Polycrystalline Metal–Organic Framework Membranes for Separation of Light Hydrocarbons

1. Introduction

As the building blocks of various organics, the global requirement of light olefins increases year by year and is expected to reach 200 million tons (ethylene and polyene) by 2023. The industrial separation of these light olefins typically relies on the technology of cryogenic distillation under high pressure and low temperature, which accounts for huge amount of energy as well as the similar great intensity of carbon emission. Finding separation systems without phase change may reduce the energy intensity by a factor of ten. As early platform, zeolites and activated carbons have shown substantial contribution to adsorption-based separations. However, when faced with these challenging mixtures (similar physical properties and molecular sizes), the intrinsic properties of the contracted or irregular pore systems either require high regeneration consumption or show very low selectivity. In addition, facing the unprecedented productions of cracked gas, the preparation of huge amount adsorbents remains a great challenging despite the cycling process.

About 40 years ago, membrane technology has been used for the recovery of hydrogen from ammonia plants. The success of these installations has attracted much attention of many researchers and experts, and this technology has been developed rapidly, such as natural gas purification, air separation. This is because membrane-based separations has attracted extensive attention owing to its smaller carbon footprint, low energy consumption, and environmental compatibility. Encouraged by zeolite-membranes and emerging pore systems of metal–organic frameworks (MOFs) materials, polycrystalline MOF membranes evoke a great deal of scientific interests. The mass transfer channel of MOF membranes can be finely designed and functionalized at molecular level. The highly crystalline nature of MOFs completely changed the traditional disordered and irregular channels in organic membranes, ensuring a steady sieving function based on the customized aperture of the channels.

Additionally, the rich nanochannel and functionalised surface promote the host–guest interaction for increased concentration gradient, which is crucial for accelerated mass transfer. Meanwhile, the soft activation of MOFs membranes, usually lower than 100 degree, indicates much lower energy consumption. Therefore, polycrystalline MOF membranes have shown tremendous potential for applications in the field of molecular separations, particularly for light hydrocarbons. This promising potential has also been predicted by a machine study.

MOFs are assembled by the coordination of metal salts and organic ligands. Different frameworks and environment of the nanospace may result in sharply different traffic for selective molecular diffusion. For membrane applications, the continuous MOF layers are necessary. However, the thin requirements and brittle characteristic make the preparation of polycrystalline MOF membranes in a great difficulty, particularly for their amplifications in meter scale. In view of this, it is an appropriate time to summarize the fabrication strategy of MOFs membranes and related applications in light hydrocarbons separation.
2. Fabrication Strategies of Polycrystalline MOF Membranes

Since the early reports of MOF-5, HKUST-1-based MOF membranes, a group of MOF membranes have been developed, including in-situ growth,[29] secondary growth,[30] layer-by-layer deposition,[31] counter-diffusion interfacial synthesis,[32,33] solvent-free conversion and fast current-driven synthesis.[34,35] However, considering the differences in types of building blocks and also the difference in selected supports, the various MOFs growth and minimal possible defects are very important. In the following sections, fabrication strategies of polycrystalline MOF membranes are discussed in detail (Figure 2).

2.1. In-situ growth

In-situ growth is the most commonly used strategy for preparing polycrystalline MOF membranes. It refers to that the substrate is directly immersed in the reaction solutions. The MOF segments nucleate and grow on the surface of the substrates, and finally forms a continuous and compact MOF membrane (Figure 3a).[36] In early of 2005, the MOF film (MOF-5) was successfully fabricated by Fischer groups, but the MOF layer features a significant defect.[37] Encouraged by this work, Lai et al. synthesized a continuous and well-intergrown MOF-5 membrane on porous α-Al₂O₃ substrate by this methodology.[38]

After this pioneering work, other researchers successively fabricated ZIF-7 membrane,[39] UiO-66 membrane,[40] HKUST-1 membrane,[41] CAU-10-H membrane,[42] MOF-303 membrane,[43] MIL-160 membrane and so on.[44] However, MOF crystal will produce competitive bulk nucleation in the reaction solution, which is unfavorable for heterogeneous nucleation of MOF crystal on the substrate so as to form poor grain boundary structure.[45]

Because the composition and aperture of the substrate may affect the permeability and selectivity of the prepared membrane, different types of substrates can be used, such as some materials with low price, flexibility, or high stability. Lu et al. selected potassium hexatitanate (K₂Ti₆O₁₆) as the substrate, due to its chemical-/thermal-stability and high affinity for Cu²⁺ in a weak acid environment. So as that, a continuous Cu-BTC...
membrane was successfully prepared on this support. Comparably, the Cu-BTC membrane that prepared by this method on an alumina support is discontinuous.

