Design of Metal-organic Framework Membranes Towards Ultimate Gas Separation

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Metal-organic framework (MOF) membranes have shown unprecedented opportunities for energy efficient separation of diverse industrially important gas pairs (e.g. H₂/CO₂, CO₂/N₂, CO₂/CH₄, and C₃H₆/C₄H₈). Among the various factors, microstructure manipulation (including thickness, orientation, and grain boundary structure) and framework tuning (including pore size, framework rigidity/flexibility, and stimuli responsiveness) of MOF membranes have been found playing dominant roles in their separation performances. In this perspective, we highlighted some recent progress in polycrystalline MOF membranes with emphasis on the elucidation of the structure-performance relationship at different scales.

1. Amorphous and low-crystalline MOF membranes

Fabrication of amorphous and low-crystalline MOF membranes has provided an opportunity for achieving better separation performance. In this regard, MOF glasses are attractive candidates for membrane fabrication due to their great potential for grain boundary defect elimination that is unavoidable for polycrystalline MOF membranes. Jiang et al.[1] prepared ZIF-62 MOF glass membranes by melt-quenching polymerization of polycrystalline ZIF-62 layers. The molten ZIF-62 phase penetrated into nanopores of substrates and precluded the generation of intercrystalline defects. Resultant glass MOF membranes exhibited excellent molecular sieving properties towards H₂/CH₄, CO₂/N₂ and CO₂/CH₄ gas pairs.

As a step further, Zhong et al.[2] fabricated low-crystallinity-state ZIF-8 membranes via interface layer polarization induction. Owing to the presence of abundant open metal sites, the diffusivity of C₂H₆ molecules through low-crystalline ZIF-8 membranes was significantly enhanced, resulting in unprecedented C₂H₆ permeance (2000~3000 GPU) and attractive C₂H₆/C₃H₈ selectivity (90~120).

2. Stimuli-responsive MOF membranes

The intrinsic structural flexibility represents a critical challenge facing precise molecular sieving of MOF membranes. Nevertheless, several recent studies indicated that stimuli-responsive MOF membranes may exhibit enhanced gas selectivity upon exposure to light irradiation, electric field, or high temperature accompanying with their structural transition. Taking ZIF-8 as a typical example, Caro et al.[3] demonstrated that gas permeation behavior of ZIF-8 membranes was switchable under a direct-current electric field poling, owing to the structural transformation of flexible ZIF-8 lattices into polymorphs (ZIF-8-Cₘ phase) with more rigid lattices. The stiffening of the ZIF-8 lattice through electric field polarization resulted in enhanced molecular sieving capability. Nevertheless, this could not be completely aligned by the electric field, leading to a limited transformation (~30%) of flexible ZIF-8 lattices into polymorphs; moreover, the rigid ZIF-8-Cₘ phase could not maintain longer than 1 h after electrical switching off. To solve this issue, Wang et al.[4] further developed a fast current-driven synthesis strategy to prepare ZIF-8 membranes with restricted linker mobility under a low direct current. Current-driven synthesized ZIF-8 membranes mainly consisted of polymorph ZIF-8-Cₘ (60% ~70%) and exhibited a C₂H₆/C₄H₁₀ selectivity >300, thereby validating the significance of linker mobility suppression in improving the C₂H₆/C₄H₁₀ selectivity.

Light irradiation as the external stimuli enables effective manipulation of the pore aperture of light-responsive MOF membranes by remote signals. Heinke et al.[5] prepared photo-switchable Cu₆(AzoBPDC)₂(AzoBiPyB) membranes employing liquid-phase epitaxy. Owing to the presence of photo-responsive azobenzene-side-groups in the framework, azobenzene moieties could be switched from trans- to cis-configuration by irradiating with ultraviolet or visible light, thereby allowing dynamic control of H₂/CO₂ selectivity. Moreover, through controlling the irradiation time or simultaneously irradiating with ultraviolet and visible light, the cis- trans-azobenzene ratio can be precisely tuned so that the H₂/CO₂ selectivity can be continuously adjusted.

