced gas permeability. Additional investigation and advancement in this field may result in the extensive utilization of COF-based membranes for effective gas separation, improving sustainability.

4.4. HOF-based MMMs

HOFs are a newly discovered type of crystalline porous material. It is created by metal-organic molecules or linking organic molecules together through intermolecular H-bonds, forming networks in 1D, 2D, or 3D[230-232]. HOFs exhibit significant potential in the domain of gas adsorption and separation due to their notable characteristics, including tunable size, favorable compatibility, metal-free high stability, low densities, high crystallinity, large surface area, convenient purification, adjustable pore size, designable structure, recrystallization through self-healing, flexibility, easy regeneration and recovery, facile regeneration, and sustainability of the environment[233]. Figure 5 shows a general structure of HOFs.

The utilization of HOF-21 ($[\text{Cu}_2(\text{ade})_4(\text{H}_2\text{O})_2] (\text{SiF}_6)_2$) nanoparticles as a filler in Pebax polymer MMMs for CO₂ separation was proven by Wang *et al.*[234]. The MMMs obtained had exceptional performance, achieving a permeability of 750 Barrer CO₂/N₂ selectivity of 60 and CO₂/CH₄ selectivity of 40, surpassing the top limit set by Robeson.

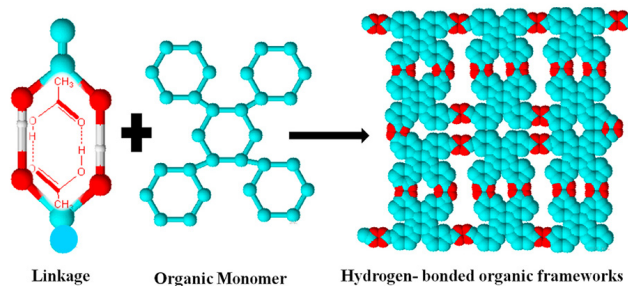


Figure 5. HOFs structure diagram. Reprint permission from reference [219], Copyright 2024, Elsevier.

4.5. MXene-based MMMs

MXenes are a new class of 2D materials with the formula $\text{M}_{n+1}\text{X}_n\text{T}_x$ ($n = 1-4$). In this formula, M represents transition metals like W, Ta, Sc, Hf, Mo, Nb, Zr, Y, Cr, or Ti. X represents C or N, while T represents surface terminal groups, for example, such as Cl, F, O, and OH[235-241]. The distinctive characteristics exhibited by MXene materials, including their robust hydrophilicity, chemical stability, minimal diffusion barriers, elevated permeability, substantial specific surface area, increased elasticity, precise sieving capabilities, versatile processability, and exceptional electrical conductivity, render them exceptionally well-suited for gas separation applications based on membranes [241]. Hence, the incorporation of MXene fillers has been shown to significantly enhance the mechanical characteristics of the MMMs [242]. Numerous approaches exist to produce membranes based on MXene, such as integrating certain additives or other materials to create MMMs, including MXenes[243].

Table 7 displays the CO₂ separation performance of MXene-incorporated MMMs in previous studies. Shamsabadi *et al.* documented the synthesis of MXene ($\text{Ti}_3\text{C}_2\text{T}_x$)@Pebax MMMs, which exhibited a CO₂/N₂ selectivity of 42 and a CO₂ permeability of 1986 GPU[244]. The $\text{Ti}_3\text{C}_2\text{T}_x$ exhibits a robust interaction with the amide group of Pebax, enhances the dispersion of $\text{Ti}_3\text{C}_2\text{T}_x$, and promotes the transit of CO₂ through the sub-nano interlayer channels of $\text{Ti}_3\text{C}_2\text{T}_x$. Guan *et al.* investigated the Pebax/m-MXene as having superior performance compared to the original Pebax membranes for the CO₂/N₂ gas permeation test through improved MMM gas separation efficiency. The MMM membrane, when doped with 0.5 wt% m-MXene, demonstrates a CO₂/N₂ selectivity of up to 93.18 and CO₂ permeability of 70.24 Barrer. These values represent an increase of 15.1% and 67.6%, respectively, compared to the original Pebax membranes[245].