Given these observations, modification of substrate surfaces have been considered, as the implanted groups on the substrate surfaces may work as a bridge to connect the building blocks of MOFs and the substrates. Typically, the polydopamine (PDA) was selected for substrate modification, where the hydroxyl groups of the PDA reacted with Al moiety on the substrate, while the N of the PDA coordinates with Zn$^{2+}$ to form a node layer of ZIF-100. Further coordination reaction of Zn$^{2+}$ and cbIM translates the building blocks into a MOF layer that tightly attached on the substrate surface (Figure 3b). Using the same methodology, they prepared a highly symbiotic, continuous, and compact MIL-160 membrane. Due to the changed ligands, 3-aminopropyl triethoxysilane (APTES) has also been selected for modification α-Al$_2$O$_3$ for exposed NH$_2$ layers by us (Figure 3c). The tightly packed NH$_2$ groups endow the formation of hydrogen bonds with the carboxylate unit from the tetrakis(4-carboxyphenyl)porphyrin (TCPP) ligand. Interestingly, due to the large π system of the ligand, as well as the assistance of the surfactant, the alternative reaction of TCPP and Cu$^{2+}$ gave a vertically packed MOF nanosheet membranes. Similarly, Caro et al. pre-modified the porous TiO$_2$ disks with APTES, of which the terminal ethoxy group of APTES react with the hydroxyl group of TiO$_2$ support, followed by a successful preparation of a well-intergrown ZIF-22 membrane.

Besides the covalent surface modification, deposit carbon nanotubes (CNTs) has also attracted attentions for membrane assembly, as the significant characteristic of uniformly distributed π-π bond. With the help of carbon nanotube, the anchored 2-methylimidazole (2-MIM) facilitates to react with Zn$^{2+}$ to form an oriented ZIF-8 membrane (Figure 3d). Meanwhile, homologous metals can also be directly used as substrates and metal center to boost the nucleation of MOF crystals. Therefore, a “twin copper source” strategy was developed by Qiu and Zhu group. For the strategy the initial configuration of various fabrication strategies for polycrystalline MOF membranes.

Figure 2. Schematic diagram of various fabrication strategies for polycrystalline MOF membranes.

In situ growth

Secondary growth

Layer-by-layer

Contour-diffusion

Secondary growth

Figure 3. Fabrication of polycrystalline MOF membranes by in situ growth. (a) Schematic representation of in situ growth synthesis. (b) Schematic illustration of the preparation of ZIF-100 membrane on PDA-modified Al$_2$O$_3$ substrate. (c) Schematic diagram of the formation of highly oriented MOF membranes on surface functionalized α-Al$_2$O$_3$ supports. (d) Schematic diagram of the synthesis of [100]-oriented ZIF-8 membrane using 2-MIM-anchored CNT. (e) Optic micrographs (left) and SEM image (right) of the net-supported Cu$_3$(BTC)$_2$ membrane. Reproduced with permission.[Ref.32] Copyright 2015, The Royal Society of Chemistry. Reproduced with permission.[Ref.33] Copyright 2023, ELSEVIER. Reproduced with permission.[Ref.36] Copyright 2022, AAAS. Reproduced with permission.[Ref.37] Copyright 2009, American Chemical Society.
oxidization of the copper mesh is very important. This is because the reaction kinetic between the ligands and CuO are faster than that of the ligand and Cu (Figure 3e).\textsuperscript{[52]} Similar strategy was extended on the membrane preparation of the Ni-based MOF on nickel mesh\textsuperscript{[53]}