Stimuli-responsive MOF membrane with thermo-switchable properties provided a great opportunity for applications in clean energy and environmental sustainability. Zhao et al.[6] fabricated a reversed thermo-switchable MAMS-1 membranes composed of MAMS-1 nanosheets exfoliated via a freeze-thaw approach. A 0.29 nm-sized pore opening within nanosheets warranted precise sieving of H₂ from CO₂; moreover, the dynamic rotation of the tert-butyl groups, which controlled the kinetic opening of in-plane pores, led to reversed thermo-switchable H₂ permeance and H₂/CO₂ selectivity during several heating/cooling cycles.

3. Ultra-thin MOF membranes

Ultra-thin MOF membranes enable us to minimize the diffusion barrier and therefore, realize ultra-high gas permeability. As the thinnest MOF membrane reported to date, Yang et al.[7] fabricated 2D Zn₄(bim)₄ membranes by first exfoliating Zn₄(bim)₄ bulk crystals into single nanosheets via low speed wet ball-milling followed by hot-drop coating on porous α-Al₂O₃ substrates, which, through warranted disorder stacking of Zn₄(bim)₄ nanosheets for sufficient exposure of in-plane pores during the separation process. Prepared Zn₄(bim)₄ membranes exhibited unprecedented H₂ permeance (760~3760 GPU) and H₂/CO₂ selectivity (53~291) due to the ultra-thin thickness (~10 nm) and ultra-small flexible pores (~2.1 Å).

In addition to ultra-thin 2D MOF membranes, recently Li et al.[8] prepared ultra-thin ZIF-8 membranes by combining sol-gel coating with gel-vapor deposition (GVD). Gel-based precursor layers were transformed into 17 nm-thick ZIF-8 membranes upon ligand vapor deposition under thermal treatment. Obtained ZIF-8 membranes exhibited excellent C₂H₆ permeance (836 GPU) as well as decent C₃H₆/C₄H₁₀ selectivity (73.4).

4. Oriented MOF membranes

Oriention control of MOF membranes not only facilitated minimization of grain boundary defects detrimental to their separation performances, but also warranted the uniformity of pore size. Nevertheless, under most conditions preferred orientation of MOF membranes was governed by the Van der Drift kinetic evolutionary selection principle so that the obtained orientation may not be optimum. Liu et al.[9] sought to address this issue through combining oriented seeding and controlled in-plane epitaxial growth. With this method, highly c-oriented NH₃-
MIL-125(Ti) membranes exhibiting superior H₂/CO₂ separation performance could be prepared. It should be noted that the use of layered TiS₂ source and single-mode microwave heating during epilatinal growth was indispensable for the desired orientation.

It is highly desirable to further reduce crystallographic misorientations and grain boundary defects via concurrent manipulation of both in-plane and out-of-plane orientations of MOF membranes. For this purpose, Liu et al.[10] further prepared NH₂-Uio-66 membranes with both (111) out-of-plane and regional in-plane orientations using uniform octahedral-shaped NH₂-Uio-66 crystals as seeds and layered ZrS₂ as metal source. Prepared NH₂-Uio-66 membranes exhibited superior H₂/CO₂ separation performances in comparison with their counterparts with random and/or mere out-of-plane orientations, thereby illustrating the significance of concurrent out-of-plane and in-plane orientation control in separation performance improvement of MOF membranes.

5. MOF membrane synthesis via non-solution protocols

Commonly used solution-based synthetic protocols easily enabled the formation of high-performance MOF membranes. Nevertheless, improper disposal or discharge of spent mother liquor may not only lead to serious environmental pollution but also make it difficult to separate unreacted reagents from solvents. To overcome the dilemma between process sustainability and performance superiority, Tsapatsis et al.[11] developed an all-vapor-phase processing method, denoted as the ligand-induced epitaxial growth, relying on atomic layer deposition of ZnO in porous support followed by ligand-vapor treatment. Prepared ZIF-8 membranes exhibited high CH₃OH/CH₄ selectivity (>10⁵ mol·Pa⁻¹·m⁻²·s⁻¹).