The performance and stability of MXene/Pebax MMMs for CO₂ separation were examined by Liu *et al.*[246]. When the MXene concentration was increased to 0.15 wt%, the CO₂/N₂ selectivity and CO₂ permeance rose by 73.4% and 81%, respectively, relative to the clean membrane. Two hypotheses were proposed to explain this excellent gas separation performance: 1) The addition of MXene nanosheets containing a high concentration of polar groups enhanced the attraction of the Pebax membrane to CO₂ rather than N₂. 2) The laminar structure of MXene facilitated efficient diffusion of CO₂ through the membrane. Nevertheless, it was observed that an increase in MXene loading from

Table 7. Evaluation of MMMs Created with Different Combinations of Polymer and MXene, Including Their Performance, Optimal and Operating Conditions, and Modifications to the MXene

Membrane material	Material	Filler loading (wt%)	Pressure (bar)	Temperature (°C)	CO ₂ /N ₂ gas pair		CO ₂ /CH ₄ gas pair		Ref.
					Permeability (Barrer)	Selectivity	Permeability (Barrer)	Selectivity	
Pebax-1657	MXene	1.0	2.0	30	148.0	63.0	-	-	[108]
		10.0	2.0	30	584.0	59.0	-	-	
PEG (600)	Ti ₃ C ₂ T _x	25.0	1.0	25	813.5	32.2	813.5	27.9	[240]
Pebax-1657	Carboxymethyl cellulose (CMC) @MXenes	6.0	1.0	25	521 GPU	40.1	444 GPU	40.4	[240]
Pebax-1657	Ti ₃ C ₂ T _x	0.1	4.0	25	1810.3 GPU	42.0	1810.3 GPU	15.0	[244]
Pebax- Ti ₃ C ₂ T _x	MXene	0.05	4.0	25	1986.5 GPU	41.8	1986.9 GPU	14.8	[244]
Pebax-1657	^{a)} m-MXene	0.5	4.0	25	70.24	93.18	-	-	[245]
Pebax-1657	Ti ₃ C ₂ T _x	0.5	4.0	25	86.2	104.8	-	-	[245]
Pebax-1657	Ti ₃ C ₂ T _x	0.15	2.0	25	21.6 GPU	72.5	-	-	[246]
^{b)} CTA	Ti ₃ C ₂ T _x	3.0	1.5	25	-	-	16.0	57.1	[247]
^{c)} SILM	MXene			25	26.35 GPU	319.2	26.4 GPU	249.0	[248]
PVDF	Pebax/PEGDA-MXene		1.0	30	765.5	54.5	-	-	[249]
PDMS	^{d)} D-MXene	1.0	1.0	35	13917.0	13.6	-	-	[250]
PDMS	^{e)} ML-MXene	3.0	1.0	35	12556.0	12.5	-	-	[250]

a) multilayered MXene (m-MXene); b) cellulose triacetate (CTA); c) supported ionic liquid membrane (SILM); d) delaminated-MXene (D-MXene); e) multilayer MXene (ML-MXene)

0.15 to 0.3 wt% resulted in a reduction in CO₂ permeance and CO₂/N₂ gas selectivity. In addition, MMMs with 0.15 wt% MXene demonstrated exceptional stability throughout the 120-hour continuous test. The membrane showed outstanding and consistent gas separation capabilities, with a CO₂ permeance of 21.6 GPU and CO₂/N₂ selectivity of 72.5.

Shi *et al.* examined the difference between Ti₃C₂T_x and GO in the context of MMMs for CO₂ separation[108]. MXenes have a notably greater maximum loading capacity than GO, primarily attributed to their enhanced polymer matrix compatibility. The MXenes@Pebax MMMs exhibit a significant improvement in CO₂ separation performance, with a 66% enhancement in CO₂ permeability under dry-gas circumstances. In contrast, a notable improvement was seen in the permeability of CO₂ (178%) and selectivity of CO₂/N₂ (74%) for wet-state membranes. However, Guan *et al.* examined the CO₂ permeability of 0.5 wt% m-MXene/Pebax MMMs. The results showed that these MMMs had a CO₂/N₂ selectivity of 104.85 and a CO₂ permeability of 86.22 Barrer[245]. This can be attributed to the improved molecular sieving effect caused by interlayer channels of different widths. MXene-based MMMs exhibit significant promise for advancement as a nascent membrane material in gas separations.

4.6. g-C₃N₄-based MMMs

The g-C₃N₄-based membranes represent a novel type of 2D microporous material with significant promise in gas separation. This is primarily attributed to its distinctive physicochemical characteristics, adjustable surface properties, extremely thin thickness, uniform nano-

pores, exceptional chemical and thermal stability, and spore structure[251-253]. Like graphene oxide (GO), this material has a layered structure resembling graphite. This structure comprises linked tri-s-triazine ring units held together by amino groups on the plane and van der Waals forces inside the interlayers[254]. The main component of the structural units consists mainly of 6-membered rings joined by sp² hybridized carbon and nitrogen atoms.