2.2. Secondary growth

The secondary growth includes two processes: pre-coating the nano-seed on the porous support by physical (dip coating, rubbing, spraying, dropping, spin coating) or chemical method (in-situ chemical reaction), and immersing the seeded support in the mother solutions for further growth (Figure 4a).\textsuperscript{[54]} Gascon et al. used a spin-coating method to prepare a crystal layer on a porous α-Al\textsubscript{2}O\textsubscript{3} substrate, then a compact and well-intergrown HKUST-1 membrane was obtained.\textsuperscript{[55]} To ensure seed crystals can strongly bind to the support surface, Jeong et al. developed a thermal coating strategy, that is, the porous α-Al\textsubscript{2}O\textsubscript{3} support is heated to 200°C, and the precursor solutions for synthesizing HKUST-1 seed crystal is directly dropped on the surface of the support until it is completely covered, followed by cleaning and ultrasonic. This process was repeated three times to form a strongly bonded crystal layer.\textsuperscript{[56]} Interestingly, Kim et al. prepared continuous Cu\textsubscript{3}(BTC)\textsubscript{2} membrane by thermal spraying seeding and secondary growth strategy.\textsuperscript{[57]} Different from physical coating, in-situ chemical reaction can also realize the planting of seeds on the support. The α-Al\textsubscript{2}O\textsubscript{3} support reacts with the 1,4-benzene dicarboxylic acid (H\textsubscript{2}BDC) to produce a seed layer at first, then an uniform MIL-53-Al membrane can be produced after the solvothermal reaction of the seed-coated support in corresponding mother solution(Figure 4c).\textsuperscript{[58]}

Compared with the in-situ growth, the isolated steps of nucleation of MOF grains and membrane assembly was expected to promote the heterogeneous nucleation and the densification of the membrane. Further, the exposed crystal surface and oriented seeds help the formation of oriented MOF membranes. By utilizing the microwave-induced thermal deposition strategy, Lai et al. found that the seed layer exhibits uniform direction along the crystal face of [1 0 –2], which
therefore benefits the preparation of the oriented MOF-5 membrane by further solvothermal reaction.\[59\] Additionally, due to the weak bonding between MOF seeds and support surfaces, the preparation process often requires addition of polymers for cohesions. Such as, the introduced polyethyleneimine (PEI) forms coordination bonds with metal salts and hydrogen bonds with free hydroxyl groups of the support surface, exemplified by the ZIF-8 membrane.\[60\] Similarly, Zhang et al. combined the surface coating and secondary growth, of which the seed crystal was prepared on the polyvinylpyrrolidone (PVP) treated AAO at first, then a well-intergrown and \([0 2 2]\) oriented UiO-67 membrane was prepared (Figure 4b).\[61\] In addition to adhesives, water may also work as a directional regent for seed layer deposition. Thanks to the interface of the water-air, tiny crystals were uniformly separated on water, which were then transferred to the surface of the porous supports. The residual water was facially removed by single-mode microwave field. Therefore, the c-oriented seed layers give perfect platform for forming of a highly c-oriented NH$_2$-MIL-125 (Ti) membrane (Figure 4d).\[54\]

2.3. Layer-by-Layer deposition

The layer-by-layer (LBL) growth is based on the alternative introduction of the reaction partners of corresponding MOFs. The cycling process can be finely controlled, which is very powerful for obtaining the membrane with desired thickness (Figure 5a).\[63\] In 2007, a crystalline HKUST-1 membrane was developed by Wöll group by applying LBL.\[63\] Encouraged by this promising strategy, the ZIF-8 SURMOF, UiO-66-NH$_2$ and SIFSIX-3-Ni membranes with thickness of 500 nm, 100 nm and 5 \(\mu\)m were synthesized.\[64–66\] For avoiding the hole or crack of the first layer, a densely arrayed living reactive groups (LRGs) was implanted on a polymeric substrate by using a high energy \(\gamma\)-irradiation, then the LBL strategy was employed to prepare the membrane. After only four cycles, an integral a UiO-66-NH$_2$ membrane with thickness of \(~ 44\) nm was obtained (Figure 5b).\[67\]

