Design of metal-organic framework membranes towards ultimate gas separation

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HIGHLIGHTS

- We highlighted major progress made in the field of MOF membranes in recent years.
- Processing innovation at microscopic, mesoscopic, and macroscopic scales of MOF membranes were highlighted.
- The relationship between structure and separation performance of MOF membranes was elucidated.

GRAPHICAL ABSTRACT
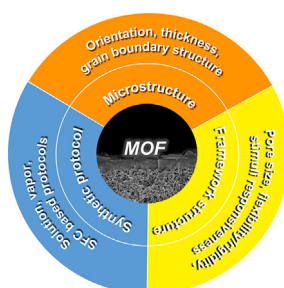
ABSTRACT

Metal-organic framework (MOF) membranes have shown unprecedented opportunities for energy efficient separation of diverse industrially important gas pairs (e.g. H_2/CO_2, CO_2/N_2, CO_2/CH_4, and C_3H_6/C_3H_8). 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 treatment 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 H_2/CH_4, CO_2/N_2 and CO_2/CH_4 gas pairs (Fig.1).

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 C_3H_6 molecules through low-crystalline ZIF-8 membranes was significantly enhanced, resulting in unprecedented C_3H_6 permeance (2000–3000 GPU) and attractive C_3H_6/C_3H_8 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
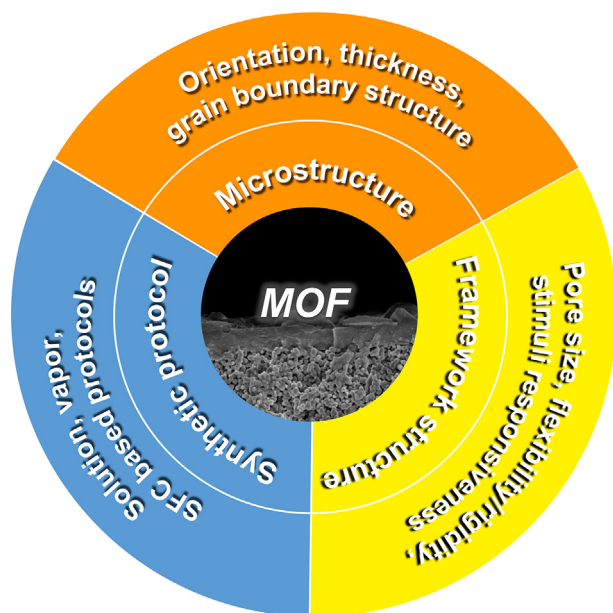

Fig. 1. Illustration of various protocols for rational design of MOF membranes at different scales.

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, linkers 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 C_3H_6/C_3H_8 selectivity > 300, thereby validating the significance of linker mobility suppression in improving the C_3H_6/C_3H_8 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 Cu$_2$(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 H_2/CO_2 selectivity. Moreover, through controlling the irradiation time or simultaneously irradiating with ultraviolet and visible light, the *cis*- : *trans*-azobenzene ratio could be precisely tuned so that the H_2/CO_2 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 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 H_2 from CO_2; moreover, the dynamic rotation of the *tert*-butyl groups, which controlled the kinetic opening of in-plane pores, led to reversed thermo-switchable H_2 permeance and H_2/CO_2 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 Zn$_2$(bim)$_4$ membranes by first exfoliating Zn$_2$(bim)$_4$ bulk crystals into single nanosheets via low speed wet ball-milling followed by hot-drop coating on porous α-Al$_2$O$_3$ substrates, which warranted disorder stacking of Zn$_2$(bim)$_4$ nanosheets for sufficient exposure of in-plane pores during the separation process. Prepared Zn$_2$(bim)$_4$ membranes exhibited unprecedented H_2 permeance (760–3760 GPU) and H_2/CO_2 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 C_3H_6 permeance (836 GPU) as well as decent C_3H_6/C_3H_8 selectivity (73.4).

4. Oriented MOF membranes

Orientation 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 NH$_2$-MIL-125(Ti) membranes exhibiting superior H_2/CO_2 separation performance could be prepared. It should be noted that the use of layered TiS$_2$ source and single-mode microwave heating during epitaxial 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 NH$_2$-UiO-66 membranes with both (111) out-of-plane and regional in-plane orientations using uniform octahedral-shaped NH$_2$-UiO-66 crystals as seeds and layered ZrS$_2$ as metal source. Prepared NH$_2$-UiO-66 membranes exhibited superior H_2/CO_2 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 permselectivation process, relying on atomic layer deposition of ZnO in porous support followed by ligand-vapor treatment. Prepared ZIF-8 membranes exhibited high C_3H_6/C_3H_8 selectivity (~100) and high C_3H_6 permeance (>10^{-8} mol Pa^{-1} m^{-2} s^{-1}).