This arrangement facilitates the formation of an aromatic p-conjugated system[253]. This particular type of 2D material exhibits the highest level of stability in the carbon nitride allotrope under normal operating circumstances for the production of MMMs used in CO₂ separation. Due to its chemical structure, the g-C₃N₄-based membrane has long-term endurance in real-world applications[255,256]. Jomekian *et al.* employed chitosan (CS)-modified g-C₃N₄ as a dopant for ZIF-8, effectively preparing CS/g-C₃N₄/ZIF-8 membranes. The findings indicate that the g-C₃N₄ membrane modified with CS and doped exhibits enhanced CO₂/CH₄ ideal selectivity compared to the pure ZIF-8 membrane. This is attributed to the amine group of CS's strong CO₂ adsorption capability. Furthermore, establishing a carbon-nitrogen bond between ZIF-8 and g-C₃N₄ has been found to have advantageous effects on enhancing the stability of the membrane[257].

Cheng *et al.* integrated g-C₃N₄ into the Pebax-1657 matrix to fabricate MMMs with enhanced CO₂ extraction capabilities. Using a thermal-etching approach, the researchers performed an initial analysis to synthesize dicyandiamide-sintered g-C₃N₄ nanosheets (DCN)[258]. The nanosheets were subjected to various processing durations (0-8 hours) to examine the impact of time on the morphology of g-C₃N₄.

Table 8. Evaluation of MMMs Created with Different Combinations of Polymer and g-C₃N₄, Including Their Performance, Optimal and Operating Conditions, and Modifications to the g-C₃N₄

Membrane material	Material	Filler loading (wt%)	Pressure (bar)	Temperature (°C)	CO ₂ /N ₂ gas pair		CO ₂ /CH ₄ gas pair		Ref.
					Permeability (Barrer)	Selectivity	Permeability (Barrer)	Selectivity	
Pebax-1657	g-C ₃ N ₄	0.25	3.0	25	33.3	67.2	-	-	[258]
PIM-1	^{a)} g-C ₃ N ₄ -D	1.00	3.5	35	3740.0	19.8	3740.0	12.4	[261]
Matrimid	protonated g-C ₃ N ₄	0.50	3.0	35	-	-	7.7	49.6	[262]
Pebax	^{b)} g-PTAP	2.50	1.0	25	154.6	83.5	154.6	22.8	[263]
Pebax	ZIF-90@g-C ₃ N ₄	3.00	2.0	25	110.5	84.4	-	-	[264]

a) g-C₃N₄ bearing with flexible propyl sulfonic acid groups formed through the reaction between 1,3-propanesultone with amino/ imino groups in g-C₃N₄ during sulfonation (g-C₃N₄-D); b) graphitic-polytriaminopyrimidine (g-PTAP)

Pebax was subjected to a loading concentration of DCN-4 nanosheets varying from 0.25 to 1 wt% to evaluate MMM's separation capability. Due to their CO₂-philic nature, DCN nanosheets improve CO₂/N₂ selectivity and CO₂ sorption solubility.

Furthermore, the produced MMMs exhibited improved selectivity in CO₂/N₂ diffusion while reducing the diffusivity coefficients of CO₂/N₂. The findings indicate that loading of 0.25 wt% is the most favorable concentration, resulting in the concurrent enhancement of CO₂ permeability and CO₂/N₂ selectivity. The cause of this could be the specificity with which g-C₃N₄ nanosheets can adsorb and transfer CO₂ over N₂[258].

Li *et al.* developed a new SILM that effectively separates CO₂/N₂ and CO₂/CH₄ by encapsulating 1-ethyl-3-methylimidazole acetate ([EMIm][AcO], IL) within 2D g-C₃N₄ nanospheres[259]. The confinement effect of g-C₃N₄ nanospheres, adding IL to the interlayer, can significantly improve the membrane's capability to separate substances.