Theoretically, the alternative reaction of the building blocks should provide a flat and integral MOF membrane, however, the introduced air bubble or evaporated solvents usually resist the further coordination in a limited space, yielding a hole or grain boundary defect. Notably, this method can be believed as a good tool for seed layer preparation. Combining the above strategy of secondary growth, a seed (HKUST-1) layer was prepared by four coordination cycles, followed by a fabrication of a continuous and well-intergrown membrane with secondary growth method (Figure 5c).\[46\]

2.4. Counter-diffusion interfacial synthesis

Counter-diffusion approach allows for fabrication of continuous and well-intergrown MOF layers based on interfacial engineering (Figure 6a).\[68\] In 2011, the first instance of ZIF-8 membrane

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Figure 5. Fabrication of polycrystalline MOF membranes by Layer-by-Layer deposition. (a) Schematic representation of layer-by-Layer deposition. (b) Schematic description of the LBL for the synthesis of ultrathin MOF coatings. (c) Schematic diagram of layer-by-layer deposition of HKUST-1 seed (left); AFM images of seeds support during different cycles (right). Reproduced with permission.\[Ref.53\] Copyright 2020, The Royal Society of Chemistry. Reproduced with permission.\[Ref.31\] Copyright 2011, American Chemical Society.
was prepared on nylon support by Yao group. Interestingly, the self-limiting characteristic of this strategy enables membrane defects to be recognized. Therefore, this strategy can be used to repair membrane defects. The inter-crystal gaps of defective ZIF-8 layers were perfectly filled with newly-grown crystals after healing process for 6 h (Figure 6b).

It is worth noting that the membrane thickness is always maintained at 1.5 μm. Similar strategy can be extended on the inter-crystalline defects reduction of the Cu-BTC membrane on α-Al₂O₃ support.

In order to apply the counter-diffusion strategy with inexpensive hollow fiber support, Brown et al. reported an interfacial microfluidic membrane processing (IMMP) approach for fabrication of ZIF-8 membranes (Figure 6c). The building blocks of MOFs were pumped into the shell side of the hollow fiber respectively. After that, a controllable growth of ZIF-8 membrane was started through continuous bore solution flow and static bore solution conditions.

**2.5. Solvent-free conversion**

Large amount solvents that used in MOF membrane preparation may cause safety and processability problems. Hence, a versatile solvent-free conversion approach is highly desired for the mass production of MOF membranes. In 2016, a chemical vapor deposition (CVD) was first reported for preparation of ultrathin ZIF-8 films on silicon wafers. With full conversion of 3 nm zinc oxide (ZnO) precursor layers, the thickness of the ZIF-8 membrane is about 52 nm. However, ZIF-8 membranes deposited on dense supports are not applicable for gas separation. Encouraged by this promising strategy, Zhang et al. proposed a novel gel-vapor deposition (GVD) for the preparation of high-quality ZIF-8 membranes on polyvinylidene difluoride (PVDF) hollow fibers (Figure 7a). Zn-based gel layer reacted with vaporized ligand, leading to a continuous ZIF-8 layer with thickness of ~87 nm. Notably, they further prepared MOF membrane modules with large effective area (~340 cm²), achieving the initial goal of scale-up production of MOF membranes.

Prior strategies mainly concentrated on depositing another porous material on the support surface. Tsapatsis et al. reported a different method for the synthesis of high-performance ZIF-8 membranes (Figure 7b). The impermeable ZnO was deposited to block the pores of Al₂O₃ with up to 50 atomic layer deposition (ALD) cycles. After that, the resultant support was exposed to vaporized ligand for formation of a ZIF-8 layer. Interestingly, the outer macroporous or mesoporous Al₂O₃ combines with the embedded microporous materials to form a highly selective MOF membrane. The same group further integrated this strategy with vapor phase ligand treatment (VPLT) to prepare high-quality ZIF-8 membranes.
2.6. Fast current-driven synthesis (FCDS)