Alternatively, recently Liu et al.[12] fabricated ZIF-8 membranes showing commercially attractive CH₃OH/CH₄ separation performance through a supercritical fluid (SCF) synthetic protocol employing supercritical CO₂ (scCO₂) as the reaction medium, relying on the near-zero surface tension, low viscosity, and high diffusivity of scCO₂; moreover, the zero pollutant discharge is facilely realized since both discharged CO₂ and unreacted ligands can be conveniently recovered and reutilized after SCF processing.

6. Pilot scale-up of MOF membranes

To realize the bulk production and applications of MOF membranes, high-performance MOF membranes should be prepared on cheap, commercial substrates in a simple, efficient, economic, and reproducible manner and easily assembled in membrane modules. Nair et al.[13] developed an interfacial microfluidic membrane processing (IMMP) for scalable fabrication of ZIF-8 membranes inside polymeric hollow-fiber substrates, relying on the growth of ZIF-8 crystals at the two-solvent interface under continuous flow. Prepared ZIF-8 membranes exhibited decent selectivity towards H₂/CH₄ (370) and CH₄/CH₃OH (12) pairs, respectively. It should be noticed that IMMP allowed independent and simultaneous processing of membranes in multiple fibers with no compromise in separation performance.

Very recently, Li et al.[14] further prepared high-performance ZIF-8 membranes with a novel dip coating-thermal conversion method. The method was extremely economic and environment-friendly because of the full utilization of the precursor solution. Prepared ZIF-8 membranes exhibited CH₄/CH₃OH selectivity up to 221 due to the preferential propylene adsorption of DMAC molecules in situ impregnated within the cages of ZIF-8. In addition, DMAC molecules remained stably confined in the ZIF-8 framework at temperatures up to 300 °C, thereby leading to long-term operational stability for 6 months. Moreover, a plate-and-frame module with an effective membrane area of 300 cm² exhibited commercial attractive CH₄/CH₃OH mixture separation performance either.

To sum up, newly emerging strategies for framework design and microstructural optimization of MOF membranes not only enable overcoming the trade-off between selectivity and permeability, but also hold great promise for their scaled-up production. However, several concerns must be fully addressed before delving into practical applications. On a microscopic scale, rational design and synthesis of new MOF materials based on reticular chemistry represents a prerequisite for high-performance MOF membrane fabrication; on a mesoscopic scale, further optimization of the microstructure of MOF membranes is required to minimize potential grain boundary defects. In this regard, the fluorescence confocal optical microscopy represents a promising tool for visualization and quantitative evaluation of grain boundary defects in MOF membranes.[15] Last but not least, positive utilization of momentum transport, energy transport, quality transport, and reaction engineering is of vital importance to successful large-scale production of high-performance MOF membranes with high reproducibility. Besides in their pure form, recently, great progress was made in MOF-based mixed matrix membranes (MMMs). Among various microstructural factors, the MOF filler-polymer compatibility commonly played decisive roles in their separation performances. In this regard, nano-sized spherical and plate-shaped MOF fillers may serve as superior candidates for reducing MOF-filler-polymer interfacial defects. Severe aggregation of MOF fillers at higher loading was another concern that should be addressed, as it may cause interfacial voids and membrane rigidity, thereby leading to inferior gas separation performances.

References

[5] Z. Wang, A. Knebel, S. Grojean, D. Wagner, S. Bräse, C. Will, J. Caro, L. Heinke, Tunable molecular separation by nanoporous micrometric roles in their separation performances. In this regard, nano-sized spherical and plate-shaped MOF fillers may serve as superior candidates for reducing MOF-filler-polymer interfacial defects. Severe aggregation of MOF fillers at higher loading was another concern that should be addressed, as it may cause interfacial voids and membrane rigidity, thereby leading to inferior gas separation performances.

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- We highlighted major progress made in the field of MOF membranes in recent years
- Processing innovation at the macroscopic scale, microstructure optimization at the mesoscopic scale, and framework manipulation at the microscopic scale of MOF membranes were highlighted
- The relationship between structure and separation performance of MOF membranes was elucidated
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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