In the year 2021, Wang *et al.* employed flexible graphene oxide (GO) nanosheets as a means to address the structural imperfections present in g-C₃N₄ nanosheets[260]. Interactions between -NH₂/-NH groups on the nanosheets' edges and -COOH groups on the surface of GO compensate for structural defects caused by the exfoliation process of g-C₃N₄ nanosheets. In this work, GO was effectively incorporated into g-C₃N₄ nanosheets. Modifying the flaws or voids of g-C₃N₄ nanosheets can be advantageous in the construction of a separation membrane that is both continuous and stable. In contrast, the g-C₃N₄ base membrane exhibits a notable enhancement in mechanical strength, accompanied by commendable long-term stability.

Table 8 presents the summary of previously reported g-C₃N₄-added MMMs. In a study by Voon *et al.*, functionalized g-C₃N₄ was integrated into the PIM-1 polymer matrix to fabricate gas separation membranes (MMMs)[261]. This study aimed to evaluate the impact of various functional groups employed for modifying g-C₃N₄ on the efficiency of MMMs in separating O₂/N₂, H₂/N₂, and CO₂/N₂. The gas separation findings indicate that the permeability of CO₂ in all manufactured MMMs containing 1 wt% was greater than that of other gaseous substances. The observed outcomes were attributed to the g-C₃N₄ nanosheets' propensity to adsorb CO₂ compared to other gaseous substances. The g-C₃N₄-D nanosheets, which were reformed with flexi-

ble propyl sulfonic acid groups, exhibited superior separation performance compared to other functionalized g-C₃N₄ nanosheets. This was evidenced by a CO₂ permeability of 3740 Barrer 19.8 and a CO₂/N₂ selectivity.

The field of gas separation is increasingly focusing on g-C₃N₄ nanosheets due to their excellent stability, variable surface characteristics, and ordered in-plane void structure. Nevertheless, more enhancements are required to address the interface fault between the filler and polymer. Furthermore, the direct involvement of nanopores on the surface of g-C₃N₄ in gas molecule transport poses a challenge, leading to a decline in the separation efficiency of the membranes. Hence, effectively harnessing the pore structure on the surface of g-C₃N₄ nanosheets remains a significant obstacle. 9 presents a summary of the gas separation statistics obtained from the literature for MMMs that are embedded with g-C₃N₄ nanosheets.

4.7. LDH-based MMMs

LDHs, typical ionic intercalated 2D materials, have the general formula[M²⁺_{1-x}M³⁺_{1-x}(OH)₂][Aⁿ⁻]_{x/n,m}H₂O, where M²⁺, M³⁺, and Aⁿ⁻ represent di-valent cations, tri-valent cations (e.g., Mn³⁺, Ga³⁺, Zn²⁺, Mg²⁺, Al³⁺, Cr³⁺, and Fe³⁺) and the interlayer anions, correspondingly[265]. The structure of LDHs consists of a host layer that is positively charged, including anions, and an interlayer of water. The exceptional gas separation performance of LDHs can be attributed to their distinctive physical and chemical properties. These properties include a versatile chemical composition, the ability to exfoliate LDHs into a single-layer nanosheet, a positive charge, adjustable size, tunable interlayer anion species, structural topology transformation, and adjustable metal elements of the host layer, among others[60]. The distinctive characteristics of LDHs have also resulted in distinct benefits for them in different areas of membrane separation and enhanced stability[266].

Table 9 exhibits the CO₂ separation performance of LDH-based MMMs reported in previous studies. Wang *et al.* used LDH laminates introduced with amino acids (AA-LDH) in the Pebax-1657 matrix to create MMMs for CO₂/CH₄ separation[267]. The MMM material, which includes 5 wt% AA-LDH, demonstrates a CO₂/CH₄ selectivity of 31 and an ideal permeability of 790 Barrer. These values are 83.9% and 64.6% greater than the original Pebax membrane. Two potential

Table 9. Evaluation of MMMs Created with Different Combinations of Polymer and LDH, Including Their Performance, Optimal and Operating Conditions, and Modifications to the LDH

Membrane material	LDH Type	Filler loading (wt%)	Pressure (bar)	Temperature (°C)	CO ₂ /N ₂ gas pair		CO ₂ /CH ₄ gas pair		Ref.
					Permeability (Barrer)	Selectivity	Permeability (Barrer)	Selectivity	
Pebax-1657	AA-LDH	5	2	30	-	-	790.0	31.0	[267]
Pebax-1657	ZIF-8@LDH	2	1	30	-	-	1307.0	31.6	[269]
Pebax-1657	3D hollow CoNi-LDH	1	8	25	172.6	71.6	-	-	[270]
Pebax-1657	LDH NSs	10	4	25	279.6	76.4	-	-	[271]
EVA	12AA-LDH	1	1	30	119.2	10.0	-	-	[272]