FCDS strategy was developed to control coordination reactions between deprotonated ligands and metal ions based on electrochemical principles. The unique self-inhibited growth function allows for fabrication of defect-free MOF membranes. Meanwhile, the membrane thickness can be finely controlled by the applied voltage. More importantly, the preparation time can be shortened to several minutes from general days or weeks in other methods. In 2018, Wang et al. reported the first instance of continuous ZIF-8 membranes that prepared in 20 min (Figure 8a).

$$\text{Zn}^{2+} \text{ ions reacted with deprotonated imidazole anions to form ZIF-8 layers with external current of 0.7 mA cm}^{-2}.$$ 

Notably, membrane defects that were once exposed to reaction solution under current-driven will be healed to form ZIF-8 crystals. Similar strategy was extended on the membranes fabrication of ZIF-8 on Polypropylene (PP) substrate and porous stainless steel hollow fiber. Recently, Eddaoudi et al. reported a versatile electrochemical directed-assembly method for preparing a series of defect-free fcu-MOF membranes. Pre-assembled hexanuclear clusters and ditopic linkers ($H_2L$) were crucial segments of high-quality membrane formation. Additionally, two guidelines of ligand concentration and pKa values of the involved ligands were investigated for optimal synthesis conditions of continuous MOF membranes (Figure 8b). Furthermore, the same group extended this strategy to prepare mixed-linker MOF membranes based on fumarate (fum) and mesaconate (mes) linkers ($fum: mes = 2:1$).

The strategies for preparing MOF membranes are diverse and their advantages and disadvantages are also very obvious (Table 1). Typically, in-situ growth is the most commonly used fabrication strategy due to its facile manipulation procedures and high reproducibility. However, it also suffers from difficult heterogeneous nucleation. Secondary growth is favorable for the formation of compact membranes and can be easily controlled, but it requires strict size requirements. Layer-by-layer deposition is accurate to control the thickness of the membrane, but it is expensive. Counter-diffusion interfacial synthesis and solvent-free conversion are self-repairing of defects and do not need any solvent, respectively, but they demand for rapid nucleation of grains and unsatisfactory membranes thickness, respectively. Fast current-driven synthesis is faster formation of membranes, but demand for the conductive supports.

![Figure 7](image-url) Fabrication of polycrystalline MOF membranes by Solvent-free conversion. (a) Schematic illustration of the GVD fabrication gel of ZIF-8 membrane. Reproduced with permission.[Ref.62] Copyright 2017, Nature Publishing Group. Reproduced with permission.[Ref.63] Copyright 2018, AAAS.

![Figure 8](image-url) Fabrication of polycrystalline MOF membranes by FCDS. (a) Schematic diagram of the formation of ZIF-8 membranes using FCDS approach (left) and different phases for membrane prepared via different methods. (b) Two guidelines allow the discovery of the optimal conditions for fabrication of continuous fcu-MOF membranes. Reproduced with permission.[Ref.65] Copyright 2018, AAAS. Reproduced with permission.[Ref.68] Copyright 2021, AAAS.

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Table 1. Summary of various fabrication strategies for polycrystalline MOF membranes.
route to fabricate membranes with facile operation procedures and high reproducibility. But the harsh synthesis conditions and difficult heterogeneous nucleation are still unignorable. In contrast, secondary growth greatly reduces the nucleation difficulty via pre-coating high-density nano seeds layer on the support. Therefore, the key segments are the formation of nanoseed crystals and uniform seeding. For many MOFs with large sizes, seed-assistant growth may be inappropriate. The above mentioned solvothermal routes may result in pinholes and cracks owing to different thermal expansion coefficients between support and MOFs. Additionally, LBL deposition was developed to finely control the membrane thickness through cycle operation. However, the introduced air bubble or evaporated solvents may lead to membrane defects. By comparison, the counter-diffusion strategy allows membrane defects to be identified and healed, where large amounts of organic solvents were consumed with increased fabrication cost. Interestingly, solvent-free conversion is promising for large-scale production of MOF membranes in a green and inexpensive route, and meanwhile, a facile FCDS strategy with self-inhibited growth provides a mild and fast route for defect-free MOF membrane fabrication. Notably, it is applicable on different inexpensive supports, displaying a promising prospect for the mass production of MOF membranes. Nowadays, in the face of the large-scale structural diversity of MOF materials, we believe that it is hopeful to develop a method, such as integral strategy, suitable for facile membrane preparation.