Alternatively, recently Liu et al. [12] fabricated ZIF-8 membranes showing commercially attractive C_3H_6/C_3H_8 separation performance through a supercritical fluid (SCF) synthetic protocol employing supercritical CO_2 (scCO$_2$) as the reaction medium, relying on the near-zero surface tension, low viscosity, and high diffusivity of scCO$_2$; moreover, the zero pollutant discharge was facilely realized since both discharged

CO_2 and unreacted ligands could 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 H_2/C_3H_8 (370) and C_3H_6/C_3H_8 (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 cost-effecitve and environmental friendly because of the full utilization of the precursor solution. Prepared ZIF-8 membranes exhibited C_3H_6/C_3H_8 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 cm^2 exhibited commercial attractive C_3H_6/C_3H_8 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 rigidification, thereby leading to inferior gas separation performances.

Declaration of competing interest

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.

References

[1] Y. Wang, H. Jin, Q. Ma, K. Mo, H. Mao, A. Feldhoff, X. Cao, Y. Li, F. Pan, Z. Jiang, A MOF glass membrane for gas separation, Angew. Chem. Int. Ed. 59 (2020) 4365–4369.

[2] Z. Qiao, Y. Liang, Z. Zhang, D. Mei, Z. Wang, M.D. Guiver, C. Zhong, Ultrathin low-crystallinity MOF membranes fabricated by interface layer polarization induction, Adv. Mater. 32 (2020) 2002165.

[3] A. Knebel, B. Geppert, K. Volgmann, D.I. Kolokolov, A.G. Stepanov, J. Twiefel, P. Heitjans, D. Volkmer, J. Caro, Defibrillation of soft porous metal-organic frameworks with electric fields, Science 358 (2017) 347–351.

[4] S. Zhou, Y. Wei, L. Li, Y. Duan, Q. Hou, L. Zhang, L.X. Ding, J. Xue, H. Wang, J. Caro, Paralyzed membrane: current-driven synthesis of a metal-organic framework with sharpened propene/propane separation, Sci. Adv. 4 (2018) eaau1393.

[5] Z. Wang, A. Knebel, S. Grosjean, D. Wagner, S. Bräse, C. Wöll, J. Caro, L. Heinke, Tunable molecular separation by nanoporous membranes, Nat. Commun. 7 (2016) 13872.

[6] X. Wang, C. Chi, K. Zhang, Y. Qian, K.M. Gupta, Z. Kang, J. Jiang, D. Zhao, Reversed thermo-switchable molecular sieving membranes composed of two-dimensional metal-organic nanosheets for gas separation, Nat. Commun. 8 (2017) 14460.

[7] Y. Peng, Y. Li, Y. Ban, H. Jin, W. Jiao, X. Liu, W. Yang, Metal-organic framework nanosheets as building blocks for molecular sieving membranes, Science 346 (2014) 1356–1359.

[8] W. Li, P. Su, Z. Li, Z. Xu, F. Wang, H. Ou, J. Zhang, G. Zhang, E. Zeng, Ultrathin metal–organic framework membrane production by gel–vapour deposition, Nat. Commun. 8 (2017) 406.

[9] Y. Sun, Y. Liu, J. Caro, X. Guo, C. Song, Y. Liu, In-plane epitaxial growth of highly *c*-oriented NH_2-MIL-125(Ti) membranes with superior H_2/CO_2 selectivity, Angew. Chem. Int. Ed. 57 (2018) 16088–16093.

[10] Y. Sun, C. Song, X. Guo, Y. Liu, Concurrent manipulation of out-of-plane and regional in-plane orientations of NH_2-UiO-66 membranes with significantly reduced anisotropic grain boundary and superior H_2/CO_2 separation performance, ACS Appl. Mater. Interfaces 12 (2020) 4494–4500.

[11] X. Ma, P. Kumar, N. Mittal, A. Khlyustova, P. Daoutidis, K.A. Mkhoyan, M. Tsapatsis, Zeolitic imidazolate framework membranes made by ligand-induced permselectivity, Science 361 (2018) 1008–1011.

[12] L. Liu, Y. Song, T. Ji, Y. Sun, D. He, H. Hu, Y. Liu, Beyond solution-based protocols: MOF membrane synthesis in supercritical environments for an elegant sustainability performance balance, ACS Mater. Lett. 2 (2020) 1142–1147.

[13] A.J. Brown, N.A. Brunelli, K. Eum, F. Rashidi, J.R. Johnson, W.J. Koros, C.W. Jones, S. Nair, Interfacial microfluidic processing of metal-organic framework hollow fiber membranes, Science 345 (2014) 72–75.

[14] Q. Ma, K. Mo, S. Gao, Y. Xie, J. Wang, H. Jin, A. Feldhoff, S. Xu, Jerry Y.S. Lin, Y. Li, Ultrafast semi-solid processing of highly durable ZIF-8 membranes for propylene/propane separation, Angew. Chem. Int. Ed. 59 (2020) 21909–21914.

[15] J. Choi, H.K. Jeong, M.A. Snyder, J.A. Stoeger, R.I. Masel, M. Tsapatsis, Grain boundary defect elimination in a zeolite membrane by rapid thermal processing, Science 325 (2009) 590–593.