explanations for this exceptional performance were hypothesized: 1) Polar amino and carboxyl groups enhance the solubility of CO₂ by interacting with quadrupole moments. 2) These groups can operate as facilitated transport carriers, reversibly reacting with CO₂. Additionally, following the intercalation of amino acids, LDH demonstrated an increased interlayer gap, hence promoting the diffusion of CO₂ into the interlayer of LDH. The combined effects of these influences improved the permeability of CO₂ and the selectivity of CO₂/N₂ in the MMM[267]. In their study, Liu *et al.* developed a membrane with an ultrathin-selective layer of LDHs that carried CO₂. This membrane was designed to effectively separate CO₂, exhibiting a CO₂/CH₄ selectivity of 33 and a CO₂ permeance of 150 GPU[268]. Zhang *et al.* successfully achieved heterogeneous structure packing by cultivating ZIF-8@LDH/Pebax, which notably improved gas separation efficiency. One advantage is that the presence of many hydroxyl groups on the surface of ZIF-8 and LDH facilitates the dissolution of CO₂, hence enhancing gas selectivity[269].

LDHs have achieved significant advancements in MMMs for CO₂ separation, leveraging their intriguing interlayer structure and characteristics. Nevertheless, it possesses considerable potential for advancing situations involving separation applications. Enhancing the compatibility of LDHs with a polymer matrix or optimizing the molecular sieving performance can be achieved by surface modification, further interlayering, or adjusting the layer spacing. Evaluation of MMMs created with different combinations of polymer and LDH, including their performance, optimal and operating conditions, and modifications to the LDH.

4.8. TMD-based MMMs

TMDs are layered compounds denoted by 2D MX₂, where M denotes transition metal atoms from groups IV-VIII such as W, Mo, Nb, Zr, Ti, and X is a chalcogen (e.g., Te, Se, and S)[273-276]. Due to their diverse crystal structures, incredibly tiny thickness, and sheet structure, they have gained attention in electronics, catalysis, energy storage, and sensors[277-282]. Furthermore, TMDs have been extensively applied as fillers in fabricating high-performance composite membranes for gas separation research[283]. 2D TMDs are typically produced using a top-down exfoliation technique[277,284]. However, recently, bottom-up methods such as CVD have been developed to create 2D TMDs with consistent layers and excellent surface area[285, 286].

Table 10 provides a concise overview of selected TMD-based MMMs used for gas separations. Shen *et al.* used a drop-coating evaporation approach to manufacture the first-ever three-layered two-dimensional Pebax/MoS₂ MMMs to separate CO₂/N₂[287]. The CO₂/N₂ selectivity was significantly improved in the gas permeation test conducted using pure CO₂ and N₂ when utilizing MMMs, including 0.15 wt% of MoS₂. The selectivity of CO₂/N₂ was significantly enhanced from 44 to 93, while the CO₂ permeability improved from 45 to 64 barrer when compared to dense mix matrix films.

Liu *et al.* created MMMs by including MoS₂ nanosheets and Pebax-1657 to facilitate the separation of CO₂/N₂ gases[288]. Incorporating 4.67 wt% MoS₂ in the MMM resulted in the highest outcome, with the CO₂ selectivity and permeability values for CO₂/N₂ being 91 and 67 Barrer. These values represent a 1.46-fold rise in CO₂ permeability and a 2.02-fold increase in CO₂/N₂ selectivity compared to the membrane

Table 10. Evaluation of MMMs Created with Different Combinations of Polymer and TMDs, Including Their Performance, Optimal and Operating Conditions, and Modifications to the TMDs

Membrane material	Material	Filler loading (wt%)	Pressure (bar)	Temperature (°C)	CO ₂ /N ₂ gas pair		CO ₂ /CH ₄ gas pair		Ref.
					Permeability (Barrer)	Selectivity	Permeability (Barrer)	Selectivity	
Pebax-1657	CuBDC-ns/MoS ₂	2.50	4.0	35	123	69	123	18.00	[202]
Pebax	MoS ₂	0.15	0.2	25	64	93	-	-	[287]
Pebax-1657	MoS ₂	4.76	2.0	30	67	91	-	-	[288]
ZIF-8	MoS ₂	10.00	5.0	25	-	-	682	19.86	[289]

without any impurities. The enhancement was ascribed to the high attraction between CO₂ adsorption and MoS₂ nanosheets and the narrow gap between the layers (0.62 nm), which promotes the selective diffusion of CO₂ gas molecules over the membranes. The results proved the constructed MMMs' strong capability without any deterioration in their gas separation efficiency. MMMs, including TMD nanosheets as fillers, are currently in their development phase relative to other 2D materials. Despite the limited number of pertinent studies, further research in the future is justified due to its benefits, including a wide range of crystal structures, strong mechanical properties, and excellent stability.