3. Light Hydrocarbons Separations

Due to their controllable structures and adjustable compositions, applications of MOF-based polycrystalline membranes in gas separation show a bright future. In recent, a large amount of continuous MOF membranes has been developed as promising candidates for applications in light hydrocarbons separation. In the following sections, typical and emerging examples of high-performance MOF membranes will be discussed.

3.1. CO$_2$/CH$_4$ separation

CH$_4$ is the main component of natural gas while accompanied by undesired impurities. Among these gases, the acidic CO$_2$ may severely corrode the pipeline, leading to increased transport costs. Therefore, efficient CO$_2$/CH$_4$ separation presents a great significance. Notably, considerable high-quality MOF-based polycrystalline membranes has been applied for CO$_2$/CH$_4$ separation. Moreover, they show higher permeability due to its uniform pore aperture. Zhu et al. successfully prepared a continuous CO$_2$(HCOO)$_2$, a type of microporous materials with one-dimensional zigzag channels (5.5 Å), membrane on macro-porous glass frits, which showed a high CO$_2$ permeance of 2.09 x 10$^{-6}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ and separation factors of 10.37–15.95. During the separation process, CO$_2$ was preferentially adsorbed by microporous and external surfaces. Due to the limitation of pore aperture, CO$_2$ and CH$_4$ cannot pass through simultaneously, which has a certain blocking effect on the diffusion of CH$_4$ molecules.

Due to appropriate pore size (3.4 Å), ZIF-8 has been regarded as an ideal membrane material for CO$_2$/CH$_4$ separation. But the intrinsic lattice flexibility will make the actual sieving pore-aperture slightly larger than 3.4 Å, leading to unsatisfactory CO$_2$/CH$_4$ separation factors. In view of this, Wang et al. reported a mixed-linker strategy to confine the lattice flexibility and narrow the pore size of ZIF-8 membranes. A series of hybrid ZIF-7x–8 membranes based on 2-MIM and benzimidazole (BIM) mixed ligands were synthesized (where x represents the molar percentage of BIM in the hybrid structure). Compared with pure ZIF-8 membranes, as the BIM loadings increased to 22%, the resultant membrane exhibited a CO$_2$/CH$_4$ separation selectivity of 25. Similarly, this strategy was extended on the hydrophobic membrane preparation of the MIL-160/CAU-10-F (Figure 9a). MIL-160 is one kind of Al-MOFs with a structure similar to the CAU-10 series. In addition, the narrowest pore window size and the largest polarity can enable the CAU-10-F to have stronger host–guest interaction with CO$_2$. Thus, the resultant membrane exhibited a CO$_2$/CH$_4$ selectivity of 78 and CO$_2$ permeance of 716 GPU, better than that of pristine MIL-160 membrane. (Figure 9b) Also, the MIL-160/CAU-10-F membrane still sustained good separation performance after a week of stability testing.

In recent, a new type of MOF glass membranes has attracted extensive interest for efficient CO$_2$/CH$_4$ separation. Some MOFs like reported ZIF-4, ZIF-62, and TIF-4 have been proven to have enough to reach the melting state before framework decomposition. Jiang et al. reported a defect-free ZIF-62 glass membrane showed an excellent CO$_2$/CH$_4$ selectivity of 36.6 and CO$_2$ permeance of 2602 Barrer, far exceeding the Robeson upper bounds (Figure 9c–9d). Afterwards, Li et al. successfully synthesized the TIF-4 and hybrid ZIF-8/262 glass membranes for CO$_2$/CH$_4$ separation, both exhibited high separation factors beyond 30.

3.2. C$_2$H$_4$/C$_2$H$_6$ separation

C$_2$H$_4$ is the most important raw material in modern chemical industry. Owing to a narrow range of molecular size differences between C$_2$H$_4$ and C$_2$H$_6$ (0.4–0.25 Å), their separation still presents significant difficulties. To date, MOF polycrystalline membrane separation has been proven to be a potential alternative technology on account of the size-sieving mechanism.

ZIFs possess narrow pore sizes to become promising membrane materials for actualizing the adsorption and separation of small molecules. Caro et al. pioneered the microwave heating synthesis of ZIF-8 polycrystalline membranes for an equimolar C$_2$H$_4$/C$_2$H$_6$ separation, with the resultant separation selectivity of 2.8. Afterwards, Dittmeyer et al. fabricated ZIF-8 SURMOF membranes via a liquid phase epitaxial (LPE)-LBL method, with relevant C$_2$H$_4$/C$_2$H$_6$ separation selectivity (5 = 2.6). To further improve separation performance, Lai et al.
fabricated high-quality ZIF-8 membranes.\textsuperscript{[31]} The resultant [100] oriented ZIF-8 has a four-membered (4-M) window, based on the “swing effects” which may enlarge the window aperture to 4.0 Å for potential C$_2$H$_4$/C$_2$H$_6$ separation. (Figure 10a–10b) Compared with the randomly oriented ZIF-8 membrane, the obtained ZIF-8 membrane exhibited an excellent C$_2$H$_4$/C$_2$H$_6$ selectivity of up to 9.6 and C$_2$H$_4$ permeance of 130.3 Barrer. (Figure 10c–10d)

Recently, Liu et al. presented a highly c-oriented Co-gallate membranes for efficient C$_3$H$_6$/C$_3$H$_8$ separation.\textsuperscript{[99]} By utilizing a novel freezing contra-diffusion method, the grain nucleation and growth kinetics were precisely regulated. The resultant membranes exhibited unprecedented C$_3$H$_6$/C$_3$H$_8$ selectivity of 8.3. In particular, the combined separation performance of C$_3$H$_6$/C$_3$H$_8$ exceeds the upper bounds of current polycrystalline MOF membranes, MOF-based mixed matrix membranes (MMMs) and polymer membranes, laying the foundation for further performance improvement.

### 3.3. C$_3$H$_6$/C$_3$H$_8$ separation

C$_3$H$_6$ is an extremely significant building block for various valuable chemicals, including polypropylene, isopropyl alcohol, and propylene oxides.\textsuperscript{[100,101]} Nevertheless, the purification of C$_3$H$_6$ is considered a challenging task in industrial separation in terms of the high affinity between C$_3$H$_6$ and C$_3$H$_8$.\textsuperscript{[2,102,103]} Generally, cryogenic distillation is the prevailing approach for C$_3$H$_6$/C$_3$H$_8$ separation in industry, which is a mature yet extremely energy and cost-intensive process.\textsuperscript{[104,105]} The difference between the kinetic diameters is very slight for C$_3$H$_6$ and C$_3$H$_8$ (~0.2 Å), although challenging, polycrystalline MOF membrane separation technology has ranked as an alternative approach based on the molecule sieving. Due to framework flexibility, sodalite zeolite structure (SOD) ZIF-8 exhibits a well-fitted effective pore-aperture (4.0–4.2 Å), allowing different kinetic diffusion of C$_3$H$_6$ and C$_3$H$_8$.\textsuperscript{[106]} Jiang et al. reported ultrathin ZIF-8 membranes with a thickness of 180 nm, which showed an excellent C$_3$H$_6$/C$_3$H$_8$ selectivity of 120 and C$_3$H$_6$ permeance of 386 GPU (Figure 11a–11b).\textsuperscript{[107]}