5. Future perspectives of 2D materials-based MMMs

This study presents a summary of the latest progress in the area of CO₂ gas separation membranes utilizing 2D materials. Three distinct categories of membrane systems exist, specifically inorganic, polymeric, and MMMs. This research comprehensively analyzes the significance of several categories of inorganic fillers in MMMs. Despite the limited availability of review reports on MMMs. Nowadays, MMMs with various inorganic fillers are the main focus of gas separation research. These membranes have the potential to offer significantly greater levels of permeability and selectivity compared to pure polymer membranes. The significant advancement in numerous novel categories of inorganic materials in recent years suggests that MMM has the potential to become a future membrane. This review aims to analyze the existing literature on gas separation using various inorganic 2D materials based on MMMs. The gas transport data for various 2D materials, including graphene, MOFs, COFs, HOFs, TMDs, MXene, and g-C₃N₄, were obtained from existing literature and subjected to a comprehensive evaluation. MMMs possess unique chemical and physical characteristics, including an expansive surface area that obstructs gas transmission and a strong affinity for CO₂, which aids in the movement of CO₂ gas. Two-dimensional materials have enabled MMMs to exceed Robeson's upper limit, a widely recognized compromise between gas selectivity and permeability. In addition, 2D materials have enhanced the plasticization resistance, mechanical stability, and aging qualities of MMMs due to their exceptional mechanical and chemical capabilities and outstanding compatibility with the polymer matrix.

The research on MMMs will continue until the development of innovative inorganic materials, as it is recognized that inorganic fillers are crucial in MMMs for attaining enhanced permeability and improved selectivity in gas separation. There have been significant advancements in the laboratory testing of 2D material-based MMMs for membrane separation. Nevertheless, the field of 2D materials is currently in its nascent phase of investigation and has obstacles regarding their actual implementation in industrial gas separation. Firstly, to achieve optimal gas separation and enhance the membrane's long-term durability. Enhancing the interfacial compatibility of membranes has emerged as a significant problem, necessitating the achievement of a uniform dispersion of 2D microporous filler inside the polymer matrix. Nanosheets of COFs and MOFs exhibit enhanced compatibility be-

tween the matrix and filler compared to other 2D inorganic materials. Additionally, it demonstrates a notable level of permeability and exceptional separation capabilities in diverse gas separation applications, encompassing the separation of carbon dioxide. However, the issue of non-selective flaws and agglomeration persists. Additionally, 2D materials possess distinct features, including changing pore size and achieving homogeneous nanopores. When preparing novel 2D materials, it is crucial to consider enhancing their sieving performance, accurately regulating pore size, and ensuring stability in strong acids, high temperatures, and aqueous solutions. The technical challenges include inadequate long-term operational stability, limited scalability, susceptibility to aging, and low resistance to pollutants. To address future challenges, it is vital to consider the following factors: enhance the techniques used for producing membranes, lower the expenses associated with membrane materials, prolong their lifespan, promote environmentally friendly membrane materials, and highlight the significance of compounding and modifying membrane materials.

To summarize, the utilization of membrane-based CO₂ separation technology can significantly impact environmental remediation and the production of clean energy. Research on developing 2D material-based MMMs for CO₂ capture is currently highly active. Significant advancements have been made in the production of MMMs using 2D microporous materials that possess atomic thickness, surface chemical characteristics, excellent ratios, and distinctive and uniform aperture distribution. Due to their small thickness and large lateral dimensions, the developing 2D materials are promising candidates for exploration as fillers in the production of MMMs. This paper offers an overview of the most recent two-dimensional-based MMMs designed for gas separation applications. The investigation's primary focus was enhancing the selectivity and permeability of 2D membranes, including graphene, MOFs, COFs, HOFs, TMDs, MXene, and g-C₃N₄. Despite unresolved issues in practical applications, this technology remains a viable method for creating membranes with consistently enhanced separation performance. This review aims to serve as a valuable reference for generating interest in 2D material-based MMMs and offering practical information for their application in membrane gas separation.

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