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**Figure 9.** (a) Crystal structures of MIL-160/CAU-10-F membranes. (b) Single-gas permeance of MIL-160/CAU-10-F membranes. (c) Comparison of the CO$_2$/CH$_4$ separation performances of MIL-160/CAU-10-F membranes with other polycrystalline membranes. (d) Schematic illustration of ZIF-62 glass. (e) Single-gas permeance of ZIF-62 glass membranes. (f) Comparison of the CO$_2$/CH$_4$ separation performances of ZIF-62 glass membranes with membranes. Reproduced with permission.[Ref.73] Copyright 2021, American Chemical Society. Reproduced with permission.[Ref.77] Copyright 2020, Wiley-VCH.
Theoretically, uncontrollable polycrystalline membrane micro-defects and intrinsic lattice flexibility show moderate separation performance, hindering the practical application. To conquer this scarcity, a high-quality polycrystalline ZIF-8 membrane with low defect density is regarded as the foundation, then suppressing the lattice flexibility to fulfill highly efficient C$_3$H$_6$/C$_3$H$_8$ separation. Wang et al. reported new rigid ZIF-8 membranes via FCDS. Based on a local in situ electric field, ZIF-8 was assembled into an inborn-distorted phase structure called ZIF-8$_{\text{Cm}}$ (Figure 11c). The ZIF-8$_{\text{Cm}}$ polymorph displayed a more rigid framework structure and better molecule sieving capacity compared with the ordinary phase structure. Molecular dynamics simulations exhibited the C$_3$H$_6$/C$_3$H$_8$ separation factor of rigid ZIF-8$_{\text{Cm}}$ polymorph membrane is three times more than that of flexible ZIF-8 membranes. Ultimately, the obtained membranes showed an unprecedented C$_3$H$_6$/C$_3$H$_8$ selectivity of 304.8 as well as C$_3$H$_6$ permeability of 52 GPU (Figure 11d).

In addition, Zhong et al. reported a new state of MOF membranes with low-crystallinity (LC–MOF) by Interface Layer Polarization Induction. Due to the Interface Layer Polarization Induction, all three types of LC–MOF membranes formatted abundant open metal sites, which formed π bond interactions with C$_3$H$_6$ for preferential affinity. DFT calculation and molecular simulation confirmed that the formation of LC–MOF ultrathin membranes was controlled by the polarized interface layer. The defect-free diethanolamine (DEA) modified ZIF-8 LC–MOF membranes prepared in this work showed unprecedented C$_3$H$_6$ permeability of 3000 GPU as well as good C$_3$H$_6$/C$_3$H$_8$ selectivity of 90.

Recently, Liu et al. prepared a high-quality ZIF-8 membranes for enhanced C$_3$H$_6$/C$_3$H$_8$ separation. Based on an epitaxial supercritical fluid processing, defect-free ZIF-8 layer was available. The resultant membranes showed a promising C$_3$H$_6$ permeance of 1.6 × 10$^{-8}$ mol m$^{-2}$ s$^{-1}$ pa$^{-1}$ and separation factors of 78.2.

4. Conclusions and Perspectives

Membrane technology is giving momentum to MOFs and will promote their applications for light hydrocarbons separations. The promising nature will definitely endow the MOFs to show a bright future. Typically, the selectivity can be finely solved by using the MOF with a suitable window aperture, or the MOFs with local dynamic, in which the olefins can be exclusively recognized. Moreover, the recovery of the changed structure may further accelerate the diffusion of the adsorbed molecules, thus promoting the permeance. Additionally, the designed and controllable interlayer space may work as the 2D mass transfer
channel for desired separation performance. Technically, the developed strategy allows oriented MOF growth with reduced thickness, which can further increase the efficiency of the sieving process, due to the straight and short mass transfer path.

Despite the fruitful fundamental achievements, there are no feasible applications of polycrystalline MOF membranes now, as the lack of prepared MOF membranes on industrialized scale. Therefore, to achieve this goal, current solutions remain need optimization. Up to now, the solvent-free conversion, CVD and FCDS methods exhibit a great promise for membrane production at large scale with low cost. Meanwhile, interfacial assembly process is readily transferred the building blocks of MOFs on different supports with large scale, including the soft the porous polymers. Therefore, the combination of the above strategies is expected to make up for each other’s shortcomings and thus achieve high-quality MOF membranes. Although the existing challenges, the fascinating structures and separation performance in lab-scale make us believe that revolutionary improvements for meeting industrial requirements can be highly expected on polycrystalline MOF membranes.

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**Conflict of Interests**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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